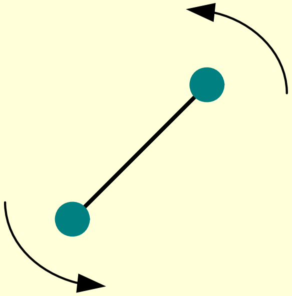
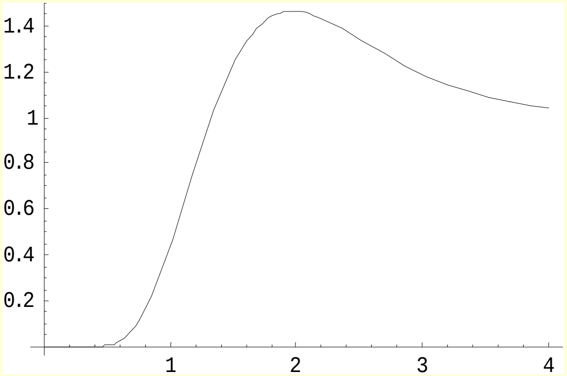
DAVID DENNISON, THE SPECIFIC HEAT OF HYDROGEN, AND THE DISCOVERY OF NUCLEAR SPIN:

EXPERIMENTAL FOUNDATIONS





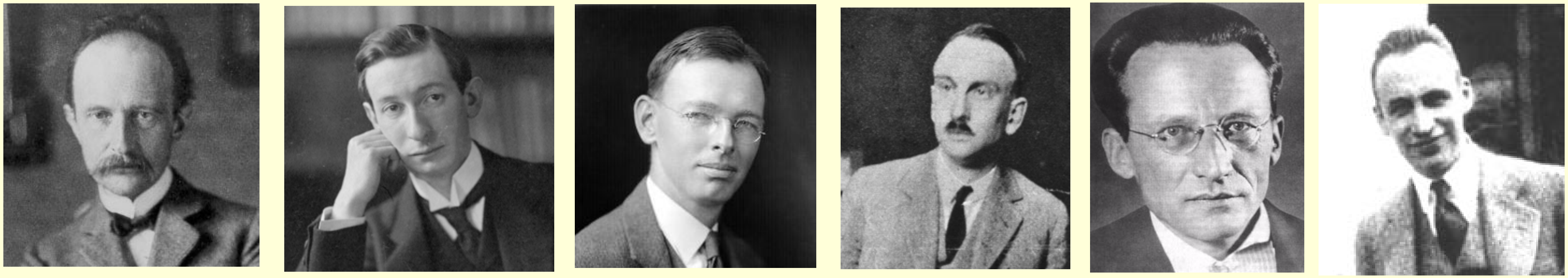
Problem: To describe the sharp decrease in the specific heat of hydrogen as rotational degrees of freedom “freeze out” at low temperatures.

Clayton Gearhart
St. John’s University
(Minnesota)

American Physical Society
St. Louis
April 2008

SPECIFIC HEAT OF HYDROGEN: AN UNSOLVED PROBLEM IN THE OLD (PRE-1925) QUANTUM THEORY

Nernst Lorentz Eucken Einstein Ehrenfest Bohr



Planck Reiche Kemble Tolman Schrödinger Van Vleck

Some of the more prominent physicists and physical chemists who worked on the specific heat of hydrogen, 1911–1926.

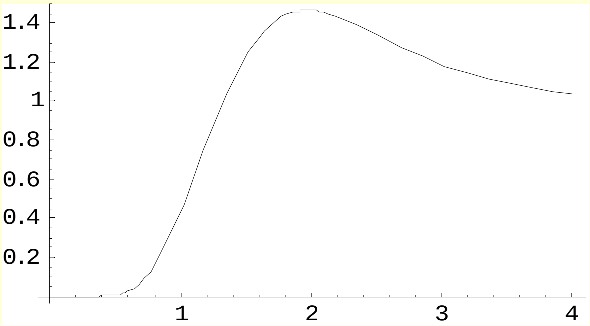
MODERN QUANTUM MECHANICAL SOLUTION (DAVID DENNISON, 1927)

Consider a hydrogen molecule (rigid rotator —two degrees of freedom)

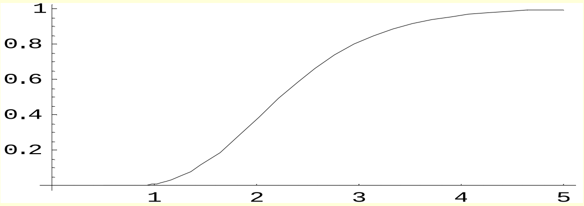
$$E_n = n(n+1)\frac{h^2}{8\pi^2 J}, \quad n = 0, 1, 2 \dots$$

The requirements of wave function symmetries and nuclear spin ⇒ **two varieties** of molecular hydrogen:

parahydrogen



orthohydrogen



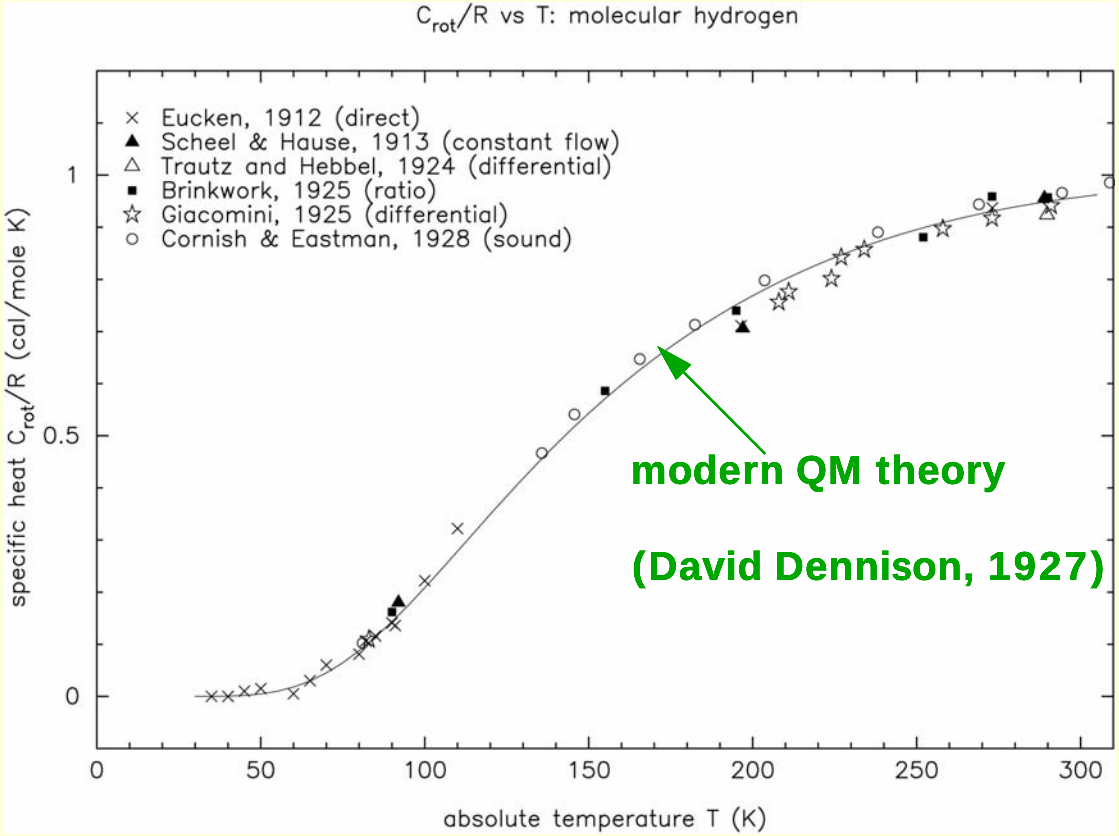
specific heats of para- and orthohydrogen are quite different at low temperatures

ORTHOHYDROGEN ⇔ PARAHYDROGEN TRANSITION IS SLOW

THEORY AND EXPERIMENT BY THE LATE 1920S

To calculate the specific heat of molecular hydrogen:

Treat hydrogen as a mixture of para- and orthohydrogen, in the ratio 1:3 (room temperature ratio for spin 1/2 fermions).



modern QM theory

(David Dennison, 1927)

Dennison's theory predicts a value for the moment of inertia of molecular hydrogen much larger than the accepted value in 1925.

MEASURING THE MOMENT OF INERTIA OF HYDROGEN:

STAGES IN THE DISCOVERY OF THE QUANTUM MECHANICAL EXPLANATION

1. Werner Heisenberg discovered the implications of identical particles in the new quantum mechanics and applied these ideas successfully to the spectrum of helium.

2. Friedrich Hund applied these ideas to molecular spectra, and (unsuccessfully) to the specific heat of hydrogen

3. **In an experimental breakthrough in 1926–27, molecular spectroscopists saw for the first time transitions involving the ground state of molecular hydrogen, and as a result, accurately measured the moment of inertia in the ground state.**

EXPERIMENTAL PHYSICS ALSO HAS A HISTORY

4. David Dennison, an American theorist from Michigan, combined all of these themes, and a few of his own, to come up with the modern theory.

All of these theorists, and a good many of the experimentalists, were at Bohr's institute in Copenhagen in 1926–1927.

THE MOMENT OF INERTIA OF HYDROGEN BEFORE 1927:

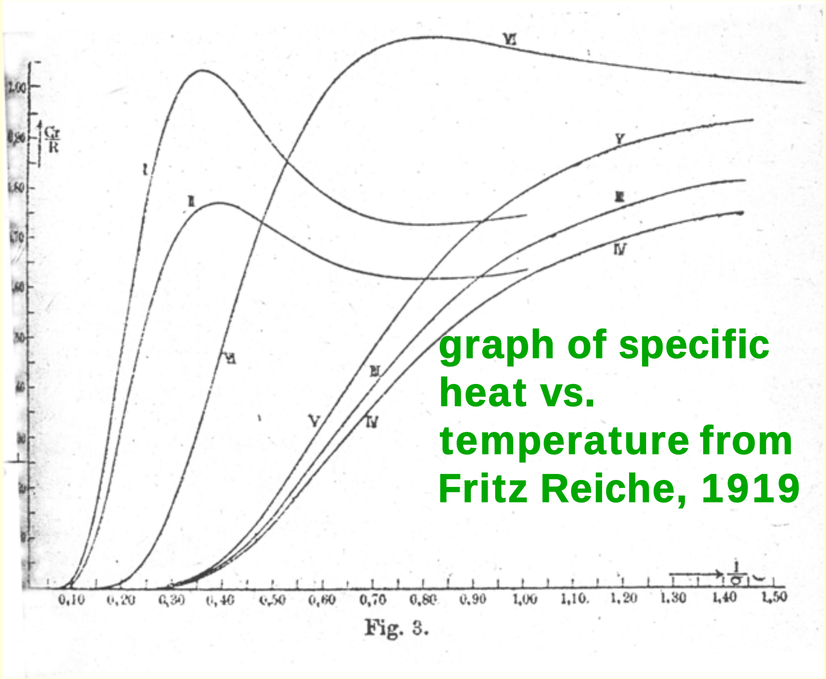


Fig. 3.

graph of specific heat vs. temperature from Fritz Reiche, 1919

$$C_R/R \text{ vs. } 1/\sigma \quad \text{where } \sigma = \frac{h^2}{8\pi^2 JkT}$$

J from specific heat of hydrogen	
	J (in gm-cm^2)
Reiche (1919)	2.2 to 2.3 × 10^{-41}
Tolman (1923)	1.39 × 10^{-41}
Schrödinger (1924)	1.43 to 1.48 × 10^{-41}
Van Vleck (1926)	2.0 to 3.0 × 10^{-41}

By early 1920s, spectroscopic measurements began to give independent values for the moment of inertia J.

J from molecular spectra	
	J (in gm-cm^2)
Lenz (1919)	1.85 × 10^{-41}
Allen (1924)	1.5 to 1.8 × 10^{-41}
Curtis (1925)	1.25 to 1.8 × 10^{-41}

THIS ROUGH AGREEMENT WOULD BE SEEN AS SPURIOUS BY 1927.

MOLECULAR (BAND) SPECTRA AND MOMENTS OF INERTIA

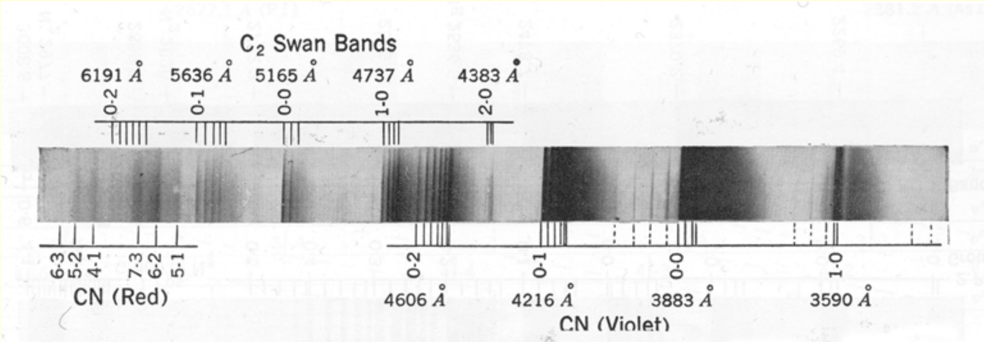
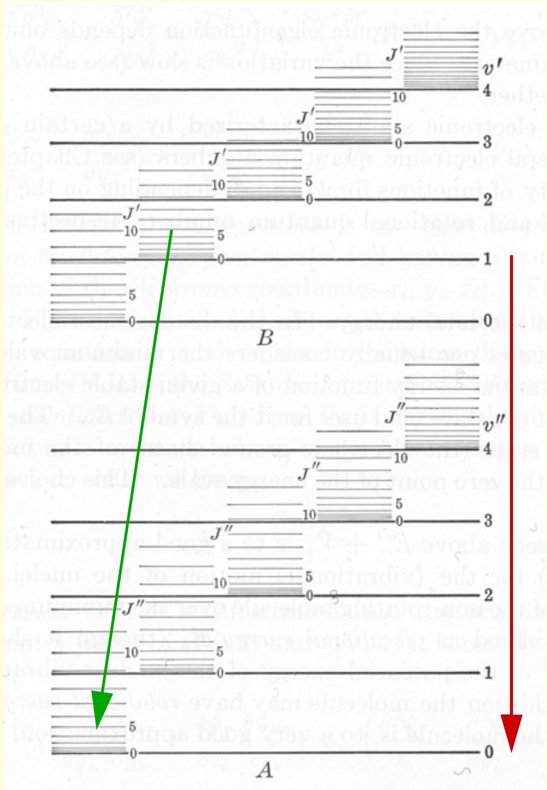


FIG. 7. Band Spectrum of the Carbon Arc in Air (Bands of the Molecules CN and C_2).



electronic state B

electronic state A

rotational quantum number

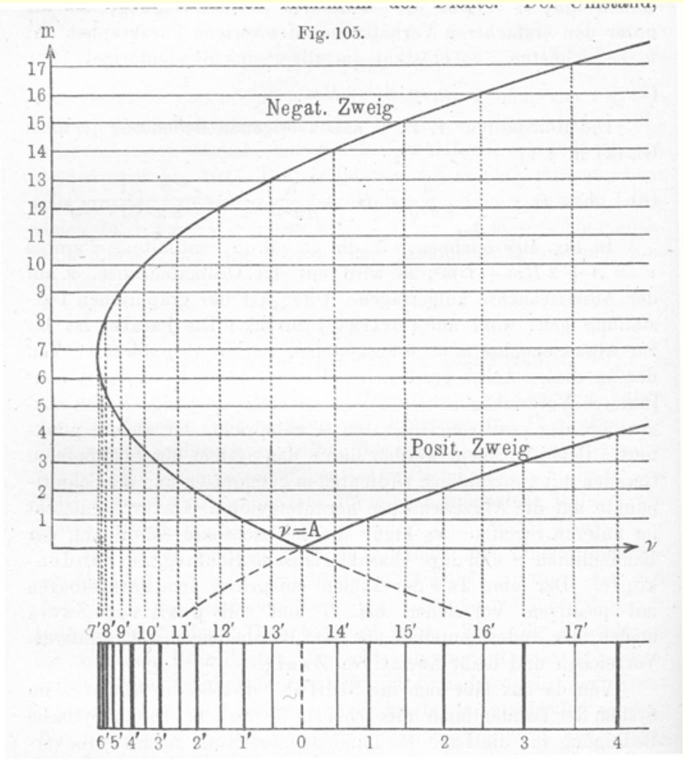


Fig. 105.

frequency

Each **band** represents a transition between specific *vibrational* levels in different electronic states.

Each band, under high resolution, consists of **lines** representing transitions among rotational states; line spacings allows the calculation of moments of inertia.

THE MANY-LINED SPECTRUM OF MOLECULAR HYDROGEN

- very complex—many hundreds of lines in visible and ultraviolet **emission** spectra
- no band heads (particularly in visible region); band structure not obvious

⇒ estimates of moments of inertia of hydrogen

- were difficult and uncertain; and
- tell us nothing about the moment of inertia in the ground state **... since as is well known, none of these series appears in absorption.** (Schrödinger, 1924)

Worse yet: Transitions to the ground state should appear in the far ultraviolet, where as Theodore Lyman tells us: **... the transparency of hydrogen [is] uncommonly great. Upon this observation is based the procedure of washing vacuum spectroscopic apparatus with this gas.** (Theodore Lyman, 1914)

- **vacuum** spectroscopy: air aborbs strongly in ultraviolet and so spectroscopes must be evacuated—adding another layer of experimental complexity!

A number of investigators are now working on the hydrogen spectrum ... but as the conclusions of various investigators are very conflicting, even in regard to the most fundamental points, we shall merely summarize as briefly as possible the main points ...

Raymond Birge (NRC report,1926)

JOHN JOSEPH HOPFIELD, GERHARD DIEKE, AND THE ABSORPTION BANDS OF MOLECULAR HYDROGEN

John Joseph Hopfield, a student of Raymond Birge, and Gerhard Dieke, who had studied with Ehrenfest and then come to California to do an experimental Ph.D., were the first to see ***absorption*** bands (and hence the ground state) in molecular hydrogen.

They also measured most of these bands in emission, including a few previously seen by Theodore Lyman.

Hopfield is doing the best vacuum spectroscopy of anyone in the world.

Raymond Birge to John Van Vleck, 1929

HOPFIELD, DIEKE, AND THE ULTRAVIOLET ABSORPTION BANDS OF MOLECULAR HYDROGEN

Dieke and Hopfield in 1926

- measured and identified bands in the extreme ultraviolet in both absorption and emission
- organized bands into "systems" that corresponded to transitions between two excited electronic states (B and C) and the ground state (A), and
- inferred an energy level diagram.

At about the same time (1926),

- all of the Lyman bands (subset of B → A, emission) published by Enos Witmer, who also did what turned out to be an incomplete rotational analysis
- Sven Warner, working at Niels Bohr's Institute of Theoretical Physics in **Copenhagen**, measured, again in emission, bands for the electronic transition C → A.

Upshot: By late 1926, the vibrational structure of the ground state A and the excited states B and C was well understood. The rotational structure was still largely unanalyzed.

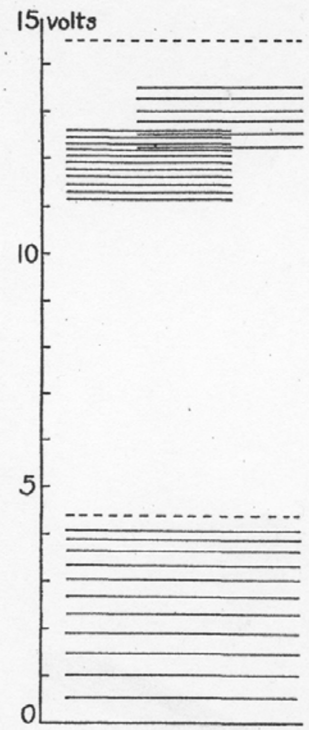


Fig. 10. Energy level diagram for the hydrogen molecule.

Dieke-Hopfield term diagram: Lines represent vibrational levels in each electronic state

EXPERIMENTAL SPECTROSCOPY IN COPENHAGEN

… the *Carlsberg Foundation* has made available to me a considerable sum of money for the construction and installation of a large *grating spectrograph*.

Niels Bohr, 1921

Dear Professor N. Bohr,

Allow me to give a brief account of my education up to the present and express my ardent wishes that I entertain now.

… I am sent by the Japanese government to Europe for the furtherance of my study.

Since I am specially interested in spectroscopy, … I am naturally attracted to your laboratory …

Takeo Hori (in Berlin) to Bohr, 9 May 1926

I am almost beside myself with joy to have received your letter, in which you have kindly permitted me to work in your laboratory …

Hori to Bohr, 21 May 1926

TAKEO HORI AND THE MOMENT OF INERTIA OF HYDROGEN

Last year Werner has found a new band system for hydrogen in the extreme ultraviolet ... At the suggestion of Professor Bohr I have carried on the investigation of these bands ...
While the work was in progress, an important work by Dieke and Hopfield appeared

Hori 1927

Hori remeasured and reanalyzed Werner bands (Dieke & Hopfield's C → A)

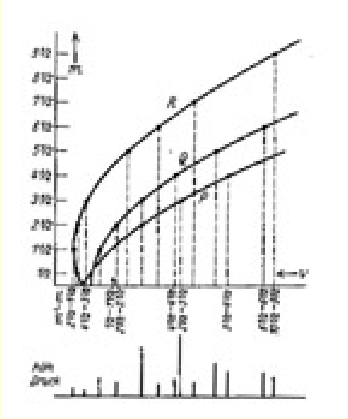
Hori reanalyzed Lyman bands (via Witmer; subset of Dieke & Hopfield's B → A)

Dieke & Hopfield: ground state, vibrational energy levels, term diagram

Result: Hori gave the first detailed analysis of the rotational structure of the H_2 ultraviolet bands, and found

$$J = 4.67 \times 10^{-41} \text{ gm-cm}^2$$

more than **double** previously accepted values; and exactly the value that David Dennison would need for his specific heat model.



I would like to thank Prof. N. Bohr ... To Dr. S. Werner I owe special thanks for unhesitating existance and valuable advice. Likewise I also thank Dr. Dennison, Dr. Fues, Dr. Hund, and Dr. Nishina for much useful advice.

Hori 1927

THE IMPORTANCE OF BEING IN COPENHAGEN

In 1924, Owen Richardson (Nobel Prize 1928, for thermionic emission) published the first in a long series of papers on the many-lined spectrum of hydrogen, primarily in the visible.

Richardson's work eventually led to a fuller understanding and integration of the visible and ultraviolet spectrum of molecular hydrogen, eventually collected in his 1932 book *Molecular Hydrogen and its Spectrum.*

In late1926 and early 1927, drawing on his own work in the visible, and on Werner, Witmer, and Dieke and Hopfield, he used an indirect method to estimate the moment of inertia of a hydrogen molecule in the ground state, and found a result about the same as Hori found later in 1927.

Nevertheless, Hori's result for the moment of inertia is almost exclusively cited. Richardson seemed a little put out. In his book he spends several pages describing his own results and Dennison's theory, and concludes dryly that

Hori's value ..., got from his analysis of the Werner and Lyman bands, was also published about the same time.

Richardson, 1932

SUMMARY AND LATER DEVELOPMENTS

- Werner Heisenberg (1926–1927)
- Friederich Hund (1927)
- **David Dennison (1927)** (modern solution)

  central: new value of *J* from band spectra measurements of 4.67×10^{-41}— more than double earlier results.

- experimental work continued through 1930s (Eucken, Paul Harteck, Karl Clusius, others) and included measurements of the specific heat of HD and D_2

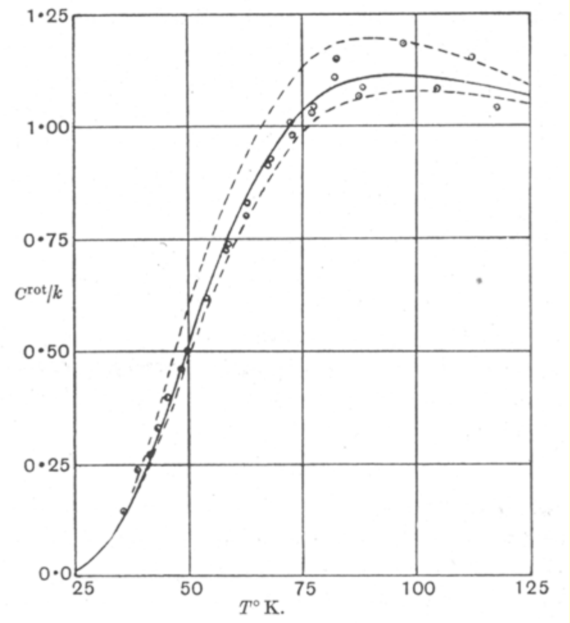


Fig. 3. The rotational molecular heat capacity of D_2.

from Fowler & Guggenheim, *Statistical Thermodynamics*, 1939

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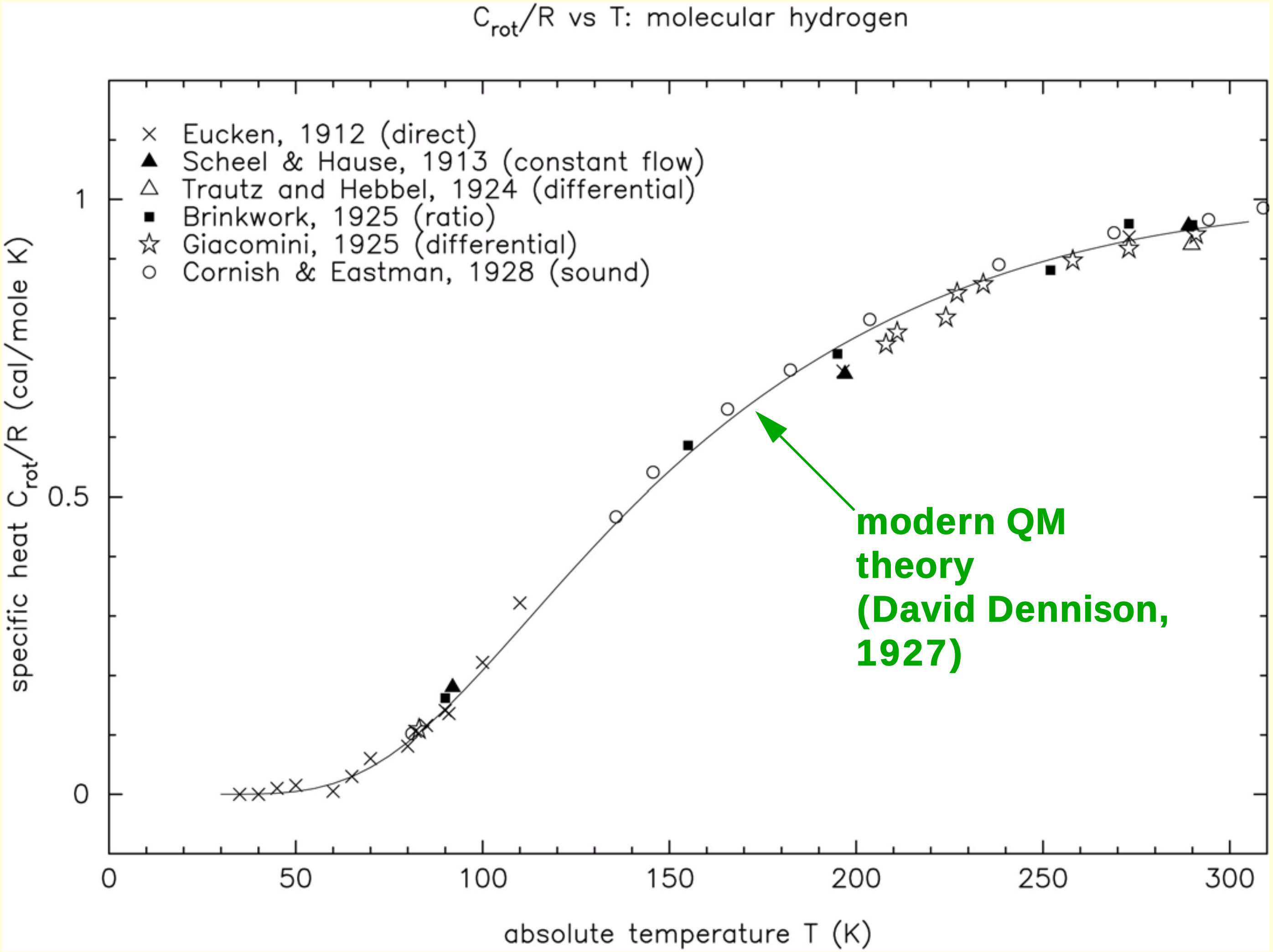
THEORY AND EXPERIMENT BY THE LATE 1920s



modern QM theory (David Dennison, 1927)

MODERN QUANTUM MECHANICS

- The energy of a rigid rotator (hydrogen molecule) is given by

$$E_n = n(n+1)\frac{h^2}{8\pi^2 J}, \quad n = 0,1,2\,\ldots$$

where *J* is the moment of intertia about axis perpendicular to a line joining the two H atoms, and passing through the center of mass.

- The two nuclei (protons) are **identical fermions** (spin 1/2)
- total nuclear spin/rotational wave function must be **anti-symmetric**

⇒ There are therefore **two varieties** of molecular hydrogen:

PARAHYDROGEN

singlet nuclear state (anti-symmetric) ⇔ symmetric rotational state (*n* even)

ORTHOHYDROGEN

triplet nuclear state (symmetric) ⇔ antisymmetric rotational state (*n* odd)

orthohydrogen ⇔ parahydrogen transition is slow