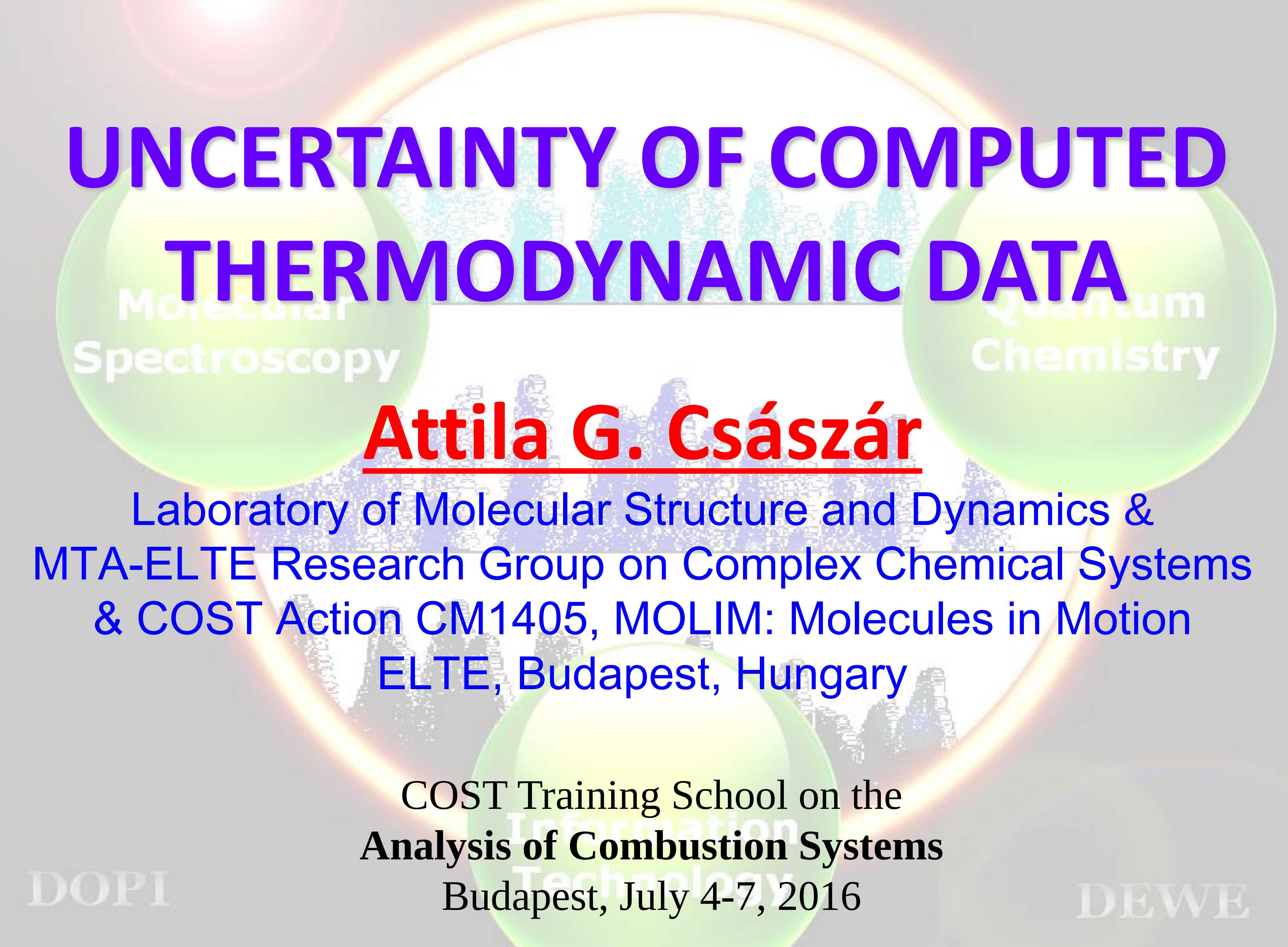


UNCERTAINTY OF COMPUTED THERMODYNAMIC DATA

Attila G. Császár

Laboratory of Molecular Structure and Dynamics &
MTA-ELTE Research Group on Complex Chemical Systems
& COST Action CM1405, MOLIM: Molecules in Motion
ELTE, Budapest, Hungary

COST Training School on the
Analysis of Combustion Systems
Budapest, July 4-7, 2016

ReSpecTh:

a joint reaction kinetics, spectroscopy, and thermochemistry information system

RE
reaction kinetics

SPEC
spectroscopy

TH
thermochemistry

http://respecth.hu

Reaction kinetics

- Respecth Kinetics Data Format
- Database of combustion experiments
- Collection of Chemkin-format mechanisms
- Programs for the analysis of reaction mechanisms

Spectroscopy

- **Experimental databases**

  The experimentally measured, assigned transitions validated by MARVEL: nine major water isotopologues, H3+, H2D+, D2H+, NH3, ketene

- **MARVEL databases**

  MARVEL energy levels with uncertainties

- **Ab initio databases**

  BT2 line list of $H_2{}^{16}O$, VTT line list of $HD^{16}O$, own $D_2{}^{16}O$ energy levels, own energy levels of H_3^+, H_2D^+, and D_2H^+

Thermochemistry

- **NEAT database**

  NEAT, standing for a “**n**etwork of computed reaction **e**nthalpies leading to **a**tom-based **t**hermochemistry”, is a simple and fast, weighted, linear least-squares refinement protocol and code for inverting the information contained in a network of quantum chemically computed 0 K reaction enthalpies.

- **Burcat’s thermochemical data**

  A mirror of Burcat’s thermodynamic data collection

“We are perhaps not far removed from the time when we shall be able to submit the bulk of chemical phenomena to calculation.”

“We are perhaps not far removed from the time when we shall be able to submit the bulk of chemical phenomena to calculation.”

L. J. Gay-Lussac (1809)

Phillip R. Bevington, D. Keith Robinson, Data reduction and error analysis for the physical sciences, 3rd edition, McGraw-Hill, 2003, ISBN 0-07-247227-8.

B. Ruscic, J. E. Boggs, A. Burcat, A. G. Császár, *et al*., IUPAC critical evaluation of thermochemical properties of selected radicals. Part I, *J. Phys. Chem. Ref. Data* **2005,** *34*, 573-656.

B. Ruscic *et al*., Introduction to active thermochemical tables: Several "key" enthalpies of formation revisited, *J. Phys. Chem. A* **2004,** *108*, 9979-9997.

B. Ruscic, Uncertainty quantification in thermochemistry, benchmarking electronic structure computations, and active thermochemical tables, *Int. J. Quant. Chem.* **2014,** *114*, 1097–1101.

Editors of PRA, Editorial: Uncertainty estimates, *Phys. Rev. A* **2011**, *83*, 040001.

H. Chung, B. J. Braams, K. Bartschaat, A. G. Császár, *et al*., Uncertainty estimates for theoretical atomic and molecular data, *J. Phys. D* **2016**, in press.

Uncertainty quantification in structural studies

- Energy level differences, such as excitation and ionization energies and for molecules also dissociation energies and barrier heights
- Configurational parameters of molecules such as bond lengths and bond angles at local minima and transition states
- Properties, such as dipole moments, oscillator strengths, lifetime, and polarizabilities
- Numerical issues such as analytical representations (fits) yielding potential energy and property (dipole moment) surfaces

Uncertainty quantification in collisional studies

- Threshold energies
- Cross sections and/or appropriate rates
- Positions and widths of key resonances
- Other observables, such as the polarization of the emitted radiation, branching ratios, etc.

Question: would experiment or theory provide more useful data for scientific and engineering applications?

Question: would experiment or theory provide more useful data for the scientific and engineering applications?

Answer: basically neither, the best approach involves both and takes advantage of the strengths of the two complementary approaches while minimizing their weaknesses. This is true for high-resolution spectroscopy and thermochemistry, as well.

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**

Objectives of the TG

The main objective of this project's activity is the continued compilation and critical evaluation of published thermochemical properties, including the computation of accurate thermochemical data for selected free radicals, that are of importance in atmospheric and combustion chemistry.

A distinguishing feature of the critical data evaluation is the systematic utilization of all available kinetic, spectroscopic, and ion thermochemical results, as well as high-level *ab initio* computations. Uncertainty (2σ) in *ab initio* results is less than 1 kJ mol^{-1}.

Radicals treated in Part I

- CH
- CH_3
- NH_2
- CH_2OH
- CH_3O
- CH_2 ($^3B_1$ and $^1A_1$)
- $C_6H_5CH_2$
- CH_3CH_2
- OH
- CH_3CH_2O

B. Ruscic et al., *J. Phys. Chem. Ref. Data* **34**, 573-656 (2005).

J. Phys. Chem. Ref. Data, Vol. 34, No. 2, 2005

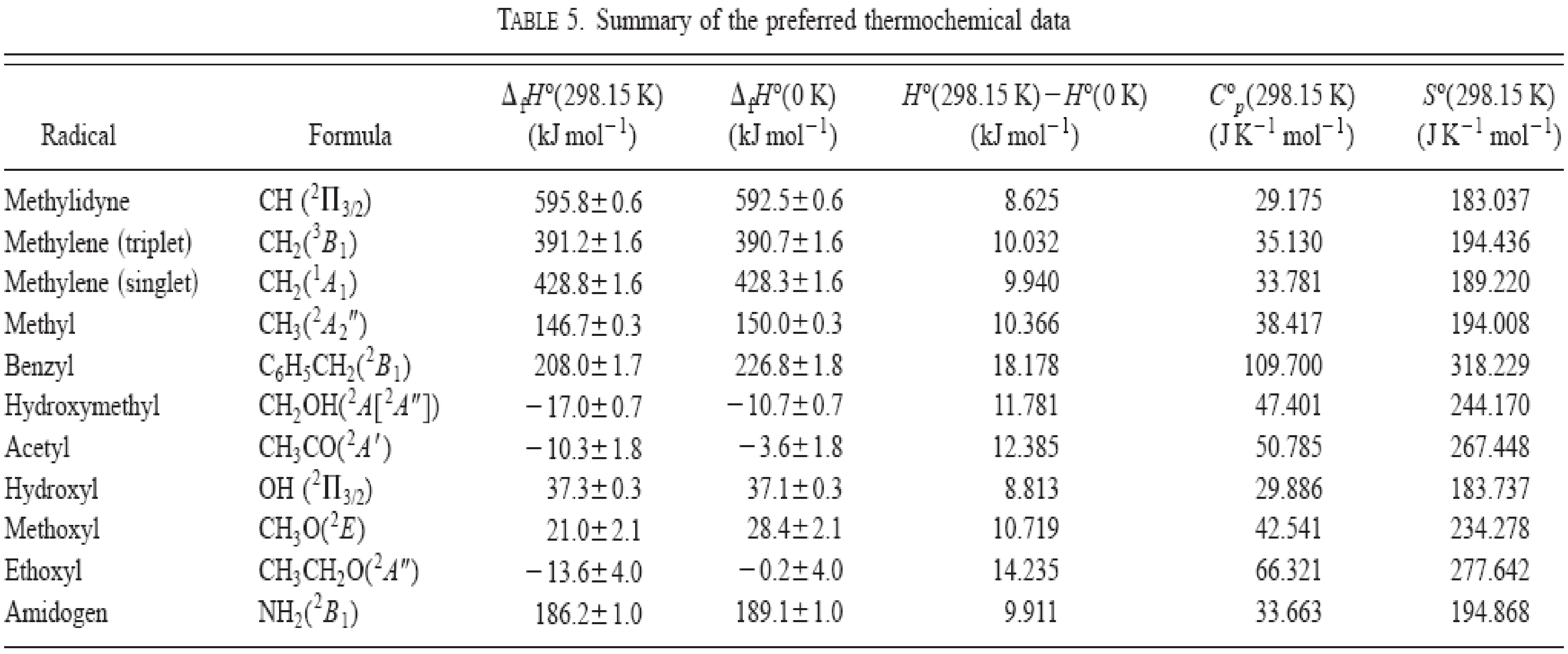


TABLE 5. Summary of the preferred thermochemical data

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	$C_6H_5CH_2(^2B_1)$	208.0 ± 1.7	226.8 ± 1.8	18.178	109.700	318.229
Hydroxymethyl	$CH_2OH(^2A[^2A''])$	-17.0 ± 0.7	-10.7 ± 0.7	11.781	47.401	244.170
Acetyl	$CH_3CO(^2A')$	-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	$CH_3O(^2E)$	21.0 ± 2.1	28.4 ± 2.1	10.719	42.541	234.278
Ethoxyl	$CH_3CH_2O(^2A'')$	-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

High-Accuracy Thermochemistry: Enthalpy of formation of CH ($^2\Pi_{3/2}$)

$\Delta_f H°$/kJ mol^{-1} (298.15 K)	Authors	Method
Measurements		
596 ± 21	Brewer and Kester (1963)	Kinetic equilibrium
593 ± 8	Linevsky (1967)	Kinetic equilibrium
597.3 ± 1.3	Herzberg and Johns (1969)	Spectroscopy
595.6 ± 1.3	Brooks and Smith (1974)	Spectroscopy
596.2 ± 1.1	Brzozowski et al. (1976)	Spectroscopy
595 ± 13	Jesinger and Squires (1999)	Collision Induced Dynamics
Computations		
613.7 ± 9.2	Zachariah et al. (1996)	BAC-MP4
596.6 ± 13	Curtiss et al. (1998)	CBS-Q
590.4 ± 7.9	Curtiss et al. (1998)	G3
596.7 ± 2.5	Peterson and Dunning (1997)	CCSD(T)
595.9 ± 1.9	Parthiban and Martin (2001)	W2
587.7 ± 7.8	Janoschek and Rossi (2002)	G3MP2B3
595.82 +0.47/-0.56	Császár et al. (2002)	FPA
595.8 ± 0.6	IUPAC recomm.	Supported by ATcT

B. Ruscic, J. E. Boggs. A. Burcat, A. G. Császár, *et al.*, *J. Phys. Chem. Ref. Data*, **34**, 573 (2005).

High-Accuracy Thermochemistry: Enthalpy of formation of CH_2 ($^3B_1$)

$\Delta_f H°$/kJ mol^{-1} (298.15 K)	Authors	Method
Measurements		
387.4 ± 2.9	Chupka and Lifshitz (1967)	PIMS-PIC
< 396 ± 2	Chupka (1968)	PIMS-PIC
391.3 ± 1.8	McCulloh and Dibeler (1976)	PIMS-PIC
388.6 ± 2.1	Lengel and Zare (1978)	Spectroscopy
389.4 ± 2.1	Feldmann et al. (1978)	Spectroscopy
394.4 ± 3.0	Hayden et al. (1982)	Spectroscopy
392.4 ± 1.6	Chen et al. (1988)	Spectroscopy
390.3 ± 0.7	Litorja and Ruscic (1998)	PIMS-PIC
391.3 ± 0.7	Willitsch et al. (2002)	PES-PIC
Computations		
387.9 ± 11.6	Melius (1990)	BAC-MP4
389.7 ± 2.5	Peterson and Dunning (1997)	CCSD(T)
389.2 ± 1.2	Doltsinis and Knowles (1997)	MRCI
396.2 ± 13	Curtiss et al. (1998)	CBS-Q
386.6 ± 7.9	Curtiss et al. (1998)	G3
391.0 ± 1.9	Parthiban and Martin (2001)	W2
385.2 ± 7.8	Janoschek and Rossi (2002)	G3MP2B3
390.87 +0.68/-0.64	Császár et al. (2003)	FPA

Motivations of the focal-point analysis (FPA) approach

- Get the right result for the right reason for polyatomic and polyelectronic systems.
- Attach uncertainties (error bars) to theoretical predictions.
- Consider small physical effects tacitly neglected in most quantum chemical studies, such as core correlation, relativistic effects, and corrections to the Born-Oppenheimer approximation.
- Approach spectroscopic accuracy (1 cm^{-1}) as opposed to chemical (1 kcal mol^{-1}) or calibration (1 kJ mol^{-1}) accuracy in predictions of spectra.

A. G. Császár, W. D. Allen, H. F. Schaefer, *J. Chem. Phys.* **1998**, *108*, 9751-9764.

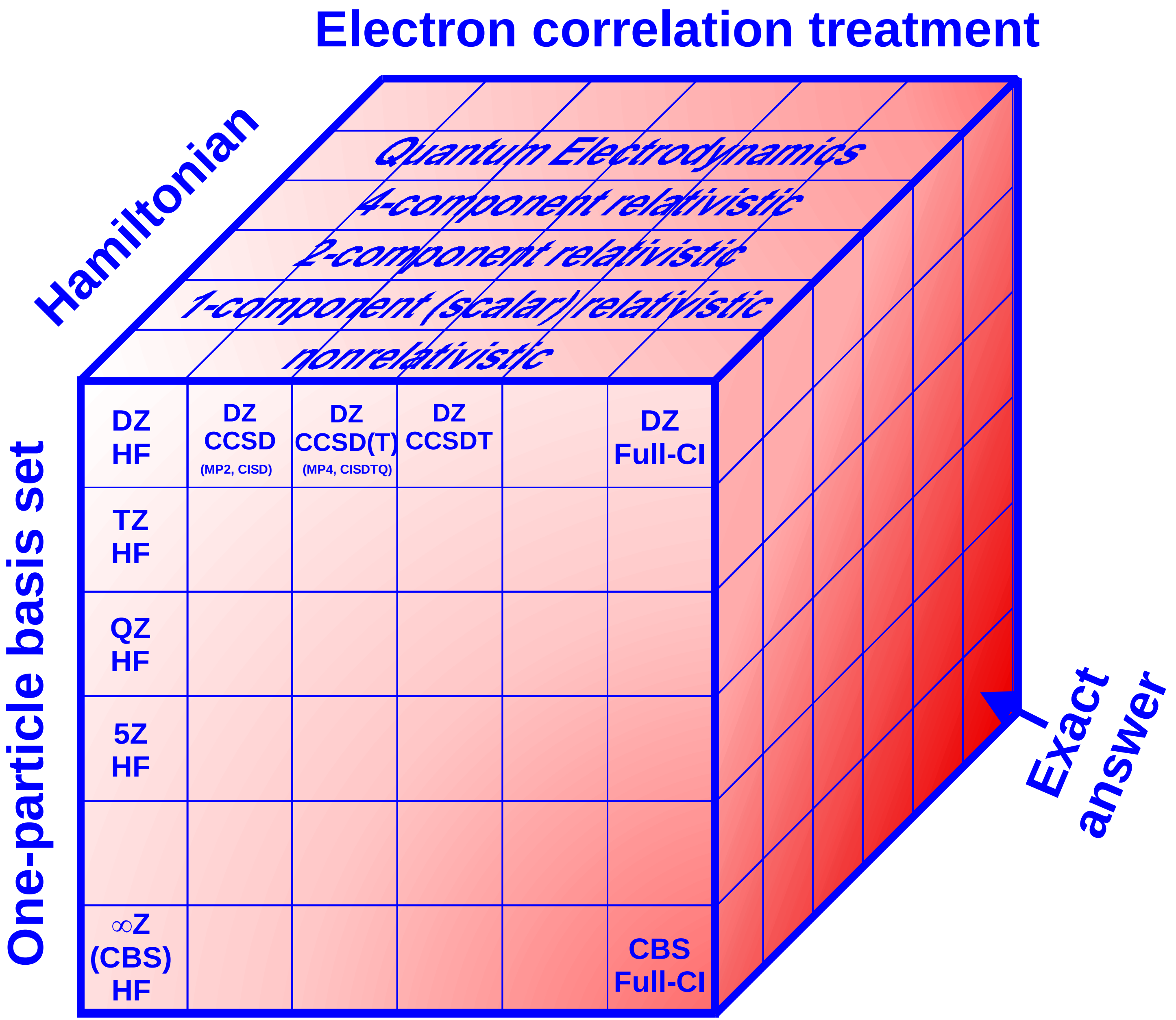
Accuracy goals in electronic structure calculations

	atomic units	kJ mol^{-1}	cm^{-1}
Chemical accuracy	$\approx 1\ \mathrm{m}E_\mathrm{h}$	4	
Calibration accuracy	$\approx 0.2\ \mathrm{m}E_\mathrm{h}$	1	≈100
Spectroscopic accuracy	$\approx 1\ \mu E_\mathrm{h}$		1
Hyperfine accuracy	$\approx 1\ \mathrm{n}E_\mathrm{h}$		

NB1: Obviously, it is much harder to achieve these accuracy goals in absolute energies than in relative energies chemists are mostly interested in.

NB2: These accuracies are characteristic of theoretical treatments, they have nothing to do with accuracies related to spectroscopic measurements.

Rubik’s cube of BO electronic structure theory



DZ HF	DZ CCSD (MP2, CISD)	DZ CCSD(T) (MP4, CISDTQ)	DZ CCSDT		DZ Full-CI
TZ HF					
QZ HF					
5Z HF					
∞Z (CBS) HF					CBS Full-CI

Characteristics of the Focal-Point Approach

- use of a family of basis sets which systematically approaches completeness (e.g., (aug-)cc-p(C)V*n*Z)
- applications of low levels of theory with prodigious basis sets (typically direct RHF and MP2 computations with up to a thousand basis functions)
- higher-order (valence) correlation (HOC) treatments [these days FCI, CCSDTQ[P], CCSDT, and CCSD(T)] with the largest possible basis sets
- layout of a two-dimensional extrapolation grid based on an assumed additivity of correlation increments
- eschewal of empirical corrections

A. G. Császár, W. D. Allen, and H. F. Schaefer III, *J. Chem. Phys.* **108,** 9751 (1998).

Accuracy to better than 10 cm^{-1} in the PEHS

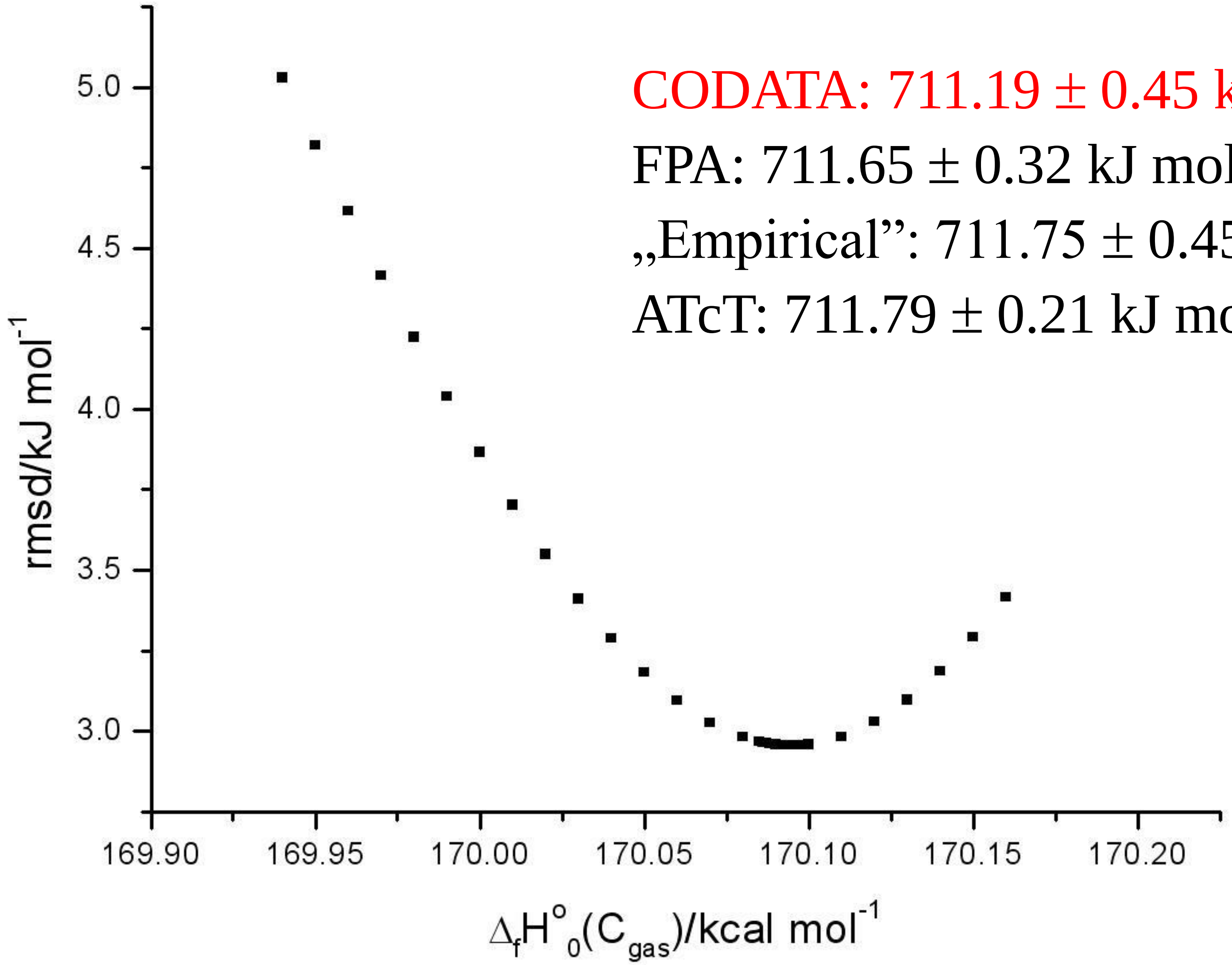
- Electronic (kinetic) relativistic effect
- Relativistic Coulomb potential (Breit effect)
- Radiative correction (Lamb shift or QED)
- Adiabatic or Diagonal Born-Oppenheimer Correction (DBOC)
- Non-adiabatic corrections for vibration and rotation

Can BO electronic structure calculations be done this accurately?

FPA computation of $D_fH_0^o(C_{gas})$ through the dissociation energy $CO \rightarrow C + O$

	Reference: UHF	Reference: ROHF
CBS Hartree-Fock	61034 ± 1	63586 ± 1
CBS CCSD(T)	90838 ± 25	90843 ± 25
CBS FCI	90873 ± 28	
Relativistic corr.	90817 ± 29	
DBOC + SO corr.	90715 ± 29	
ZPE	**89627 ± 30**	
Expt.	**89595 ± 30**	

Dependence of the computed enthalpies of formation of C_1-C_{13} alkanes on the enthalpy of formation of C_{gas}



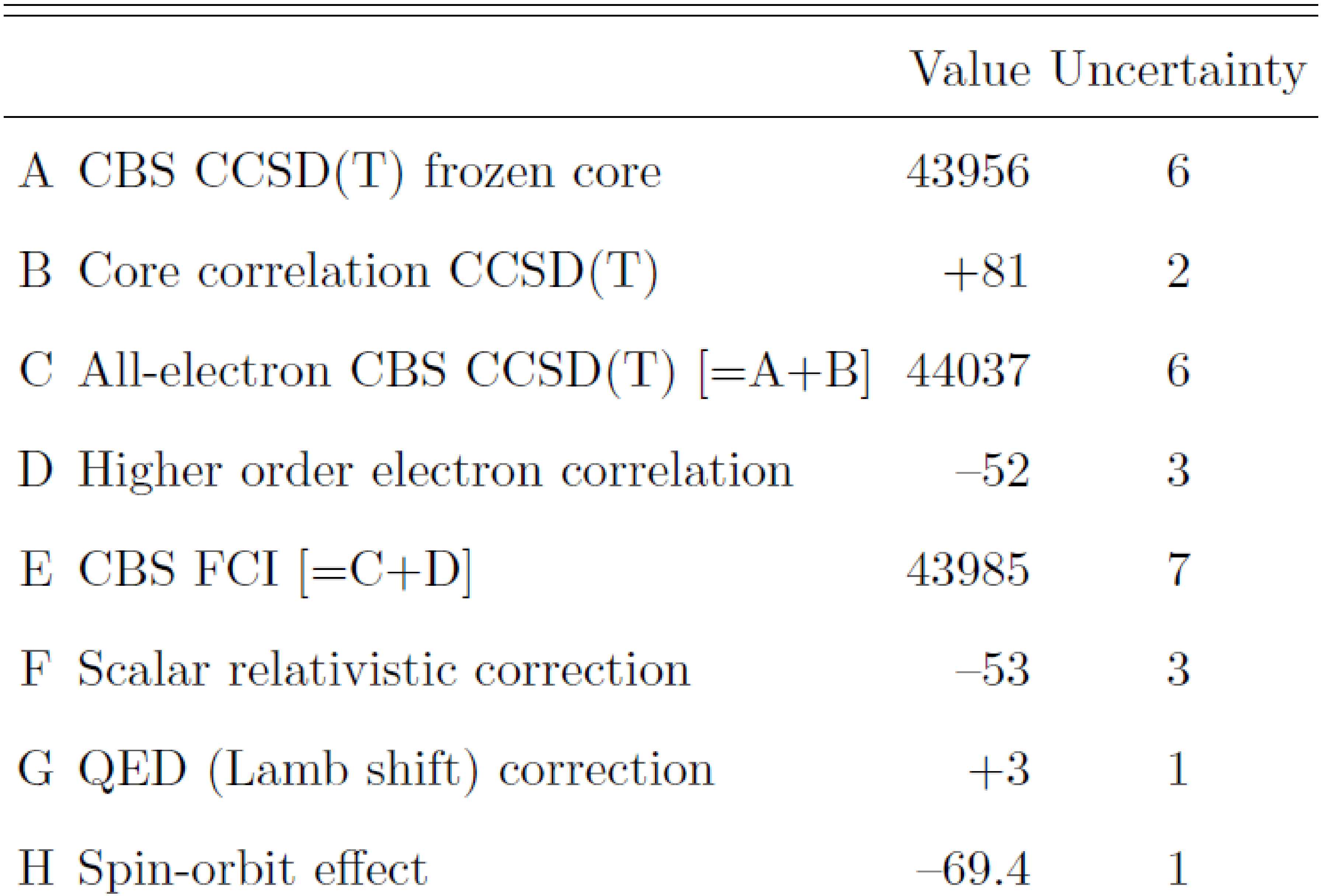
CODATA: 711.19 ± 0.45 kJ mol^{-1}

FPA: 711.65 ± 0.32 kJ mol^{-1}

„Empirical”: 711.75 ± 0.45 kJ mol^{-1}

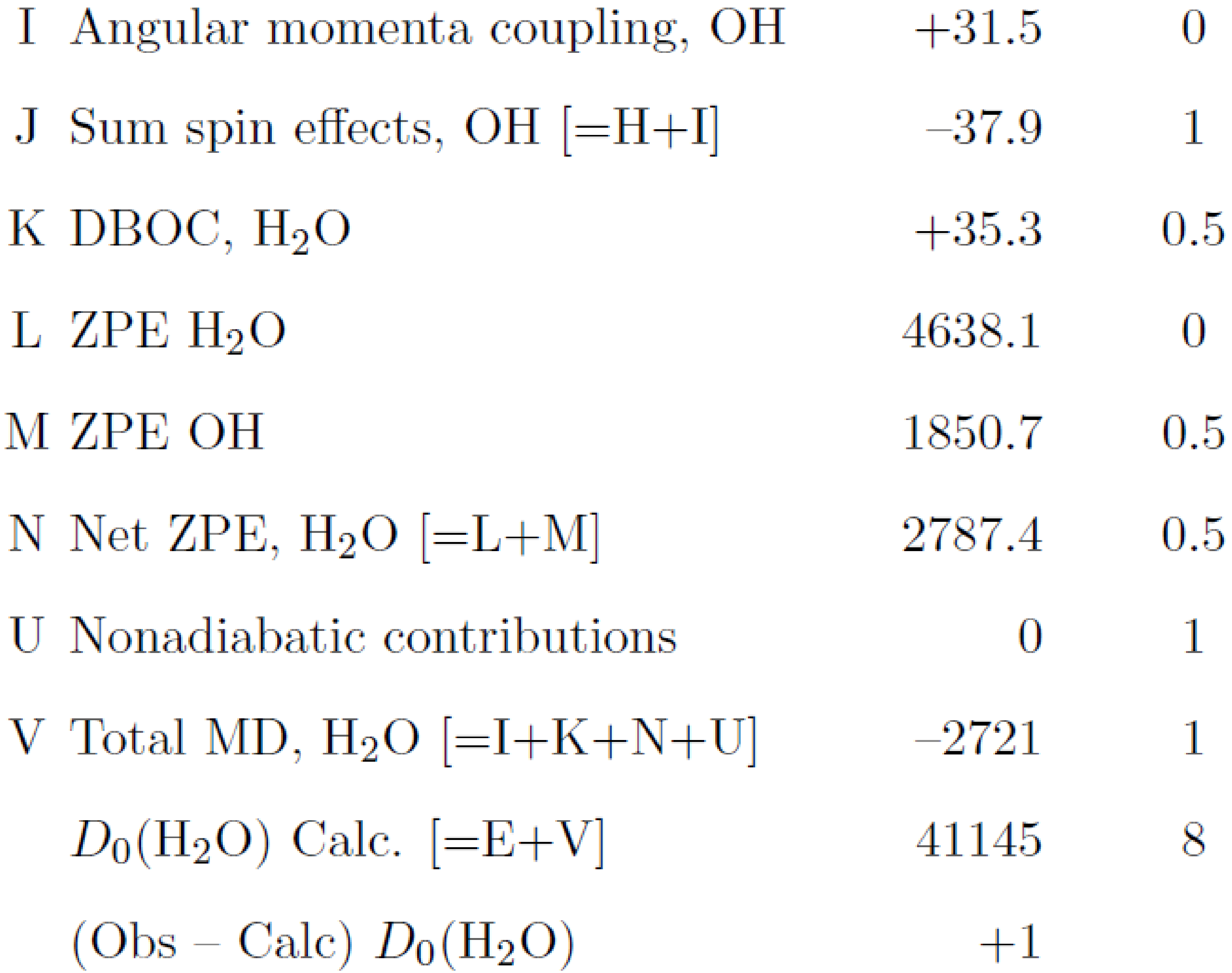
ATcT: 711.79 ± 0.21 kJ mol^{-1}

Dissociation energy of $H_2{}^{16}O$



		Value	Uncertainty
A	CBS CCSD(T) frozen core	43956	6
B	Core correlation CCSD(T)	+81	2
C	All-electron CBS CCSD(T) [=A+B]	44037	6
D	Higher order electron correlation	–52	3
E	CBS FCI [=C+D]	43985	7
F	Scalar relativistic correction	–53	3
G	QED (Lamb shift) correction	+3	1
H	Spin-orbit effect	–69.4	1

Dissociation energy of $H_2{}^{16}O$



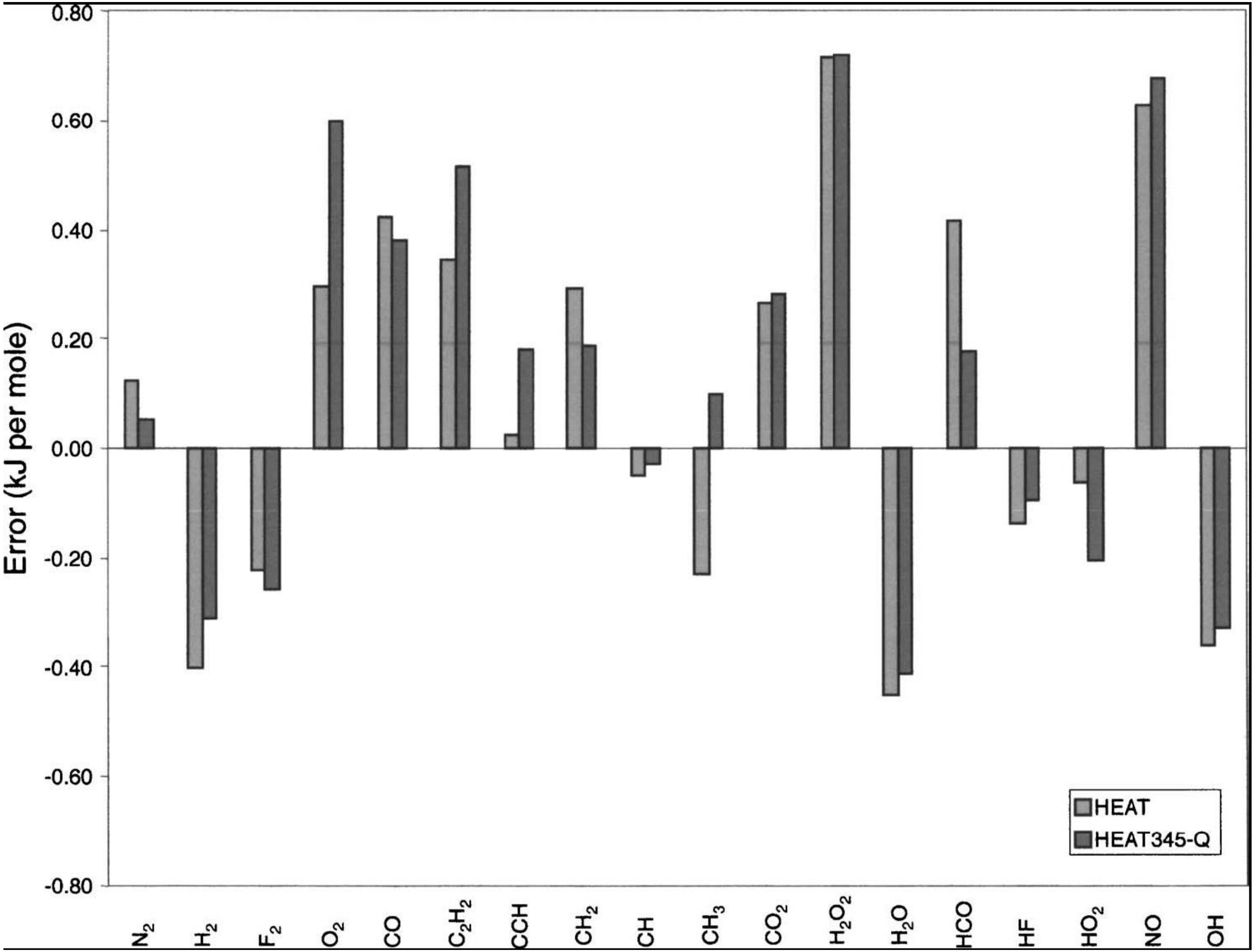
I	Angular momenta coupling, OH	+31.5	0
J	Sum spin effects, OH [=H+I]	–37.9	1
K	DBOC, H_2O	+35.3	0.5
L	ZPE H_2O	4638.1	0
M	ZPE OH	1850.7	0.5
N	Net ZPE, H_2O [=L+M]	2787.4	0.5
U	Nonadiabatic contributions	0	1
V	Total MD, H_2O [=I+K+N+U]	–2721	1
	$D_0(H_2O)$ Calc. [=E+V]	41145	8
	(Obs – Calc) $D_0(H_2O)$	+1	

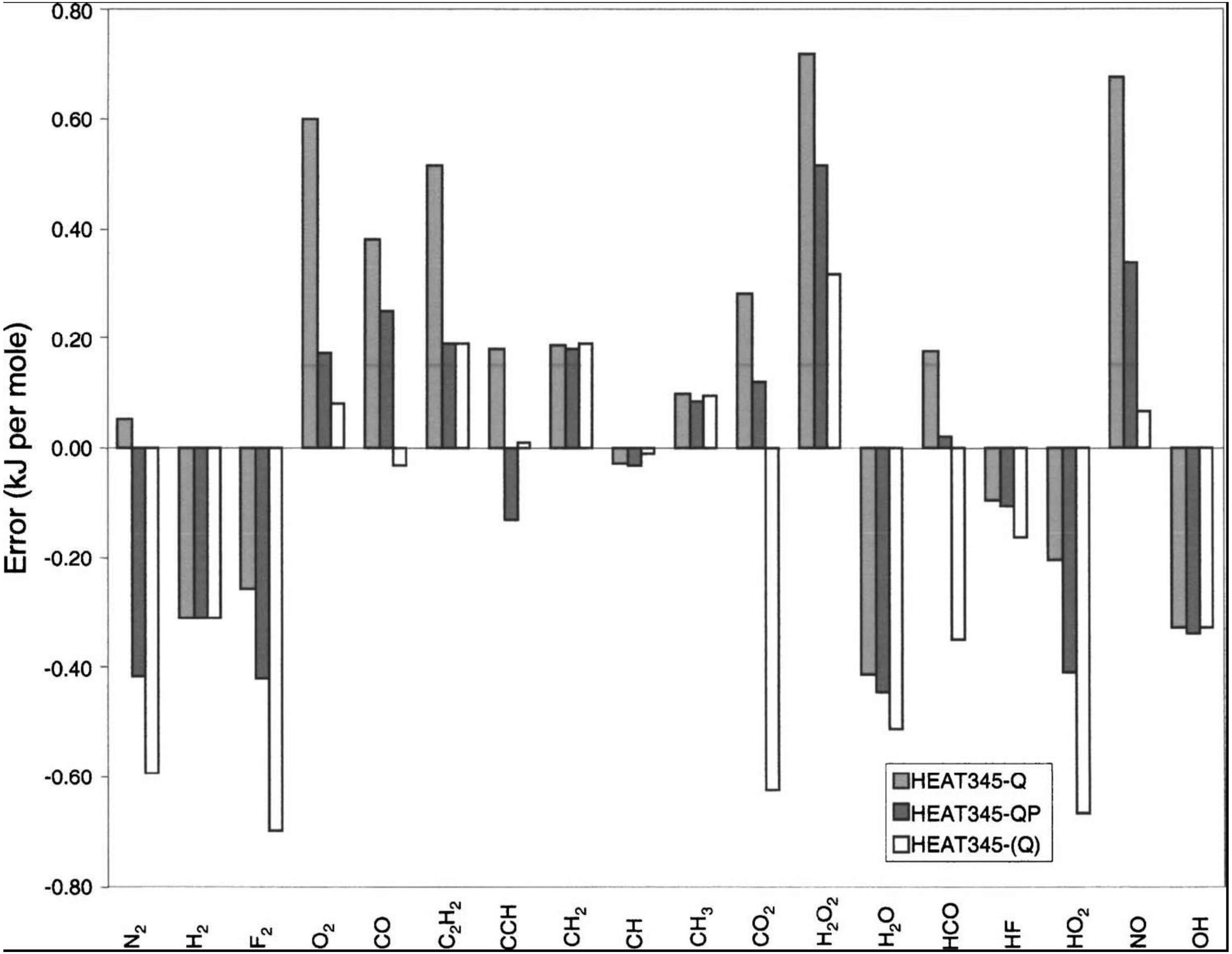
HEAT:
High accuracy extrapolated *ab initio* thermochemistry

The 31 species treated:

N_2, H_2, F_2, O_2, C, F, H, N, O, CO, C_2H_2,
CCH, CH_2, CH, CH_3, CO_2, H_2O_2, H_2O,
HCO, HF, HO_2, NO, OH, HNO, CN,
HCN, CF, NH_2, NH_3, NH, OF

A. Tajti, P. G. Szalay, A. G. Császár, M. Kállay, J. Gauss, E. F. Valeev,
B. A. Flowers, J. Vázquez, J. F. Stanton, *J. Chem. Phys.* **121**, 11599 (2004).


Error (kJ per mole)
0.80
0.60
0.40
0.20
0.00
-0.20
-0.40
-0.60
-0.80
N_2
H_2
F_2
O_2
CO
C_2H_2
CCH
CH_2
CH
CH_3
CO_2
H_2O_2
H_2O
HCO
HF
HO_2
NO
OH
HEAT
HEAT345-Q


0.80
0.60
0.40
0.20
0.00
-0.20
-0.40
-0.60
-0.80
Error (kJ per mole)
HEAT345-Q
HEAT345-QP
HEAT345-(Q)
N2
H2
F2
O2
CO
C2H2
CCH
CH2
CH
CH3
CO2
H2O2
H2O
HCO
HF
HO2
NO
OH

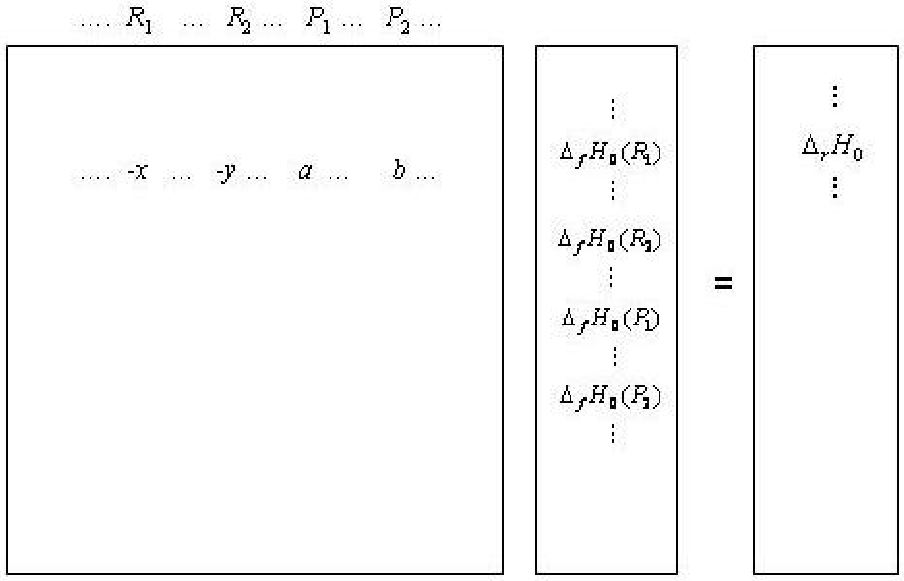
NEAT

NEAT: Network of computed reaction Enthalpies leading toward Atom-based Thermochemistry

Database: $xR_1(\mathrm{g}) + yR_2(\mathrm{g}) \rightarrow aP_1(\mathrm{g}) + bP_2(\mathrm{g})$

Base equation:

$$\Delta_r H_0 = [a\,\Delta_f H_0(P_1) + b\,\Delta_f H_0(P_2)) - (x\,\Delta_f H_0(R_1) + y\,\Delta_f H_0(R_2)]$$



NEAT

NEAT database contains only *ab initio* 0 K reaction enthalpies from 31 publications

Convention: atom-based thermochemistry

Conversion between AT and element-based approches:

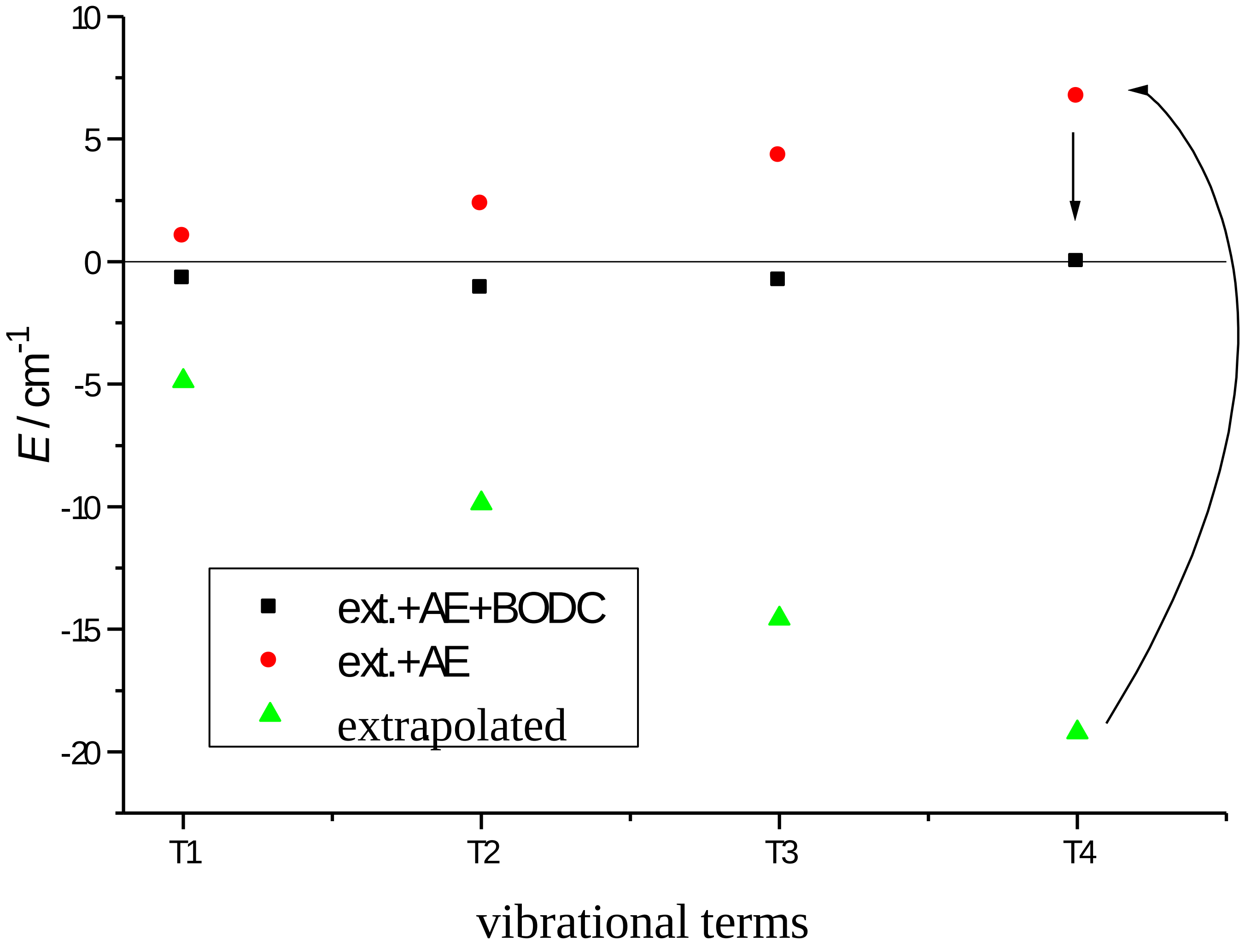
$$\Delta_f H_0^\circ(\mathrm{A}_a\mathrm{B}_b) = \Delta_f H_0^{\mathrm{AT}}(\mathrm{A}_a\mathrm{B}_b) + a \cdot \Delta_f H_0^\circ(\mathrm{A}) + b \cdot \Delta_f H_0^\circ(\mathrm{B})$$

Comparison with ATcT: Active Thermochemical Tables of Ruscic accepted as containing the ‘experimental’ enthalpies of formation

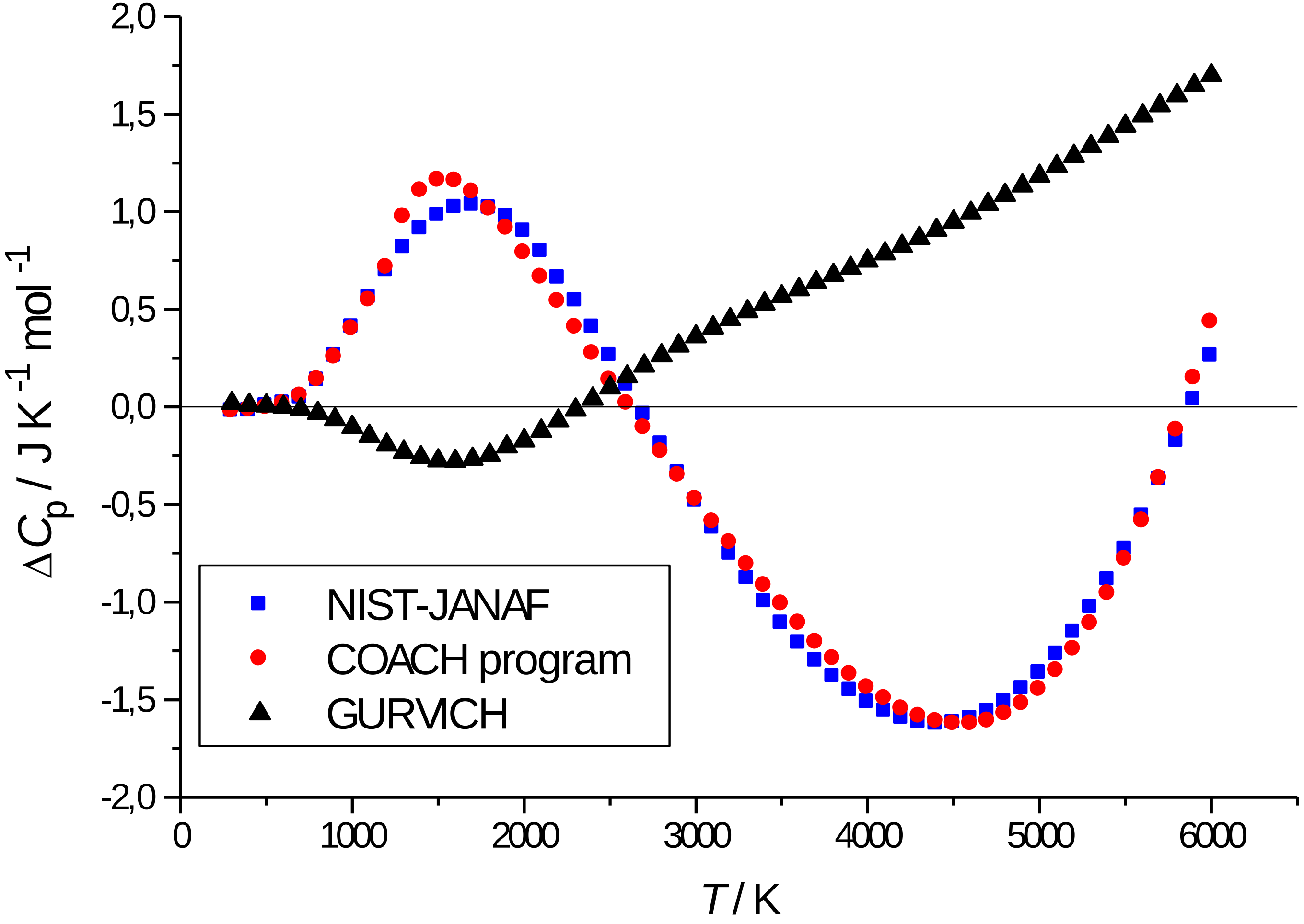
NEAT

Species	No. of reactions		NEAT		ATcT
	2010	2013	2010	2013	
H_2O	17	21	918.05 (20)	918.04(15)	917.83(3)
C_2H_2	13	16	1625.71(37)	1625.83(36)	1626.16(24)
CH ($X^2\Pi_{3/2}$)	13	25	334.61(15)	334.67(15)	334.66(23)
NH_3	12	14	1157.47(34)	1157.34(29)	1157.25(4)
CO	13	17	1072.08(28)	1071.94(26)	1072.13(9)
CH_3	11	13	1209.81(33)	1209.58(28)	1209.63(13)
CH_2 ($^3B_1$)	10	14	752.45(23)	752.41(20)	752.70(26)
OH	12	19	425.93(21)	425.84(15)	425.62(3)
CH_4	10	13	1641.76(41)	1641.87(36)	1642.24(12)
CO_2	10	12	1597.77(40)	1597.92(37)	1598.27(9)
H_2	11	16	432.07(0)	432.07(0)	432.07(0)
NH	9	12	327.69(25)	327.68(21)	328.43(29)
HO_2	7	8	694.51(34)	694.50(31)	694.46(22)
HF	7	9	566.12(31)	566.10(26)	565.97(1)

Differences between experimental and theoretical VBOs for $^2\Pi$ CH



Differences between first-principles and established heat capacities for CH



Partition function of $H_2{}^{16}O$

- 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:

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

Partition function of $H_2{}^{16}O$

- The simplest way to approximate the partition function: the RRHO (rigid rotor, harmonic oscillator) model

$$Q^{\mathrm{HO}}(T)=\left(\sum_{v_1} e^{-c_2 v_1/T}\right)\left(\sum_{v_2} e^{-c_2 v_2/T}\right)\left(\sum_{v_3} e^{-c_2 v_3/T}\right)$$

Integrate

$$Q^{\mathrm{HO}}(T)=(1-e^{-c_2 v_1/T})^{-1}(1-e^{-c_2 v_2/T})^{-1}(1-e^{-c_2 v_3/T})^{-1}$$

Partition function of $H_2{}^{16}O$

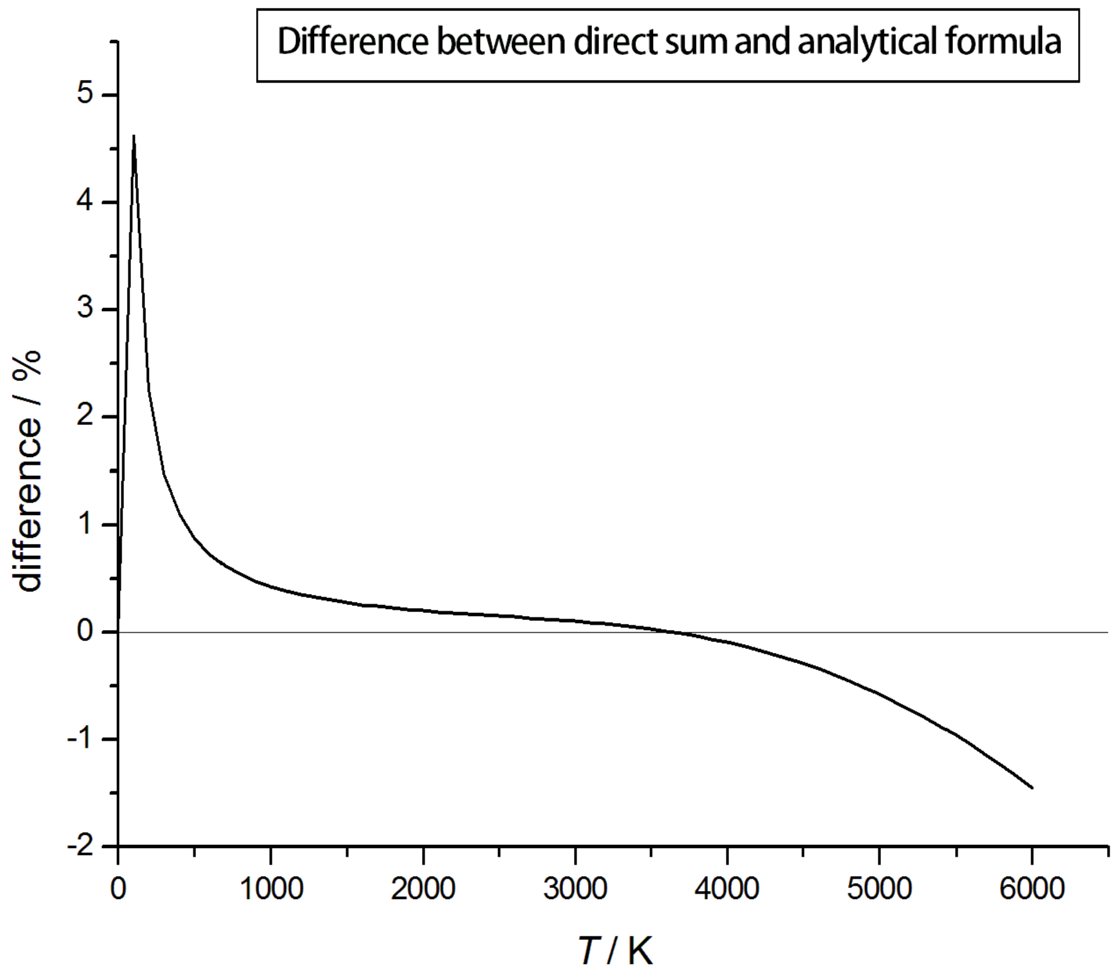
- The simplest way to approximate the partition function: the RRHO (rigid rotor, harmonic oscillator) model

$$Q^{\mathrm{RR}}(T)=\sum_{J}(2J+1)e^{-c_2E^{\mathrm{RR}}(J)/T}$$

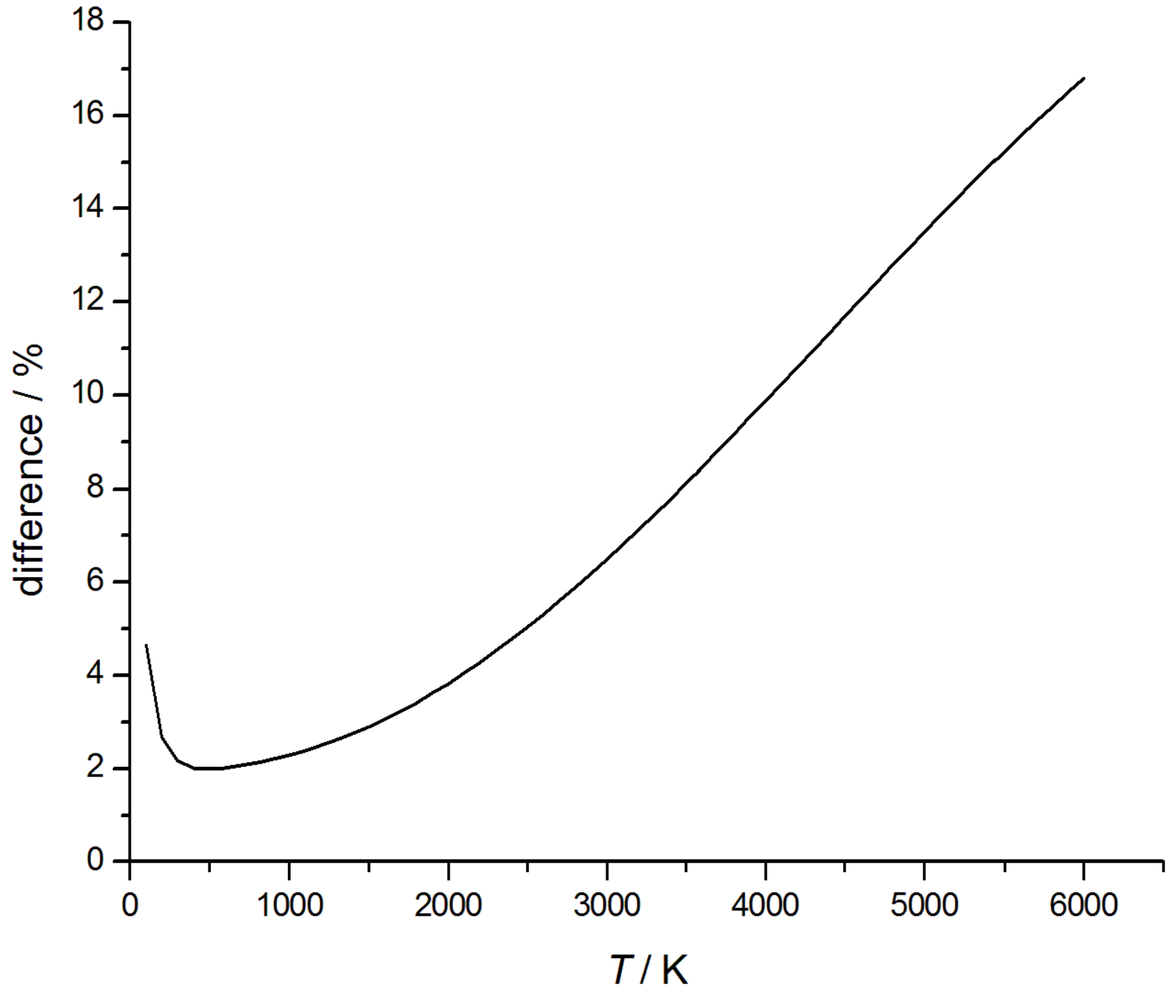
Integrate

$$Q^{\mathrm{RR}}(T)=1.027\sqrt{\frac{T^3}{ABC}}$$

Partition function of $H_2{}^{16}O$



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



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* calculation (completeness)
- unbound states

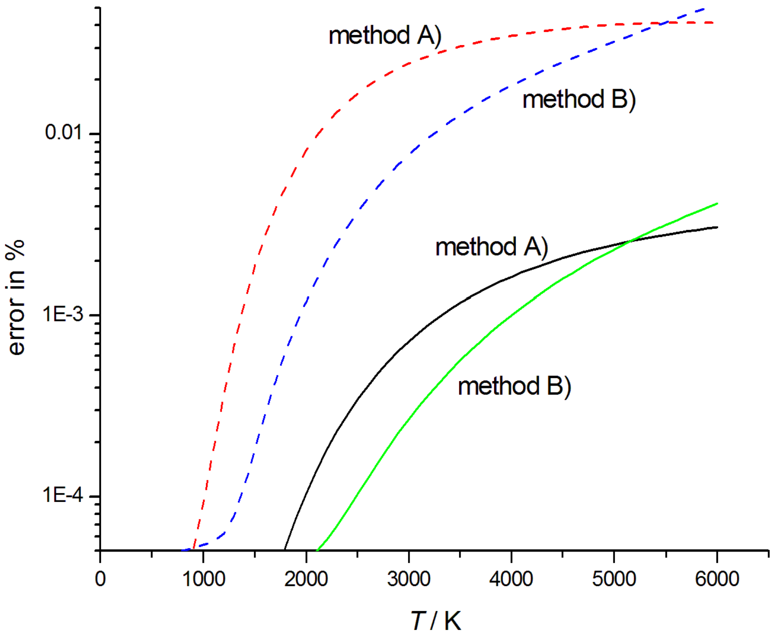
Uncertainty of partition functions

1. Each energy level has its own uncertainty

$$E_i \pm \varepsilon_i$$

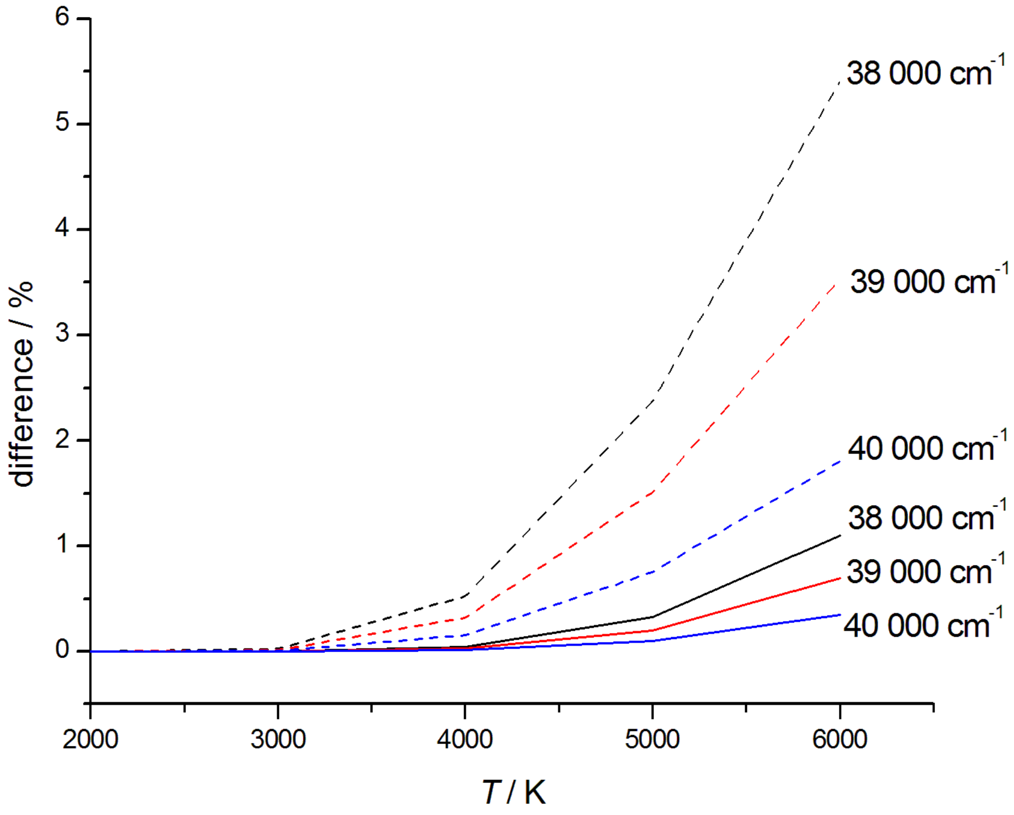
method A: error propagation formula

method B: two extrema method (Q^+-Q^-)



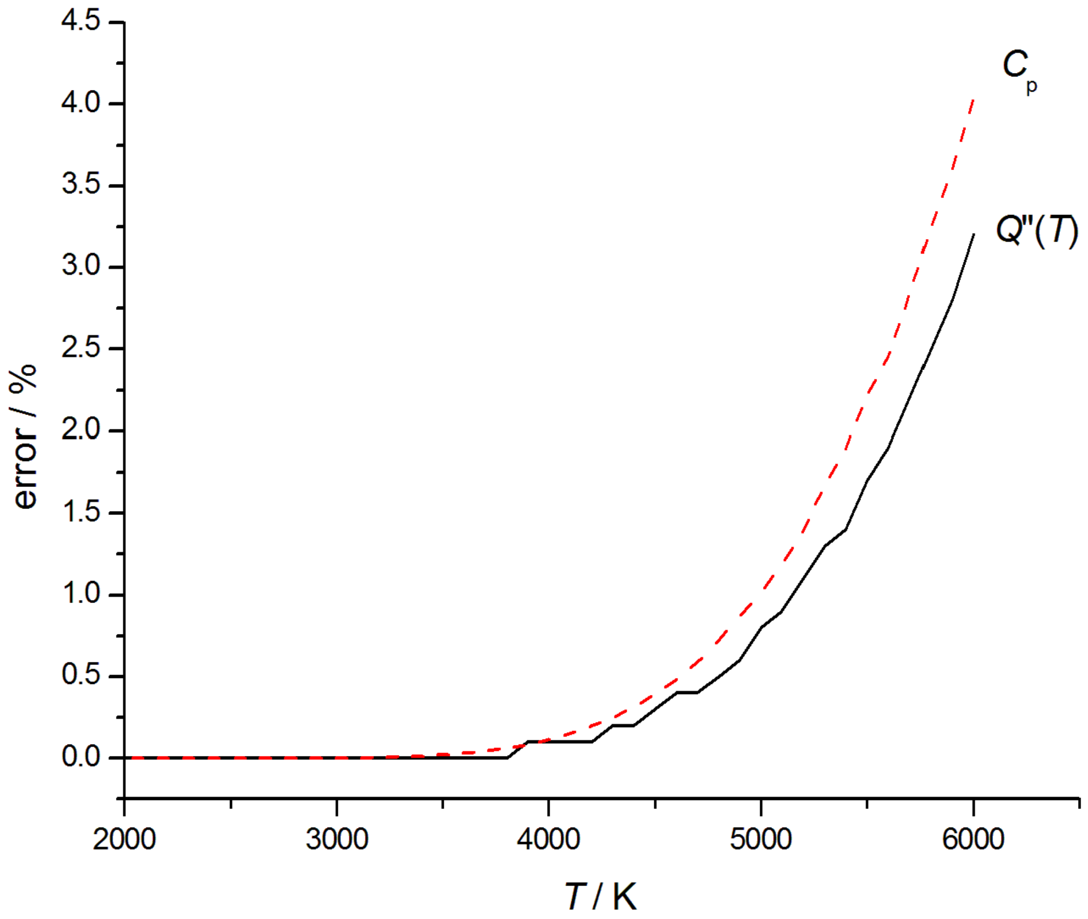
Uncertainty of partition functions

2. The “missing” energy levels, assuming that the set of first-principles levels is not complete



Uncertainty of partition functions

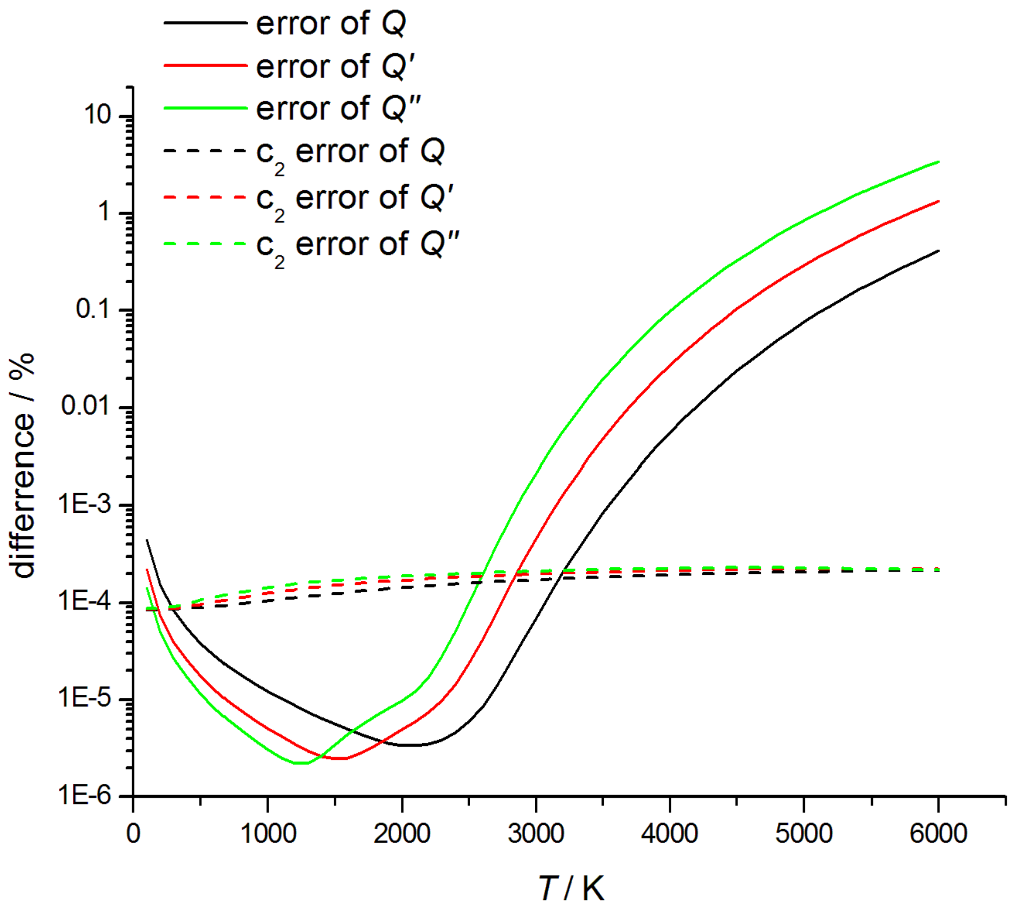
3. The effect of unbound states



Uncertainty of partition functions

4. Uncertainty of physical constants

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



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

$$Q(T) = Q_{\mathrm{B}}(T) + Q_{\mathrm{U}}(T)$$

$$Q_{\mathrm{U}}(T) = Q_{\mathrm{R}}(T) + Q_{\mathrm{F}}(T)$$

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

$$\rho_{\mathrm{B}}(E) = \sum_n \delta(E - E_n) \qquad \rho_{\mathrm{R}}(E) = \frac{1}{\pi} \sum_r \frac{\frac{\Gamma_r}{2}}{(E - E_r)^2 + \frac{\Gamma_r^2}{4}}$$

$$\boxed{\begin{aligned} Q(T) = \int_0^\infty \rho(E) e^{-\beta E} dE &= \sum_n g_n e^{-\beta E_n} \\ &+ \frac{1}{2\pi} \sum_r g_r \int_{D_{\mathrm{e}}}^\infty \frac{\Gamma_r e^{-\beta E}}{(E - E_r)^2 + \frac{\Gamma_r^2}{4}} dE \end{aligned}}$$

Partition functions and resonances

$$\lim_{\gamma_r \to 0} \frac{\frac{\Gamma_r}{2\pi}}{(E-E_r)^2 + \frac{\Gamma_r^2}{4}} = \delta(E-E_r) \quad \Longrightarrow \quad \frac{1}{2\pi}\int_{D_\mathrm{e}}^{\infty} \frac{\Gamma_\mathrm{r} e^{-\beta E}}{(E-E_r)^2 + \frac{\Gamma_r^2}{4}} dE \cong e^{-\beta E_r}$$

$$\rho_\mathrm{U}(E) = \frac{1}{\pi}\frac{d\eta(E)}{dE} \qquad\qquad \rho(E) = \rho_\mathrm{B}(E) + \rho_\mathrm{U}(E)$$

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

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

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

Partition functions and resonances

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

$$\left. - \int_{\substack{0\\ \mathrm{ArgSqrt}>0}}^{\infty} \sqrt{E - \frac{\hbar^2 N(N+1)}{2\mu R^2}}\, dR \right] + \frac{\pi}{4}\delta_{0,N},$$

$$Q'(T) = \sum_n g_n \beta E_n e^{-\beta E_n}$$

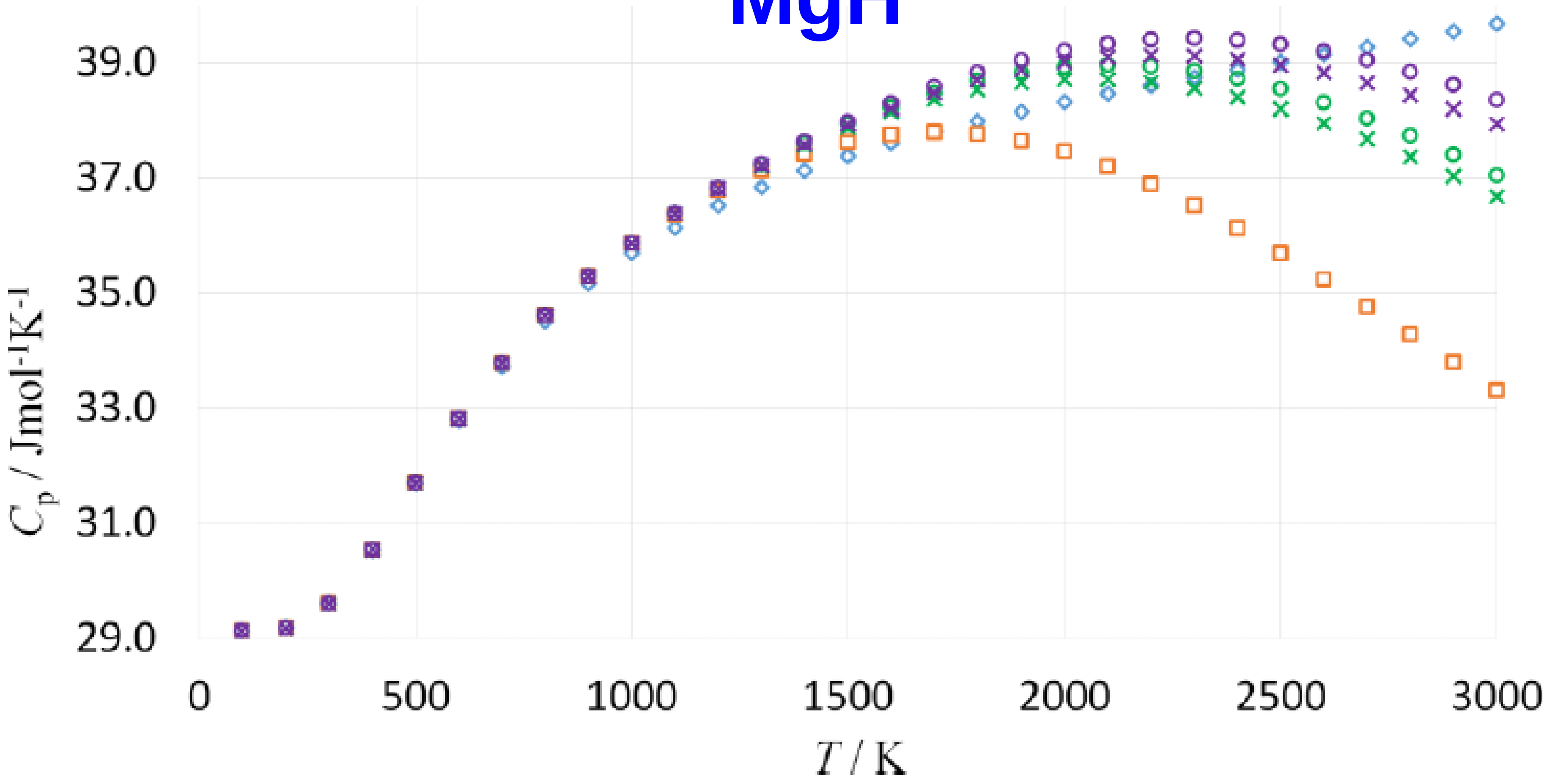
$$+ \frac{1}{2\pi} \sum_{\mathrm{r}} g_r \int_{D_{\mathrm{e}}}^{\infty} \frac{\Gamma_r \beta E e^{-\beta E}}{(E - E_r)^2 + \frac{\Gamma_r^2}{4}}\, dE$$

$$Q''(T) = \sum_n g_n (\beta E_{\mathrm{n}})^2 e^{-\beta E_n}$$

$$+ \frac{1}{2\pi} \sum_{r} g_r \int_{D_{\mathrm{e}}}^{\infty} \frac{\Gamma_r (\beta E)^2 e^{-\beta E}}{(E - E_r)^2 + \frac{\Gamma_r^2}{4}}\, dE$$

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

^{24}MgH



blue diamond: NIST-JANAF

orange square: bound only (638)

green circle: bound + sharp res.

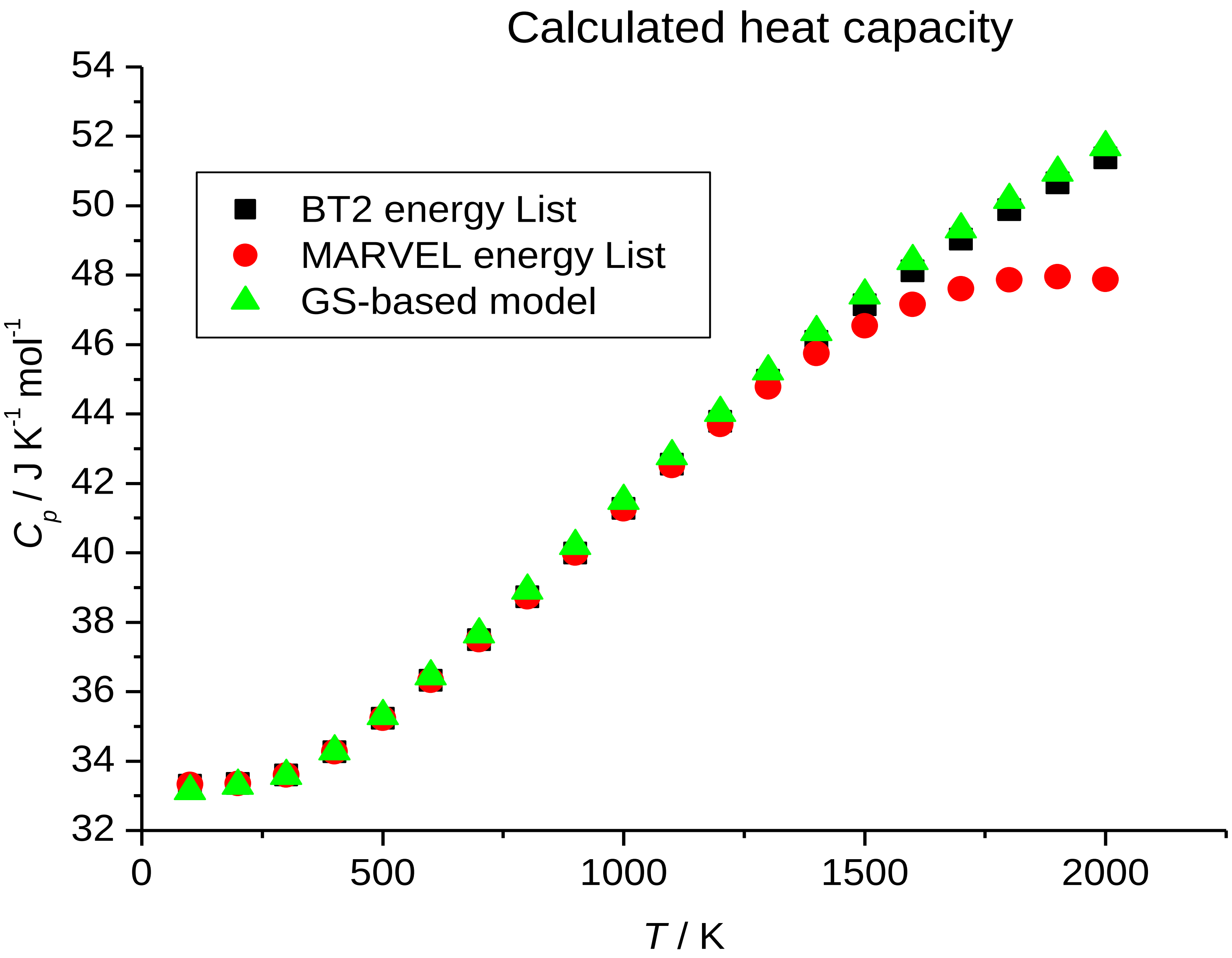
green cross: B + sharp R + int. form

violet circle: B + R + simple sum

violet cross: B + R + integral form

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

From quantum chemistry to steam tables (IAPWS, Int. Association for the Properties of Water and Steam)



Summary

- It is possible to compute highly accurate thermochemical data up to very high temperatures, well above those needed for combustion modeling, using the focal-point analysis (FPA) approach.
- The weighted linear-least-squares ATcT and NEAT approaches yield the best enthalpies of formation.
- Under nearly ideal circumstances highly accurate thermochemical functions can be computed via the “direct summation” technique.
- Unbound states may play a significant role in the accuracy of high-temperature thermochemical functions, especially C_p.