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A review on determining the equilibrium ortho-parahydrogen ratio

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Introduction

Knowledge of the equilibrium ortho-parahydrogen ratio is of fundamental importance for many liquid hydrogen applications in engineering and science.

Some examples with particularly high requirements for accuracy are:

- Calibration and testing of **ortho-para measurement methods**
- The production of **referece gas samples** of known ortho-para ratio
- Measurements and modelling of **thermophysical properties**

The equilibrium ortho-para ratio is described by the Boltzmann distribution, which requires assumptions regarding the modeling of the rotational energy levels of the hydrogen molecule. However, there seems to be ongoing confusion regarding the choice of modeling approach and molecular constants.

This work compares the methods reported in literature and aims to provide clarity and practical advice on how the calculation should be performed.

Literature review

Literature values for characteristic rotational temperature $\boldsymbol{\theta_R}$

References	θ_R [K]
Eisenhut 2024	**85.24**
Green 2012, Parrot 2019, Atkins 2022,	87.6
Essler 2013, Kinard 1998	86.2
Sonntag 1986	85.4
McQuarrie 2000	85.3

Literature values for molecular constants $\mathbf{B_0}$ and $\mathbf{D_0}$

References	B_0 [cm^{-1}]	D_0 [cm^{-1}]
Brannon 1968 (reference)	**59.3343 ± 0.003**	**0.0457 ± 0.0003**
Edwards 1978	59.339 ± 0.005	0.0460 ± 0.0003
Stoicheff 1957	59.3392 ± 0.005	0.04599 ± 0.003
Foltz 1966	59.3362	0.04584

Boltzmann distribution

The Boltzmann distribution describes the ortho-para ratio in thermal equilibrium:

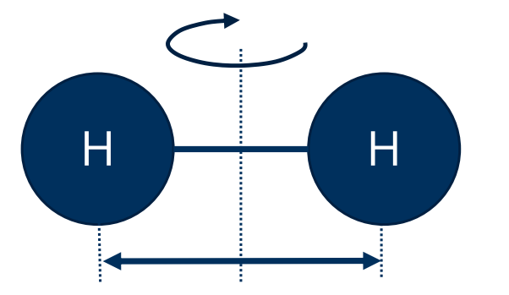
$$\frac{N_{ortho}}{N_{para}} = \frac{3\sum_{J=1,3,5,\ldots}\left[(2J+1)\,e^{-\frac{\boxed{F(J)}}{k_B T}}\right]}{1\sum_{J=0,2,4,\ldots}\left[(2J+1)\,e^{-\frac{\boxed{F(J)}}{k_B T}}\right]}$$

N_{ortho} ... Orthohydrogen population
N_{para} ... Parahydrogen population
J ... Rotational quantum number
k_B ... Boltzmann constant
T ... Temperature
$F(J)$ ... Rotational energy level
θ_R ... Characteristic rot. temperature
B_0, D_0, H_0 ... Molecular constants

Rotational energy level *F(J)*

Rigid rotor model

Assumes that the Hydrogen molecule has a fixed bond length. It is commonly used but inherently less accurate.

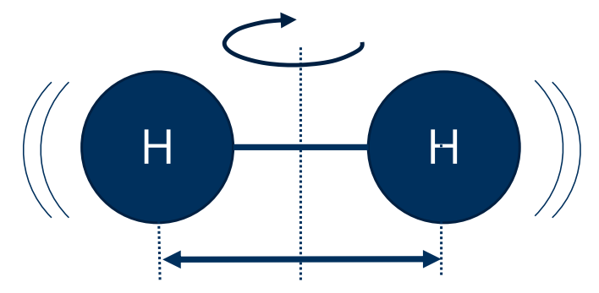


R = const.

$$\boxed{F(J)} = \Theta_R\, k_B\, J\,(J+1)$$

Non-rigid rotor model

Takes the distortion of the molecule in dependence of rotational quantum number J into account.

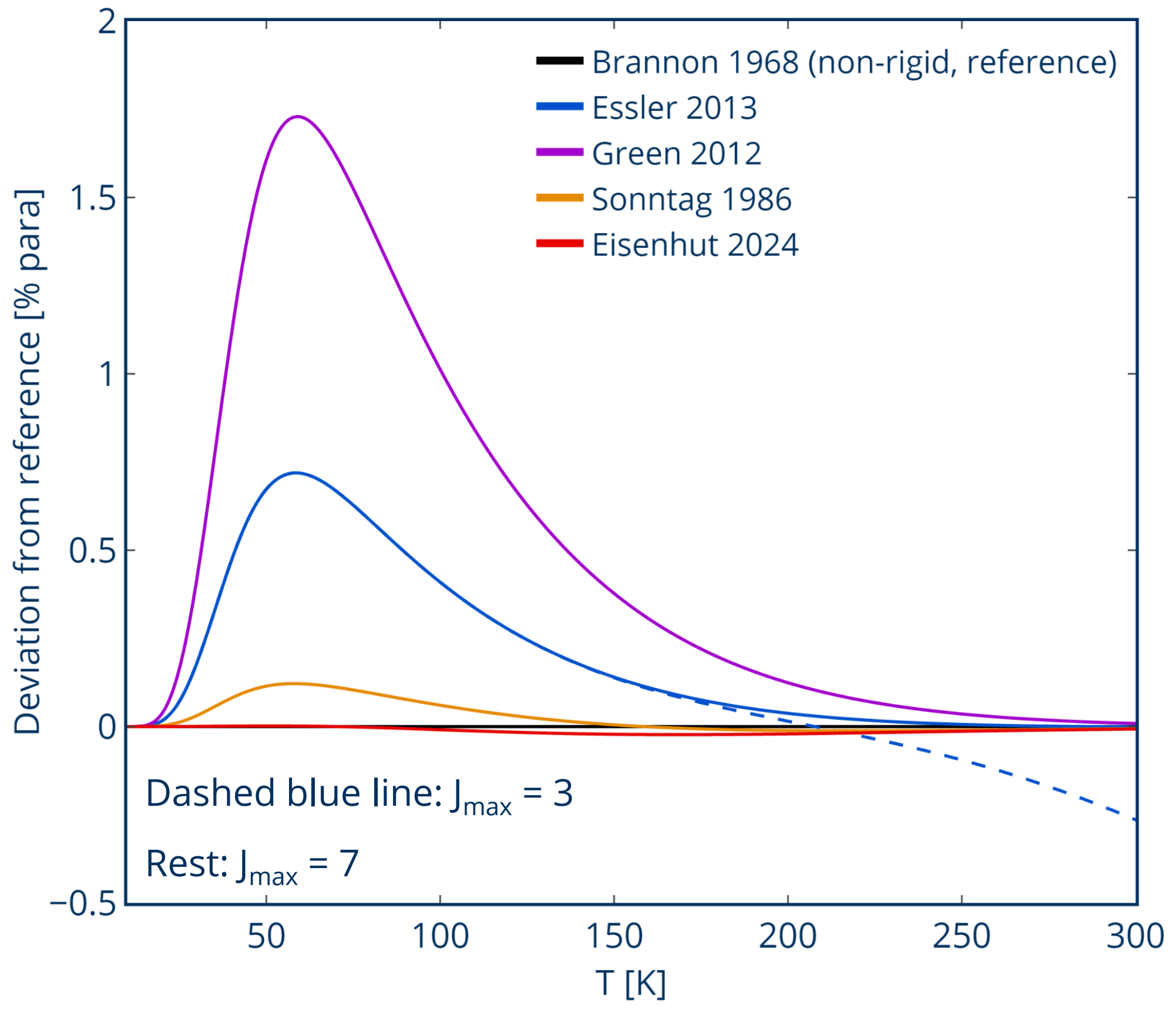


R ≠ const.

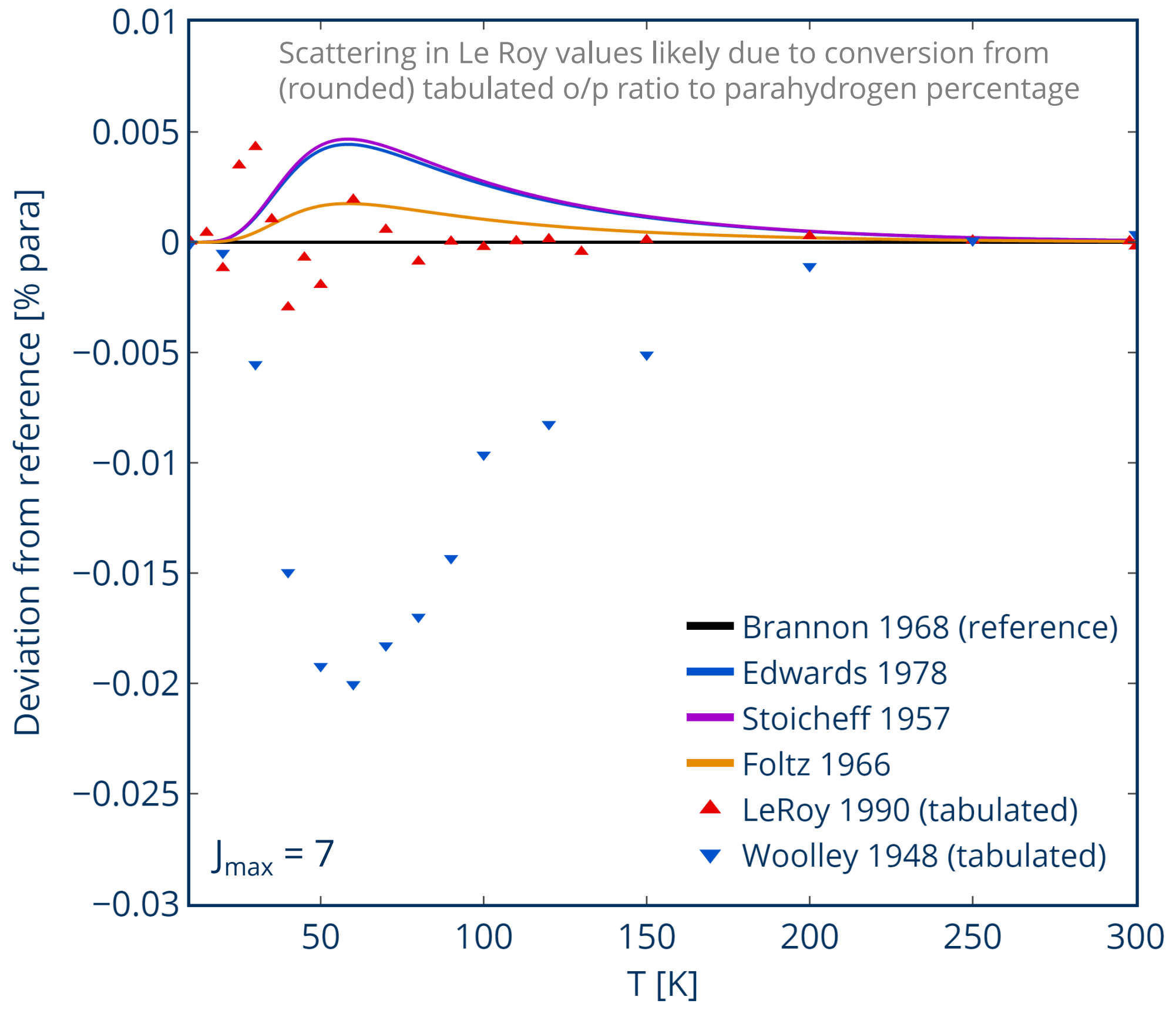
Effect on equilibrium para percentage ~ $1 \cdot 10^{-4}$% p-H_2

$$\boxed{F(J)} = B_0\, J\,(J+1) - D_0\, J^2 (J+1)^2 + H_0\, J^3 (J+1)^3$$

Rigid rotor model: effect of θ_R



Non-rigid rotor model: effect of B_0 and D_0



Conclusion

The aim of this work is to propose a reliable way to calculate the equilibrium ortho-para ratio. An in-depth literature review was conducted to reveal the most reliable set of molecular constants required for the calculation of the rotational energy levels *F(J)*. The effect of these constants on the equilibrium composition was compared quantitatively. The result is a list of practical advice:

- **Use the non-rigid rotor model** for most accurate results:
  - The equilibrium parahydrogen fraction varies by less than 0.005 % for all the published values of B_0 and D_0
  - The parameter set **from Brannon 1968 was chosen as a reference** (lowest measurement uncertainty, best agreement with the currently most accurate ab initio simulations by Le Roy 1990)
  - The **third-order term $\boldsymbol{H_0 J^3 (J+1)^3}$ has only a minor effect** on the equilibrium composition (~ 1 x 10^{-4}% p-H_2)
- When using the **rigid-rotor model**, **use $\boldsymbol{\theta_R}$ = 85.24 K** for best agreement with the reference non-rigid rotor model (deviation < 0.02 % p-H_2)
- **Integrate up to at least J = 7** for accurate and physically consistent results at room temperature and above

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