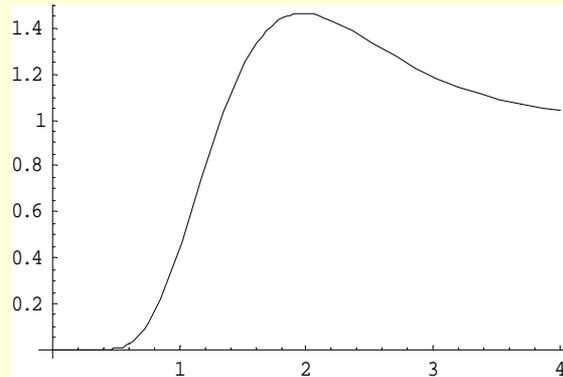
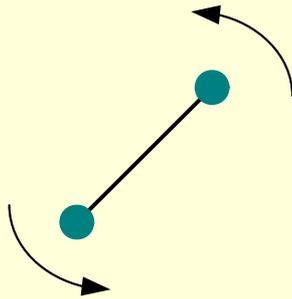


# THE ROTATIONAL SPECIFIC HEAT OF MOLECULAR HYDROGEN IN THE OLD QUANTUM THEORY

“ASTONISHING SUCCESSES” “BITTER DISAPPOINTMENT”

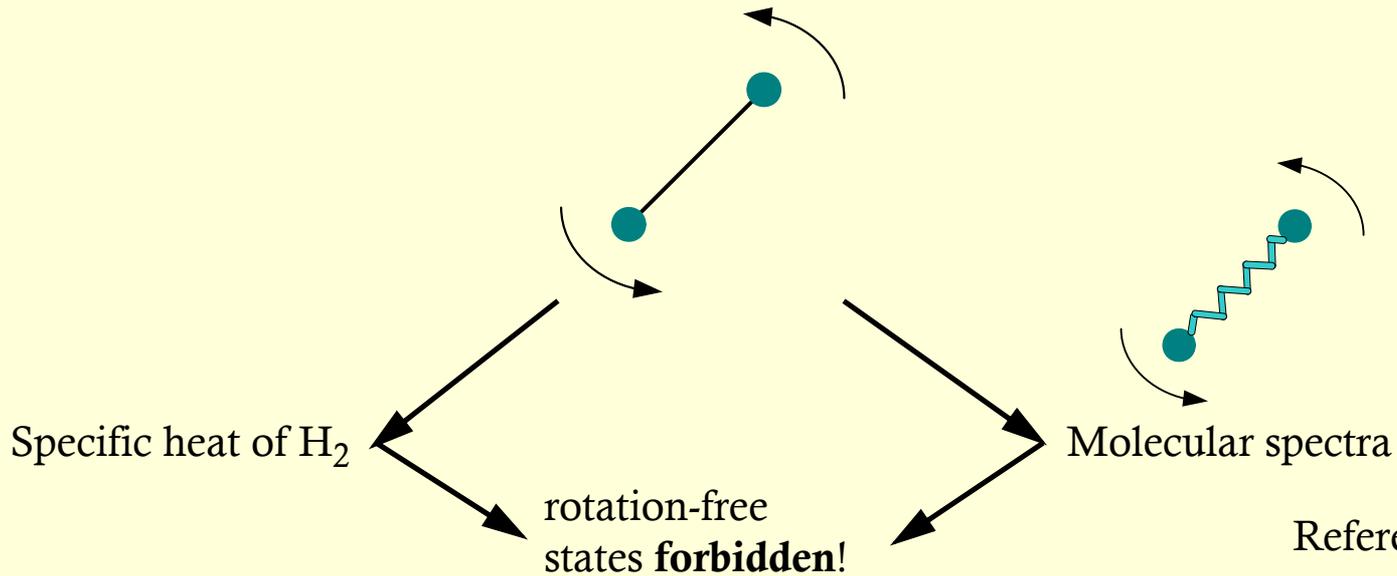
--Fritz Reiche, 1921



**Clayton Gearhart**  
**St. John's University**  
**(Minnesota)**

Max-Planck-Institut für Wissenschaftsgeschichte  
Berlin  
June 2006

# RIGID ROTATOR (ROTATING DUMBBELL)



References:

Chiyoko Fujisaki,  
*Historia scientiarum* **24**,  
53–75 and **25**, 57–86  
(1983)

Alexi Assmus, *Historical  
Studies in the Physical and  
Biological Sciences* **22**,  
209–231 and **23**, 1–34  
(1992)

- The rigid rotator was among the earliest problems taken up in the **old (pre-1925) quantum theory**.
- **The problem should have been simple**
  - relatively uncomplicated theory
  - only one adjustable parameter (moment of inertia)
- Nevertheless, **no accurate theoretical description emerged** in the old quantum theory
- Today: indistinguishable particles applied to wave function symmetry central to explanation

# MODERN QUANTUM MECHANICS

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

- 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)  $\Leftrightarrow$  symmetric rotational state ( $n$  even)

## ORTHOHYDROGEN

- triplet nuclear state (symmetric)  $\Leftrightarrow$  antisymmetric rotational state ( $n$  odd)

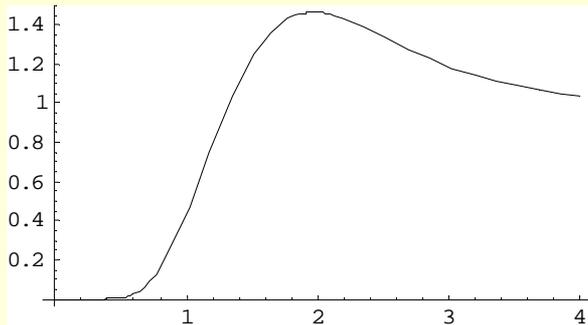
**ORTHOHYDROGEN  $\Leftrightarrow$  PARAHYDROGEN TRANSITION IS SLOW**

# MODERN QUANTUM MECHANICS

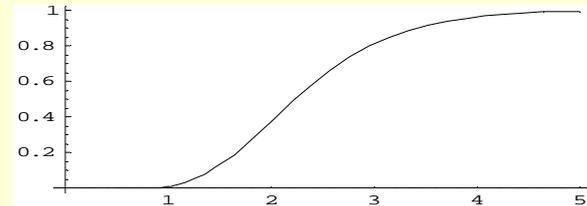
To calculate the specific heat of molecular hydrogen:

- Treat hydrogen as a (weakly interacting) mixture of para- and ortho-hydrogen, in the ratio 1:3 (room temperature ratio).

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



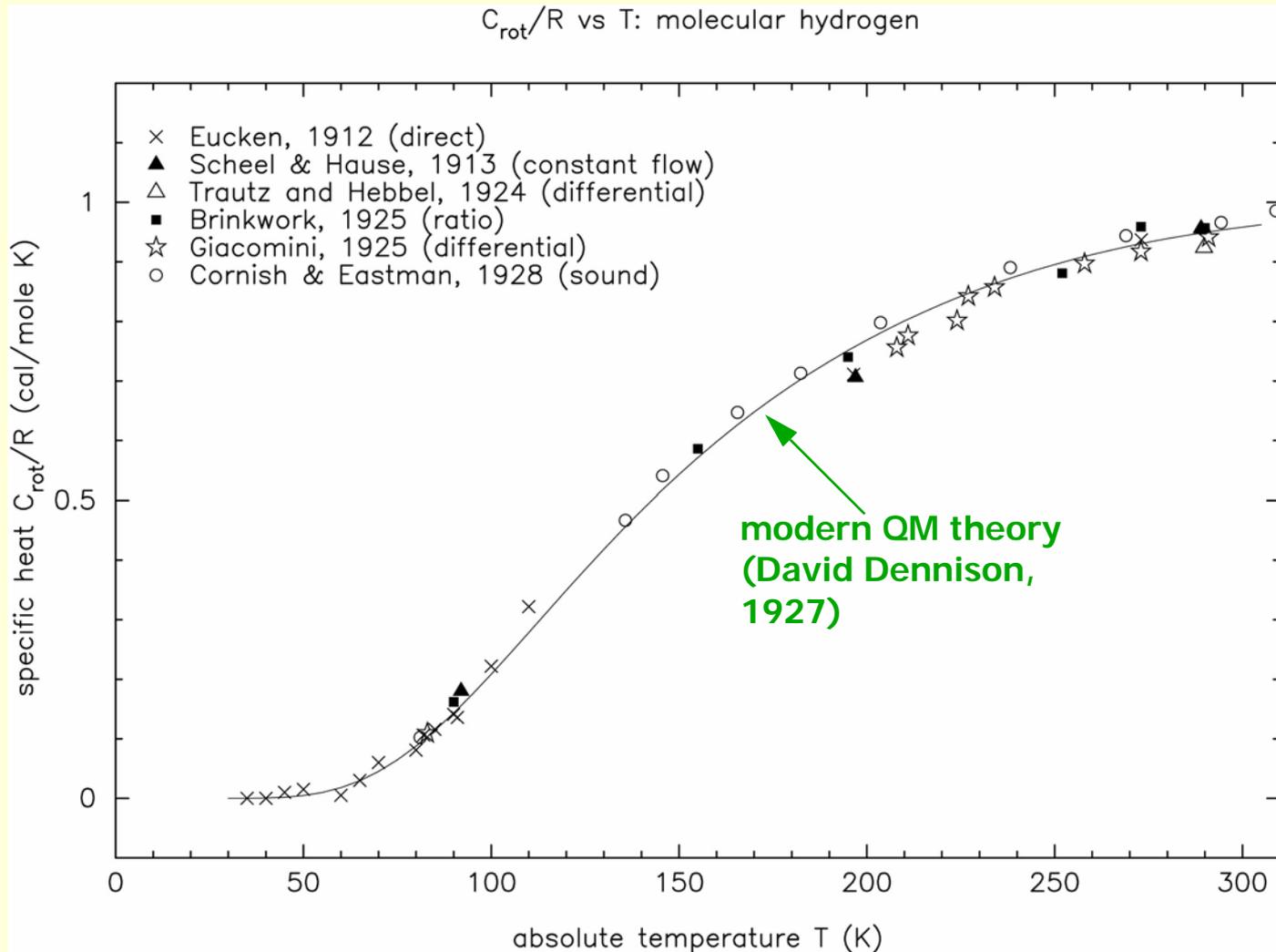
parahydrogen



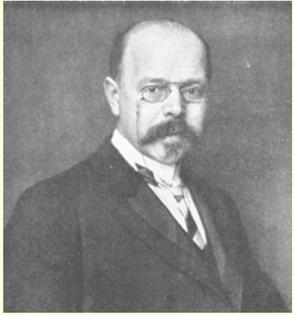
orthohydrogen

If one combines these two curves in the ratio 1 part para to 3 parts ortho, one obtains a smoothly decreasing curve that agrees well with experiment.

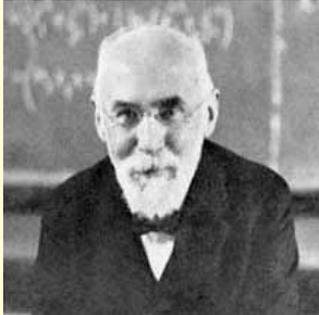
# THEORY AND EXPERIMENT BY THE LATE 1920s



# SPECIFIC HEAT OF HYDROGEN: WIDELY INVESTIGATED IN THE OLD QUANTUM THEORY



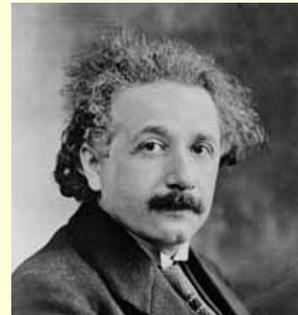
Nernst



Lorentz



Eucken



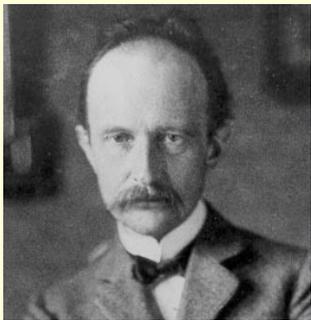
Einstein



Ehrenfest



Bohr



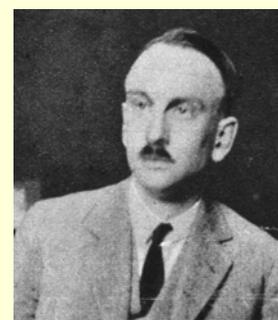
Planck



Reiche



Kemble



Tolman



Schrödinger



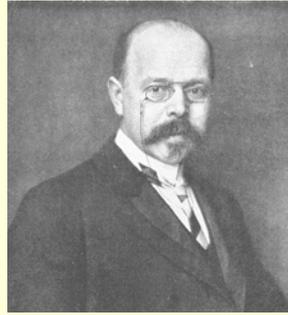
Van Vleck

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

I will be particularly interested in the work of **Fritz Reiche** in Germany, and **Edwin C. Kemble** in the U. S. in the years around 1920.

**OUR STORY BEGINS WITH**

# NERNST'S HEAT THEOREM



## Walther Nernst 1864 – 1941

- physical chemist
- studied with Boltzmann
- 1889: lecturer, then professor at Göttingen
- 1905: professor at Berlin

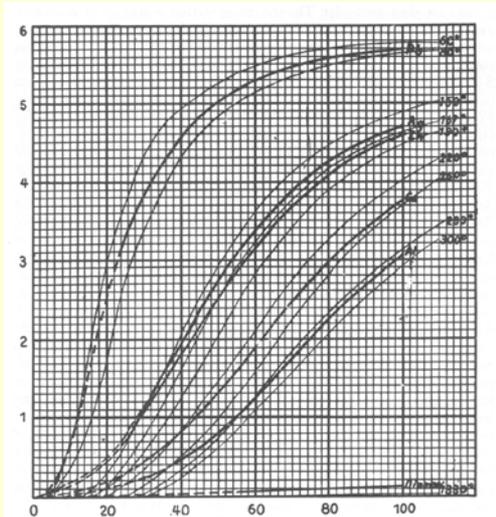
Nernst formulated his **heat theorem** (Third Law) in 1906, shortly after appointment as professor in Berlin.

# NERNST'S THEOREM AND QUANTUM THEORY

- Initially, had nothing to do with quantum theory.
- Understand the equilibrium point of chemical reactions.
- **Nernst's theorem had implications for specific heats at low temperatures.**
- 1906–1910: Nernst and his students undertook extensive measurements of specific heats of solids at low (down to liquid hydrogen) temperatures.

**“... one gets the impression that the specific heats are converging to zero as required by Einstein's theory.”** (Nernst 1910)

- Einstein in 1907: If one treated a solid as a collection of quantized harmonic oscillators, the specific heat should go to zero as  $T \rightarrow 0$ .
- As a result, Nernst became an enthusiastic promotor of quantum ideas.



Nernst's data (February 1911)

**... Nernst, who rescued all the results pertaining to this question from their theoretical limbo...**

Einstein (1911)  
(Solvay Conference)

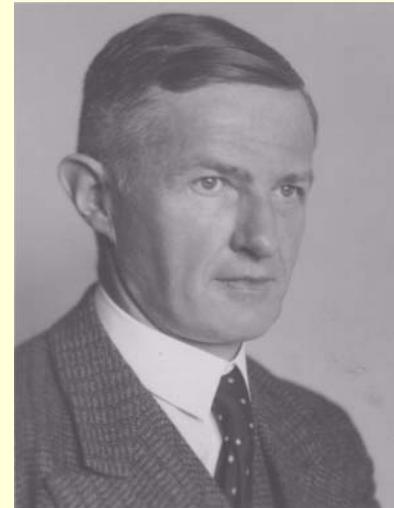
# THE SPECIFIC HEAT OF MOLECULAR HYDROGEN

- Initially, Nernst's Heat Theorem applied only to solids and liquids
- Early in 1911, Nernst speculated that the rotational (and for diatomic gases, vibrational) degrees of freedom **for gases** might show quantum behavior.
- Because of its low mass and low liquification temperature,  
**... The determination of the specific heat of hydrogen at low temperatures would therefore be especially interesting.** (Nernst 1911)

Arnold Eucken was one of Nernst's assistants, and had been closely involved in the measurements of the specific heats of solids.

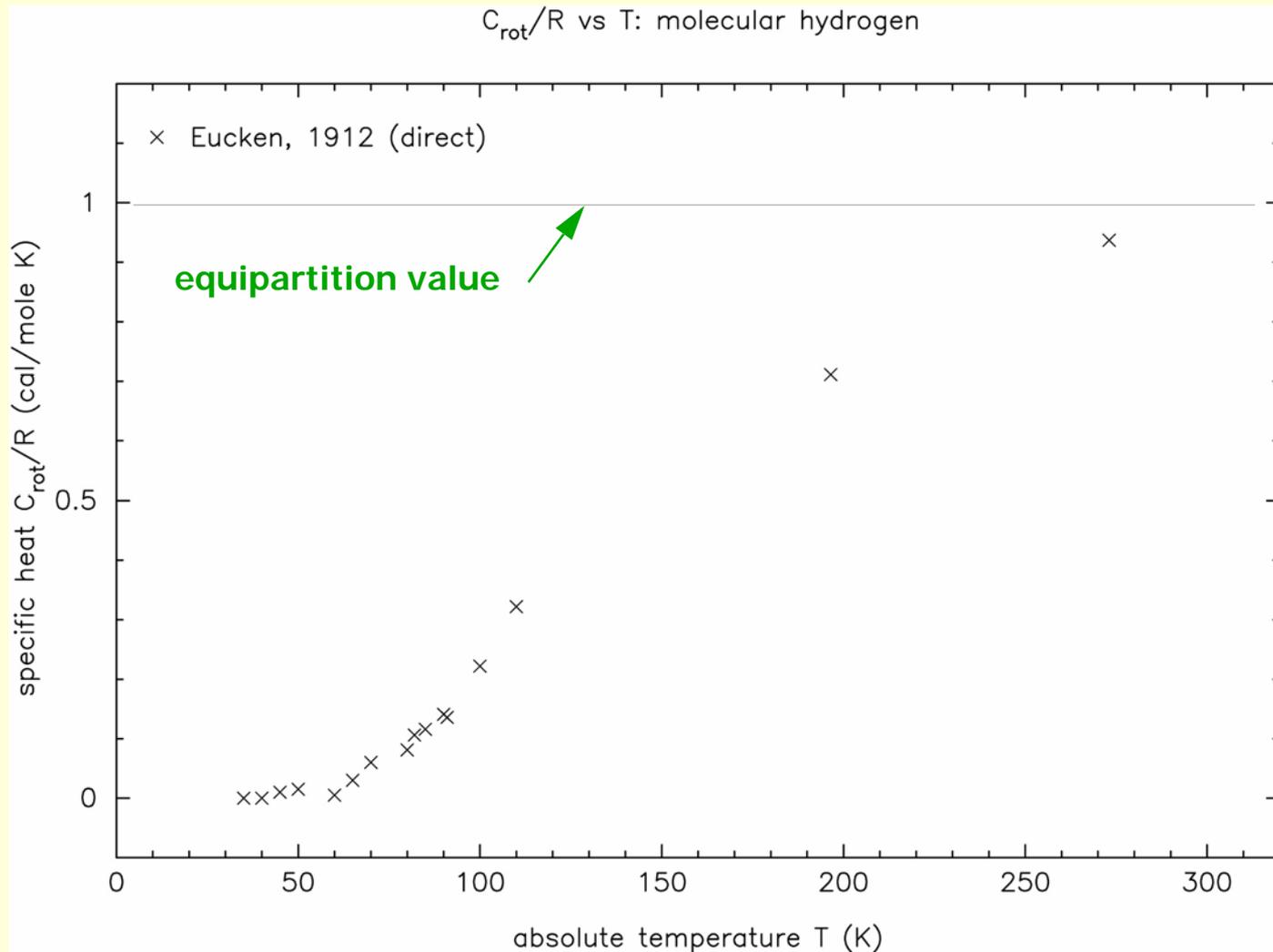
In 1912, he packed about 0.2 moles of  $H_2$  into a 39  $cm^3$  thin-walled steel chamber (pressure about 100 atm!), measured the specific heat down to about 30K.

Both the experiment and the data reduction were difficult. Eucken found ...



Arnold Eucken

# EUCKEN'S DATA



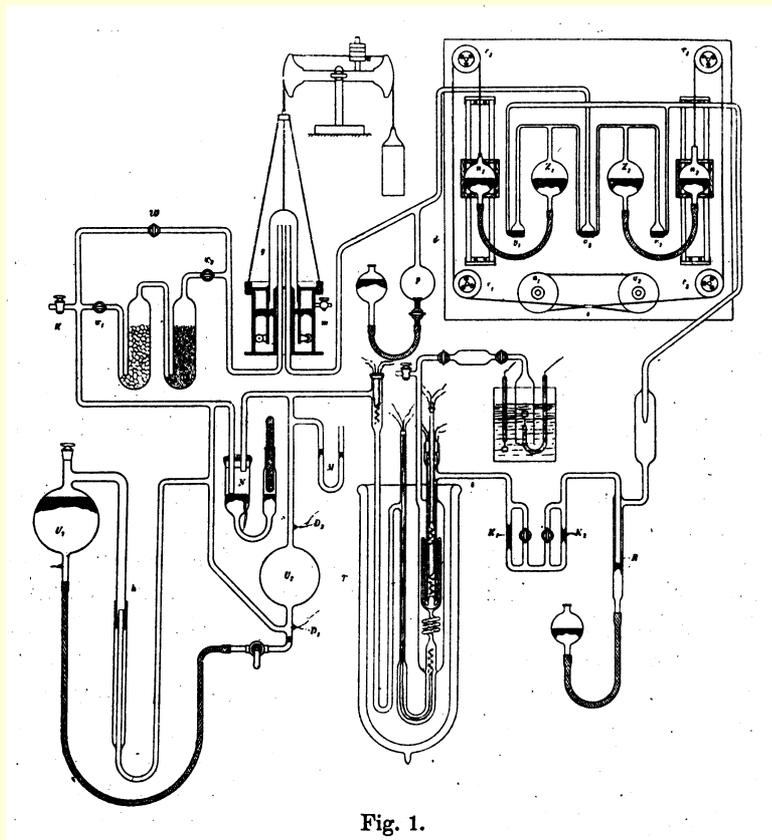
Eucken attempted to fit these data to Einstein's 1907 result for the specific heat of solids.

## MORE DATA

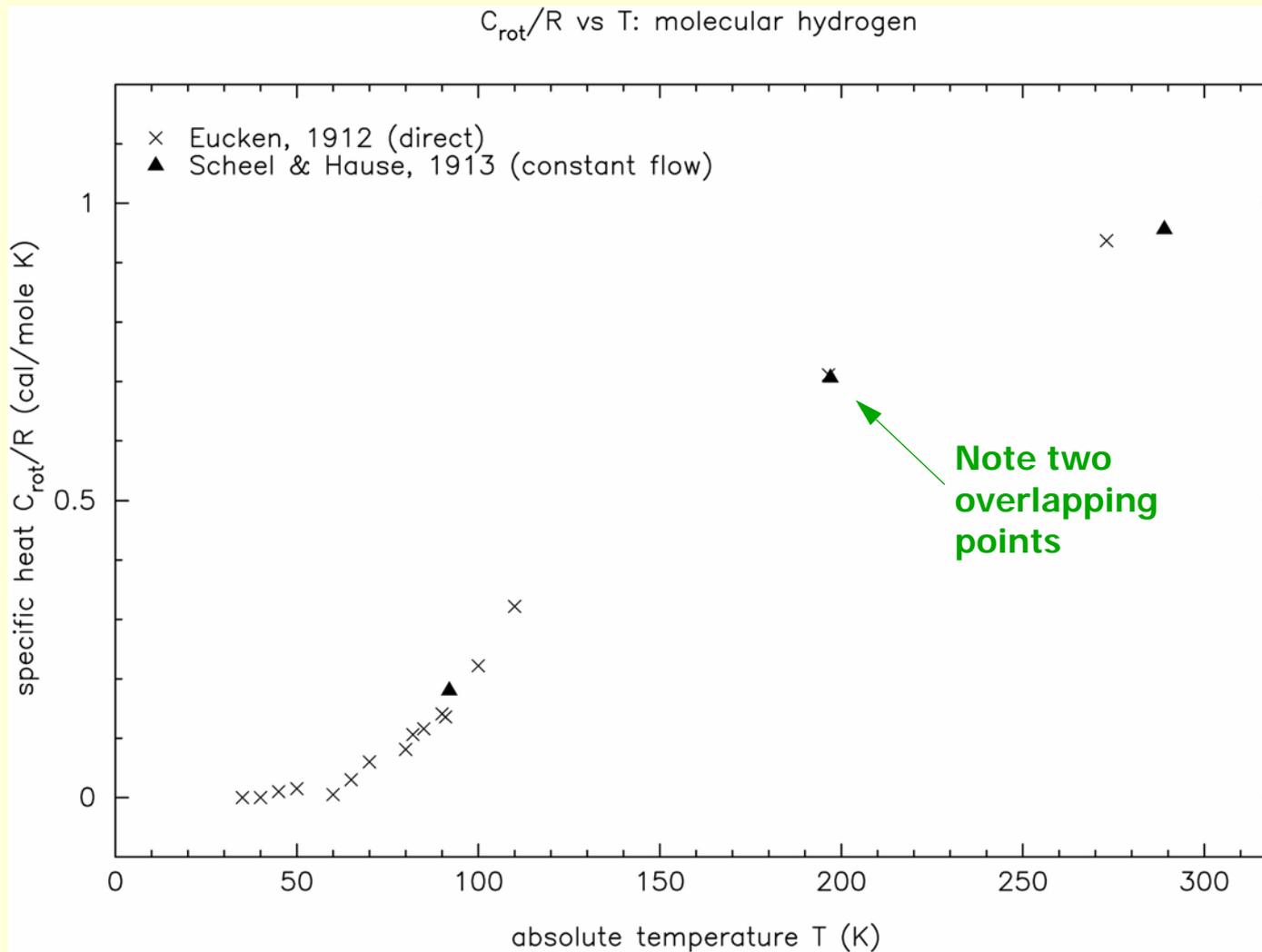
1913: Karl Scheel and Wilhelm Hause, working at the Physicalisch-Technische Reichsanstalt just outside Berlin, using the impressive-looking apparatus shown below (“Method of Constant Flow”), measured the specific heat of  $H_2$  at three temperatures, as part of a more general program of measuring specific heats of gases.

“The specific heats of helium and several diatomic gases”

*Annalen der Physik*, 1913



# DATA IN 1913



# AND NOW, THE THEORY

## QUANTUM THEORY OF THE RIGID ROTATOR APPLIED TO THE SPECIFIC HEAT OF HYDROGEN

### STAGES

1. The unquantized rotator: Nernst, Einstein, and Otto Stern, 1911–1913
2. Quantized rotators with one degree of freedom: Lorentz, Paul Ehrenfest, Erik Holm, others; 1913–1916 or so
3. Quantized rotators with two degrees of freedom: Max Planck, Fritz Reiche, Edwin C. Kemble, Niels Bohr, others; 1915–1925

Molecular spectra became increasingly important

- First, vibration-rotation spectra (e.g., HCl)
  - Later, vibration/rotation transitions in electronic spectra of H<sub>2</sub> (extremely complex, with thousands of lines); allowed for the independent measurement of the moment of inertia
4. Modern quantum mechanics: John Van Vleck, Friedrich Hund, David Dennison, others; 1926 on

# NERNST, FEBRUARY 1911

“Towards a theory of specific heats and on the application of the doctrine of energy quanta to physical chemical questions in general”

Zeitschrift für Electrochemie, 1911

In the following I would like to communicate the views of Einstein in a somewhat different form, and to be sure I will derive Einstein's formula not deductively from the general principles of statistical mechanics, but on the contrary through the direct calculation of a special simple case, through which I hope to formulate the views transparently and visually.

Nernst 1911

## EINSTEIN ON NERNST:

Nernst's standard work, "Theoretical Chemistry," offers, not only to the student but also to the scholar, an abundance of stimulating ideas; it is theoretically elementary, but clever, vivid, and full of intimations of manifold interrelations. It truly reflects his intellectual character.

Einstein (1942)

# NERNST AND SPECIFIC HEATS: FEBRUARY 1911

Nernst reviewed his results for the specific heats of solids; but the 1911 paper is as much about gases as about solids.

Nernst began by pointing out problems with equipartition in monatomic and diatomic gases:

- monatomic gases: no rotational degrees of freedom. **The theory furnishes not even a clue ...**
- diatomic gases: value  $5/2 R$  is ok for most gases, but halogens have considerably higher values, and the specific heats of all gases increase at higher temperatures.

**The theory can account for a new degree of freedom, as in the oscillation of an atom around its equilibrium position, but the gradual emergence of a new degree of freedom is (without new arbitrary assumptions) entirely senseless.**

# NERNST AND SPECIFIC HEATS: FEBRUARY 1911

Nernst first considered a mass point oscillating in a solid, and attempted to treat its three degrees of freedom:

**we can so visualize the motion of a point, that we project its path onto three mutually perpendicular planes, whereby we obtain three "oscillation circles" ["Schwingungskreise"].**

**Since we at first disregard the quantum theory and make the assumption, that the kinetic energy of the Schwingungskreise projected on a plane ... sits in equilibrium with the kinetic energy of the gas molecule projected on the same plane, we arrive at the second consequence, that in both cases the same distribution law obtains.**

That distribution turns out to be the Maxwell-Boltzmann **velocity** (not speed) distribution. Nernst applies the Maxwell-Boltzmann distribution to a solid. He then assumes that **a gas molecule which crashes (anprallt) onto a rotating atom is able to take on or withdraw only the energy quantum**

$$\varepsilon = h\nu = \frac{R}{N_0} \beta \nu$$

Nernst then supposes that the MB distribution is replaced by a stepwise one, and uses this approach to derive Einstein's result for the specific heat of a solid.

# NERNST AND SPECIFIC HEATS: FEBRUARY 1911

Rotational motion:

We have seen above, that a departure from the laws of statistical mechanics then emerges, if one concerns oneself with the rotation of atoms around an equilibrium position. If we make the certainly obvious generalization of the quantum hypothesis, that energy always will be absorbed only in fixed quanta not only for an oscillation about an equilibrium position, but also for an arbitrary rotation of masses, then we arrive at the wider conclusion that certain contradictions of the old theory may perhaps be clarified. It will for example be understandable, that a molecule of a monatomic gas may take on no noticeable rotational energy, since because of the smallness of the dimension of an individual atom, such a rotation could be identified with a Schwingungskreis of very high frequency.

We thus have an odd situation:

- Unlike an oscillator, a rotator has no fixed frequency.
- In Nernst's theory, a diatomic gas molecule exchanges rotational energy in fixed (harmonic oscillator) quanta (in collisions with a Schwingungskreis? with other molecules??). rotation frequency of molecule = frequency of oscillator?
- Nevertheless, neither the rotational velocity nor the energy is quantized.
- comment on rotational energy of a monatomic gas molecule is particularly hard to understand.
- Nernst notes that although the rotational velocities will be given by a MB distribution, he takes as a first approximation a constant rotational velocity equal to the square root of the temperature (equipartition result)! Einstein pointed out the inconsistency at the first Solvay conference.

# NERNST AND SPECIFIC HEATS: FEBRUARY 1911

Through this chain of reasoning, Nernst writes the following results:

Nernst's result for the average energy of a collection of quantized oscillators

$$W = 3R \frac{\beta\nu}{e^{\frac{\beta\nu}{T}} - 1}$$

derivative  $\Rightarrow$  Einstein's result for the specific heat

$$\frac{dW}{dT} = 3R \frac{e^{\frac{\beta\nu}{T}} \left( \frac{\beta\nu}{T} \right)^2}{\left( e^{\frac{\beta\nu}{T}} - 1 \right)^2}$$

↓

$$\beta\nu = a\sqrt{T}$$

equipartition result, substituted into  $W$

↓ derivative now leads to

$$\frac{R}{4} \left[ \frac{a}{\sqrt{T} \left( e^{\frac{a}{\sqrt{T}}} - 1 \right)} + \left( \frac{a}{\sqrt{T} \left( e^{\frac{a}{\sqrt{T}}} - 1 \right)} \right)^2 e^{\frac{a}{\sqrt{T}}} \right]$$

Nernst's result for the specific heat per degree of freedom of a diatomic molecule.

Nernst concludes this section by showing that this expression leads to the expected result (rotational contribution to specific heat =  $R$ ) for oxygen molecule at room  $T$ .

# FIRST SOLVAY CONFERENCE (NOV 1911): NERNST

At the first Solvay Conference in November 1911, Nernst repeated his February derivation of Einstein's specific heat result, but said comparatively little about gases.

- “Schwingungskreis” did draw some fire—how e.g. can energy be decomposed into components (Lorentz)?; led to discussion of multiple degrees of freedom
- Nernst did refer to his February paper, but otherwise made only a few brief allusions to the specific heats of gases.
- In the discussion after his talk, in an exchange with Poincaré, Nernst did say:

**The variable frequency  $\nu$  [of rotation] is determined by the rotational energy and the dimensions of the molecule. The difficulties that stand here in the way of the application of quantum theory are very substantial.**

**HOWEVER ...**

# FIRST SOLVAY CONFERENCE: EINSTEIN

Einstein devoted a short section to the rigid rotator in his talk:

- several letters suggest an earlier interest in this problem, and in talk, he said

**I tried to solve this problem, but did not succeed because of mathematical difficulties.**

- Then, adopted a sanitized version of Nernst's model:

**If, with Nernst, we assume for the sake of simplicity that all molecules of the diatomic gas being considered have a definite angular frequency  $\nu$ , which is the same for all molecules, then the relation between the rotational energy  $E$ , the frequency, and the temperature will not differ substantially from the corresponding relation for the linear oscillator. We have approximately**

$$E = \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1}$$

**... we must assume in accordance with mechanics**

$$E = \frac{1}{2} I (2\pi\nu)^2$$

**These two equations contain the relation between  $E$  and  $T$  we have been looking for; all that remains is to eliminate  $\nu$**

He added in a footnote:

**Instead of the second of these relations, Nernst assumed the relation  $\beta\nu = a\sqrt{T}$ . But this relation could only be satisfied if the specific heat were independent of the temperature.**

# FIRST SOLVAY CONFERENCE: EINSTEIN

Einstein said nothing about Nernst's conceptual framework, nor about how he was interpreting these equations.

## Einstein:

- Assume all rotators have same rotational frequency
- Equate rotator kinetic energy to average kinetic energy of a Planck "resonator" (harmonic oscillator) with same frequency

Earlier, Einstein had pointed out that a monatomic gas molecule could not be treated in this way, and added

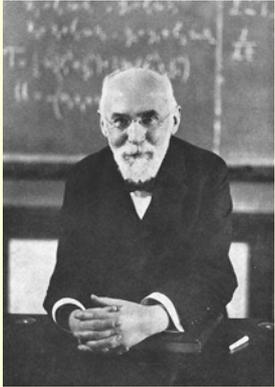
**We thus see that we should greet with skepticism each new application of the method of deducing the thermal properties of matter from the radiation formula.**

$$\frac{1}{2} J (2\pi\nu)^2 = \frac{h\nu}{e^{h\nu/kT} - 1}$$

The rotator is **not** actually quantized. Does it nevertheless absorb/give off quanta  $h\nu$ ?

**THERE WAS ONE MORE CONTRIBUTION TO THE DISCUSSION:**

# FIRST SOLVAY CONFERENCE: LORENTZ



## QUANTIZING THE RIGID ROTATOR

**Lorentz:**

Quantize the rotator energy directly (comment following Einstein's report):

$$\frac{1}{2}J(2\pi\nu)^2 = nh\nu, \quad n = 0, 1, 2, \dots$$

$J$  = moment of inertia

$\nu$  = frequency of rotation

**But then, this remark is of no great significance. When applying the hypothesis of energy elements, one can confine oneself to systems for which a definite frequency determined by the nature of the process is given in advance.**

**BOTH SUGGESTIONS WERE PURSUED.**

# EINSTEIN AND OTTO STERN, 1913

“Some arguments for the Assumption of Molecular Agitation at Absolute Zero”



Otto Stern

Stern did his Ph.D. with Otto Sakur in Breslau in 1912. Sakur had worked with Nernst, and published a series of papers (“Sakur-Tetrode equation”) on quantizing the monatomic ideal gas.

$$\frac{1}{2} J (2\pi\nu)^2 = \frac{h\nu}{e^{h\nu/kT} - 1} + \frac{h\nu}{2}$$

zero-point energy

“Planck’s first theory:”

- Quantized energy levels
- No zero-point energy

“Planck’s second theory:”

- Continuous energies
- Quantized energies emitted when resonator is on the boundary of a **finite** phase-space cell
- Quantized energy replaced by the **average** energy within a **finite** phase-space cell.

⇒ leads to “zero-point energy” of sorts

... [the specific heats] **are equivalent for structures with unchanging  $\nu$ , whereas the theory of those structures whose  $\nu$  has different values for different states is substantially affected by the assumption of a zero-point energy.**

# EINSTEIN AND STERN, 1913

$$E = \frac{1}{2} J (2\pi\nu)^2 = \frac{h\nu}{e^{h\nu/kT} - 1} + \frac{h\nu}{2}$$

zero-point energy

$dE/dT$  gives the specific heat; one solves (numerically) a transcendental equation to find  $\nu(T)$

Einstein and Stern say nothing about the physical picture that underlies this equation. Note however that:

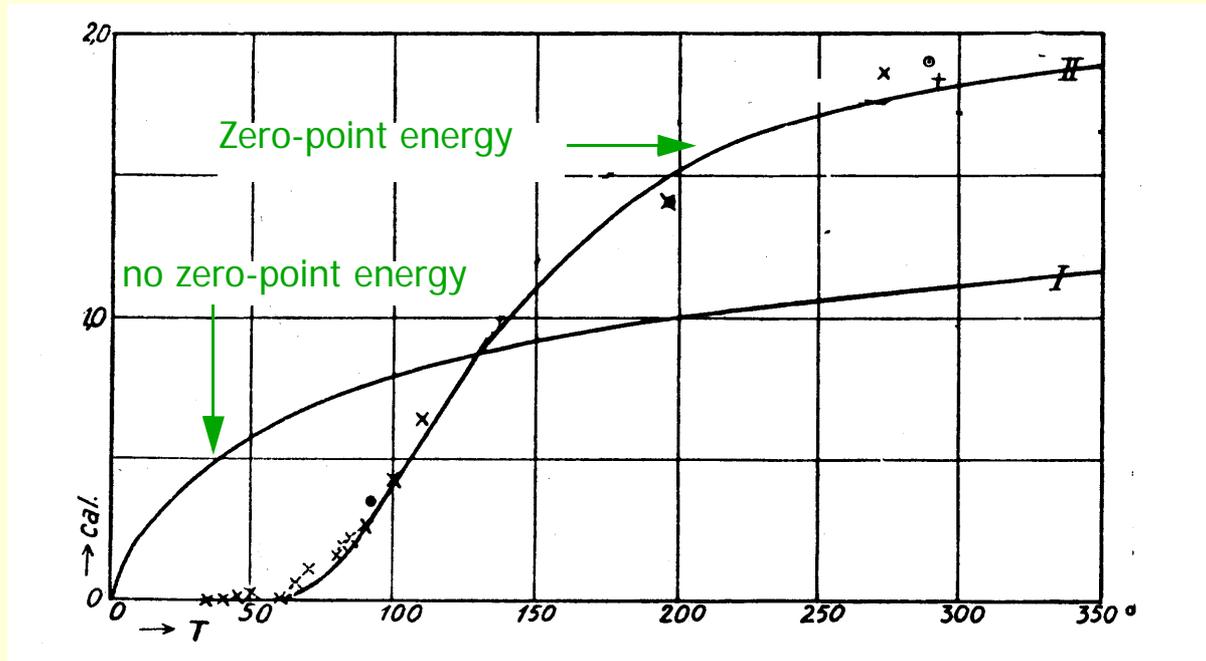
- “**for the sake of simplicity**” the rotational speed is the same for all molecules
- interest is as much about the harmonic oscillator and Planck’s two theories as it is about the specific heat of hydrogen.
- rotator frequency  $\nu(T)$  and energy are *continuous* functions of temperature! The rotators are *not* quantized, but do rotate at the frequency of the oscillator.
- $\nu(T)$  is nevertheless not “classical”—as Nernst’s was. In particular, for the zero-point case,  $\nu(T = 0) = \pi^2 / J \neq 0$  ; so rotator also has zero-point energy.
- rotator presumably absorbs/emits resonator quanta when interacting with a resonator.

**... the thermal energy of every structure depends on the temperature in the same way as that of the resonators in Planck’s theory does.**

Einstein, “Max Planck as Scientist,” 1913

**Aside:** In same paper, they give a derivation of Planck radiation law that assumes no discontinuities. But zero-point energy is  $h\nu$ , not  $h\nu/2$ .

# EINSTEIN AND STERN: RESULTS



In spite of what Einstein and Stern called “splendid agreement” for the zero-point motion result, Einstein soon lost confidence in this calculation, and it vanished from sight. By the end of 1913, in a letter to Ehrenfest (V, 481), Einstein pronounced zero-point motion “**dead as a doornail**” (“**maustot ist**”).

## **Kein Teufel weiss warum and nach welchem Gesetz.**

Einstein on Eucken’s data, summer 1913, notes of Walter Dällenbach (CPAE 4)

Nevertheless, this work inspired another calculation by ...

# THEORY: QUANTIZING THE RIGID ROTATOR

## PAUL EHRENFEST, 1913



“Remark concerning the specific heat of diatomic gases”

It is at any rate worth pointing out, that the snuggling up [Anschmiegen] [of a specific heat curve] to the horizontal axis at  $T = 0$ , to infinitely high order, may be produced entirely without the introduction of a zero-point energy.

# EHRENFEST'S CALCULATION OF THE SPECIFIC HEAT

## Three Steps:

1. **Calculate energy of a rotator:** Ehrenfest, following Lorentz, quantized the rotators

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

$$\Rightarrow \varepsilon_n = \frac{1}{2} J (2\pi\nu)^2 = n^2 \frac{h^2}{8\pi^2 J}$$

Ehrenfest noted enigmatically that his factor of 2

**... may be demonstrated from a very general point of view.**

Adiabatic hypothesis! See for example Klein, *Ehrenfest*.

Ehrenfest did not call attention to the sharp difference in approach

# EHRENFEST'S CALCULATION OF THE SPECIFIC HEAT

1. Calculate energy of a rotator:

$$\Rightarrow \varepsilon_n = n^2 \frac{h^2}{8\pi^2 J}$$

2. Calculate the dependence of the specific heat on temperature:

$$Q = \sum_{n=0}^{\infty} e^{-\varepsilon_n / kT}$$

$$c_R = Nk\sigma^2 \frac{d^2 \ln Q(\sigma)}{d\sigma^2}, \quad \sigma = \frac{h^2}{8\pi^2 JkT}$$

**Aside:** Einstein would have found it straightforward to have adopted this technique.

# EHRENFEST'S CALCULATION OF THE SPECIFIC HEAT

1. Calculate energy of a rotator:

$$\Rightarrow \varepsilon_n = n^2 \frac{h^2}{8\pi^2 J}$$

2. Calculate the dependence of the specific heat on temperature:

$$Q = \sum_0^{\infty} e^{-\varepsilon_n/kT} \quad c_R = Nk\sigma^2 \frac{d^2 \ln Q(\sigma)}{d\sigma^2}, \quad \sigma = \frac{h^2}{8\pi^2 JkT}$$

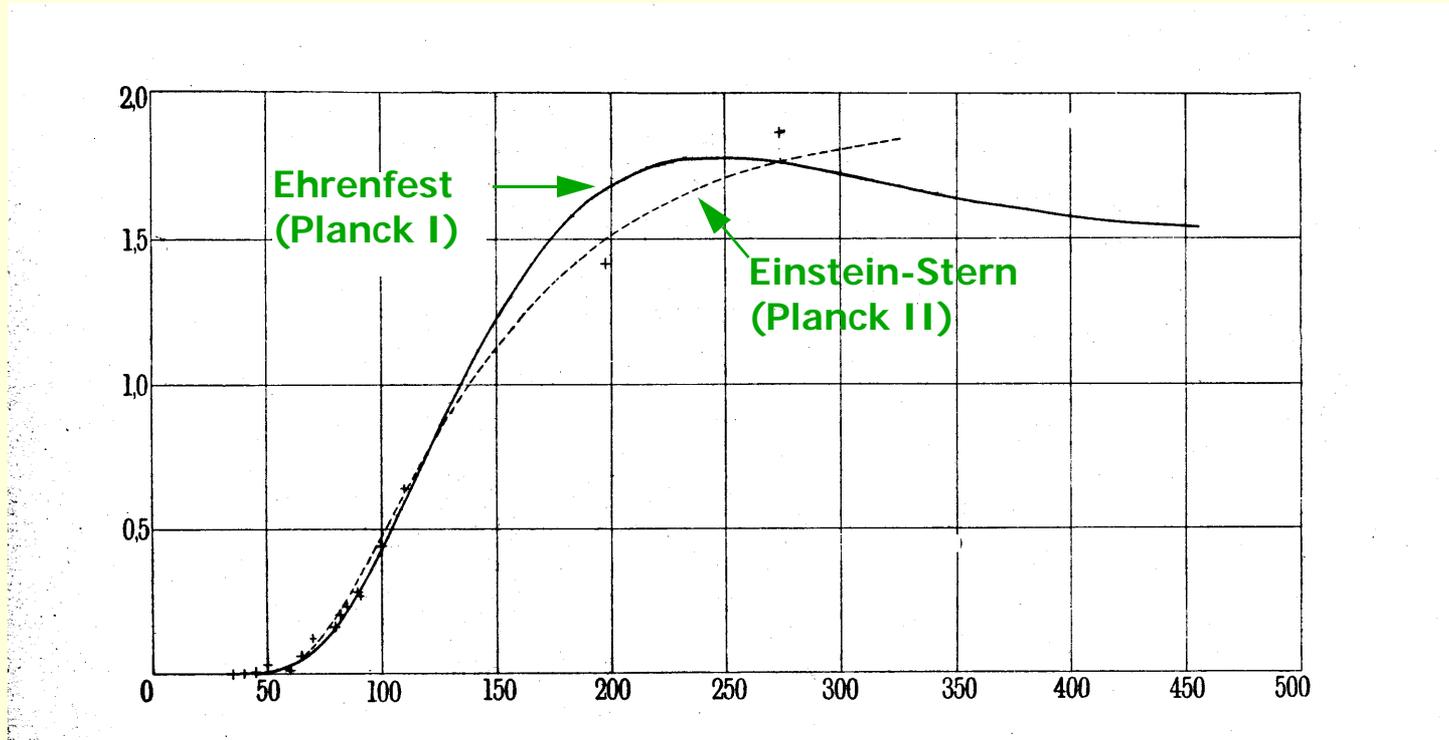
**3. Take into account both rotational degrees of freedom:**

$$c_R = 2Nk\sigma^2 \frac{d^2 \ln Q(\sigma)}{d\sigma^2}$$

The sum  $Q$  and the specific heat are not easy to calculate (series converges slowly for large  $\sigma$ ); Ehrenfest used a Jacobian theta function to get around this problem. He found ...

# EHRENFEST'S RESULT

Specific heat (cal/mole-K) vs absolute Temperature

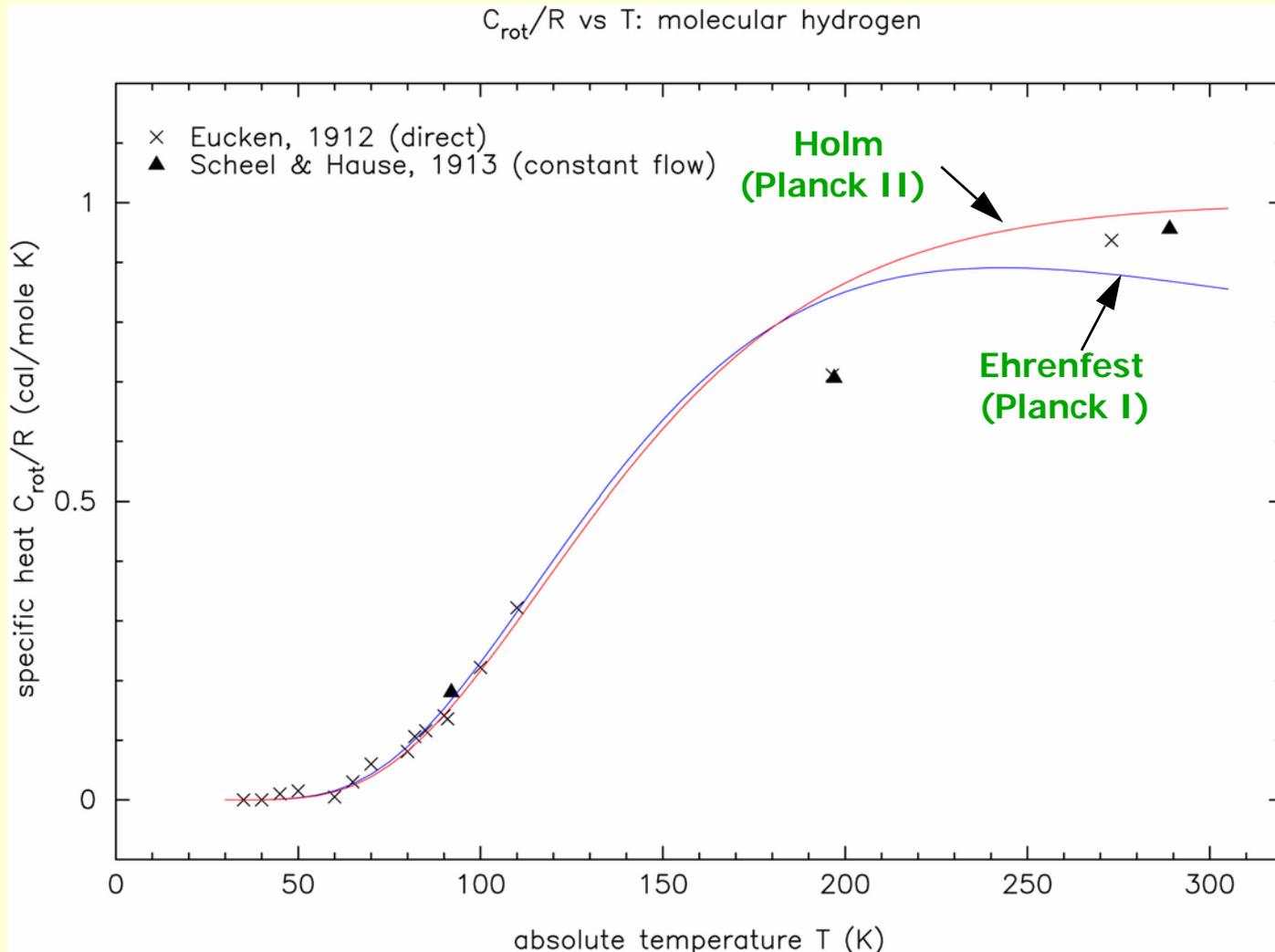


Ehrenfest noted the peak in the specific heat curve, but did not say much about it.

# ERIK HOLM AND PLANCK'S SECOND THEORY

Later in 1913, Erik Holm used Ehrenfest's calculational methods, but Planck's *second* theory (*continuous* energies, zero-point energy) to find the specific heat:

Swedish;  
former  
mining  
engineer;  
Ph.D.  
thesis

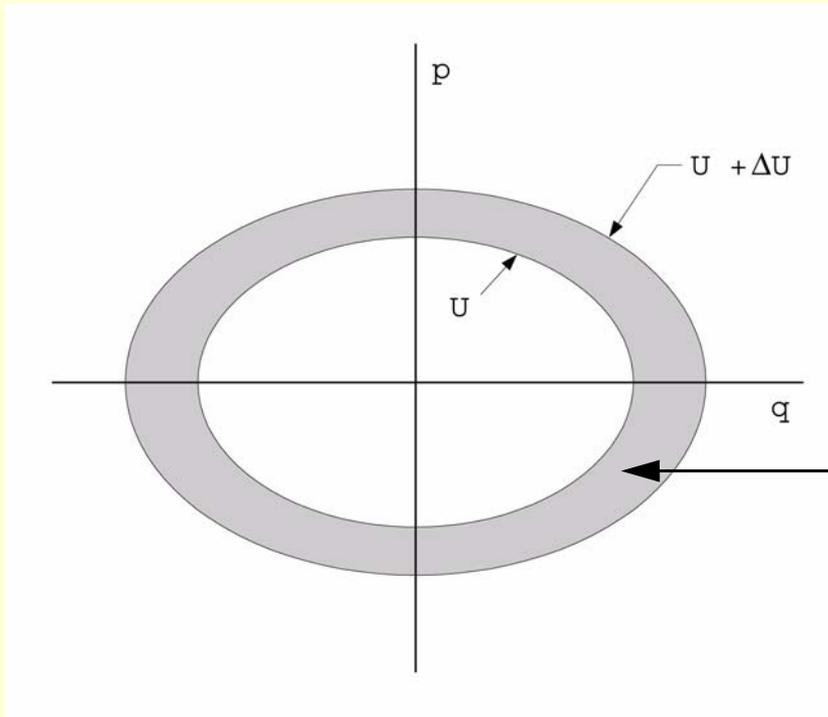


Jan von Weissenhoff, a student of Simon Ratnowski (Privatdocent in Zürich), published a similar theory in 1916, in which he investigated paramagnetism as well as the specific heat of  $\text{H}_2$ .

# PLANCK AND THE PHYSICAL STRUCTURE OF PHASE SPACE

Ehrenfest's and Holm's work seem to have caught Planck's attention.

In 1906, Max Planck showed that his one-dimensional “resonators” could be described by a “surface” of constant energy in “phase space,” a graph of momentum  $p$  vs. position  $q$ .



$$\text{Energy } = U = \frac{p^2}{2m} + \frac{1}{2}kq^2$$

path of constant energy is an ellipse in phase space

If  $U = nh\nu$  then the area of a finite “cell” (grey area) in phase space is Planck's constant. Plank called these cells “elementary domains of probability.”

This area of a cell is proportional to the probability of finding an oscillator in a particular cell. This result justified his assumption that all “complexions” are equally probable.

# PLANCK AND THE PHYSICAL STRUCTURE OF PHASE SPACE

In a series of three papers submitted in November and December of 1915, Planck generalized his treatment to **several degrees of freedom**

- “**hypersurfaces**” in multi-dimensional phase space determined quantum condition and the “volume” of finite phase space cells.
- energies are continuous (Planck’s “second theory”); average energy within the  $n$ th phase space cell used to calculate thermal properties, using same partition function technique as Ehrenfest (with which Planck was in any case familiar).

In the first paper, “The Quantum Hypothesis for Molecules with Several Degrees of Freedom (First Part),” Planck noted

**It is characteristic of the quantum hypothesis, in opposition to the classical theory, that the elementary domains of probability possess a definite form and size; in particular, their boundaries will be defined by certain  $(2f-1)$  dimensional hypersurfaces.**

**Their determination constitutes the most important but also the most difficult part of the problem. The simplest case is the one in which these hypersurfaces are simultaneously the surfaces of constant energy...**

In this case, the volume of the  $f$  dimensional phase space bounded by an energy  $u_n$  is

$$\int_{u=0}^{u=u_n} d\phi_1 \cdots d\psi_n = (nh)^f$$

# COHERENT AND INCOHERENT DEGREES OF FREEDOM

From Edwin P. Adams, *Quantum Theory*, NRC Bulletin 1920 and 1923

**In general, each degree of freedom furnishes one hypersurface; but it often happens that two or more degrees of freedom lead to the same hypersurface. Such degrees of freedom, with common hypersurfaces, Planck calls “coherent” degrees of freedom.**

Adams, 1920, p. 309

(Planck’s definition is more technical, and involves the details of how one calculates the volume of phase space.) Thus, Planck’s model for hydrogen is an example of a problem displaying coherent degrees of freedom. He did not introduce this terminology until the second paper in the series.

# PLANCK AND THE SPECIFIC HEAT OF HYDROGEN

Planck took a rigid rotator, with two degrees of freedom, as a simple example. **He applied this model to the specific heat of hydrogen**, using the same mathematics as Holm and Ehrenfest

- The average energy within a cell turns out to be.

$$\bar{u}_n = \frac{h^2}{8\pi^2 J} \left( n^2 + n + \frac{1}{2} \right)$$

- The size of the corresponding phase space cell and the related probability of finding a molecule in that cell are.

$$G_n = \left\{ (n+1)^2 - n^2 \right\} h^2 = (2n+1)h^2 \quad p_n = 2n+1$$

Planck calculated the specific heat from the partition function, in a manner similar to Ehrenfest. Planck was in any event thoroughly familiar with this formalism. He wrote his “thermodynamic potential” (the free energy divided by the temperature) in terms of the logarithm of the partition function (to which, at this stage, he gave no name and no symbol):

$$\Psi = Nk \ln \sum_0^{\infty} (2n+1) e^{-(n^2+n+\frac{1}{2})\sigma} \quad \sigma = \frac{h^2}{8\pi^2 JkT}$$

The specific heat is just the second derivative. Planck found correct limiting behavior at high and low temperatures. However, the calculations for intermediate temperatures were more difficult than for Ehrenfest and Holm:

**Unfortunately, the sum does not reduce so simply to a Jacobean theta function...**

Planck 1915

He did not do a graph.

# By 1916

By 1916, **two sets** of techniques had been developed for treating

- systems with **several degrees of freedom**; and
- **degenerate** energy states (**several quantum states with the same energy**)

action integral ( Sommerfeld and others)

$$\oint p dq = nh$$

led to quantized momentum and quantized energy states for several degrees of freedom.

Paul Epstein and Karl Schwarzschild independently treated multiple degrees of freedom and degenerate systems:

- Stark effect
- Epstein: **unsuccessful model for specific heat of hydrogen**, based on Bohr molecular model

Planck's "Physical Structure of Phase Space"

Context: Planck's "second theory"

"**Surfaces**" in multi-dimensional phase space defined both quantum conditions and phase space cells

Distinguished between

- "**coherent**" degrees of freedom (several degrees of freedom coalesce into one)
- "**incoherent**" degrees of freedom

The "volume" of a cell in phase space played a role similar to that of degenerate states

Planck had applied his theory to the specific heat of hydrogen, but had not done a graph.

**Fritz Reiche** in Germany, **Niels Bohr** in Denmark, and **Edwin C. Kemple** in the U.S., applied the new formalism to the specific heat of molecular hydrogen.

# FRITZ REICHE (1883–1969)



- Ph.D. with Planck, 1907
- 1908–11: in Breslau
- 1913: Privatdocent in Berlin
- 1915–18: assistant to Planck
- 1919–1920: advisor to Fritz Haber in the Physical Chemistry Institute in Berlin
- 1921–1933: Professor in Breslau
- 1921: widely read quantum theory textbook

**Fritz Reiche was one of the very few research pupils of Max Planck ... He was a tiny delicate Jew who combined the typical humor of the Berliner with a deep melancholy and pessimism. ... I learned from him a great deal about radiation and quantum theory which he had studied at the source, in personal contact with Planck.**

--Max Born

**1919: “On the Quantum Theory of the Rotational Heat of Hydrogen”**

# IMMEDIATE CONTEXT OF REICHE 1919

## Paul Epstein (1916)

Used Bohr's (1913) model of H<sub>2</sub> molecule (3 degrees of freedom), in which moment of inertia was not a free parameter; poor agreement.

## Simon Ratnowski

Privatdocent at Zürich; Ph.D. advisor to both Jan von Weysenhoff (SP?) and Sophie Rotszajn.

## Jan von Weysenhoff (1916)

One degree of freedom (had completed thesis in 1915); specific heat calculation similar to Holm; also did paramagnetism based on rotator.

## Adolf Smekal (1918)

Treated paramagnetism based on Planck's first theory (quantized energies, Hamilton-Jacobi formalism).

## Sophie Rotsaijn (1918)

Ph.D. student at Zürich. Used Planck's phase space theory, but with "incoherent" degrees of freedom. Reasonable agreement with specific heat data (see later); did not plot Planck's "coherent" degrees of freedom theory; also did paramagnetism.

## Reiche 1917

Treated paramagnetism using Planck's phase space formalism applied to rigid rotator (spherical pendulum).

Used Hamilton-Jacobi formalism to find energies of phase space hypersurfaces (same energies are quantized energies in Planck's "first theory.")

Thus, Reiche developed much of formalism he used in 1919 in this paper.

These theories of paramagnetism seem not to have gone anywhere; Reiche did not so much as mention them in his 1921 textbook.

But Reiche's & Rotsaijn's treatments were mentioned favorable in E. P. Adams, *The Quantum Theory* (NRC 1920; not mentioned in 1923 edition)

# REICHE AND THE SPECIFIC HEAT OF H<sub>2</sub>

- Had first tackled the rigid rotator with two degrees of freedom in 1917 (paramagnetism)
- Thoroughly explored and clearly explained the theoretical possibilities for calculating  $c_R$  using the quantum theory of 1919
- Worked primarily with Planck's "first quantum theory"

Calculations: **Three Steps:**

**1. Calculate energy for rotator with two degrees of freedom:**

$$W_{n_1, n_2} = (n_1 + n_2)^2 \frac{h^2}{8\pi^2 J}$$

$n_1$  and  $n_2$  are the quantum numbers associated with two rotational degrees of freedom

**Since in spite of the two degrees of freedom, the probability of a state is determined by a single quantity (the energy), we have to deal with a "degenerate" problem.**

# REICHE'S CALCULATIONS

1. Calculate energy for rotator with two degrees of freedom:

$$W_{n_1, n_2} = (n_1 + n_2)^2 \frac{h^2}{8\pi^2 J}$$

1. Calculate  $Q$  (usually to 6 terms)

$$Q = \sum_{n_1} \sum_{n_2} e^{-W_{n_1, n_2} / kT} = \sum_{n_1} \sum_{n_2} e^{-\sigma(n_1 + n_2)^2} \quad \sigma = \frac{h^2}{8\pi^2 JkT}$$

If one writes out the first few terms, it becomes evident that

$$Q = \sum_{n=0}^{\infty} (2n + 1) e^{-\sigma n^2}$$

“weight,” or number of degenerate quantum states for a given energy

**IF** one counts positive and negative rotations separately.

# REICHE'S CALCULATIONS

1. Calculate energy for rotator with two degrees of freedom:

$$W_{n_1, n_2} = (n_1 + n_2)^2 \frac{h^2}{8\pi^2 J}$$

1. Calculate  $Q$  (usually to six terms)

$$Q = \sum_{n=0}^{\infty} (2n + 1) e^{-\sigma n^2}$$

### 3. Calculate the specific heat

$$c_R = Nk\sigma^2 \frac{d^2 \ln Q(\sigma)}{d\sigma^2}$$

The calculation is difficult. It is not hard to show that

$$c_R \rightarrow 0 \quad \text{as} \quad T \rightarrow 0$$

$$c_R \rightarrow R \quad \text{as} \quad T \rightarrow \infty$$

The intermediate case is harder, as Planck had already discovered.

# REICHE'S CALCULATIONS

$$c_R = Nk\sigma^2 \frac{d^2 \ln Q(\sigma)}{d\sigma^2} \quad \sigma = \frac{h^2}{8\pi^2 JkT}$$

The calculations become horrendous!

If we let  $x = e^{-\sigma}$  then

$$\frac{c_R}{R} = \sigma^2 \frac{f(x)}{g(x)} \quad \text{where}$$

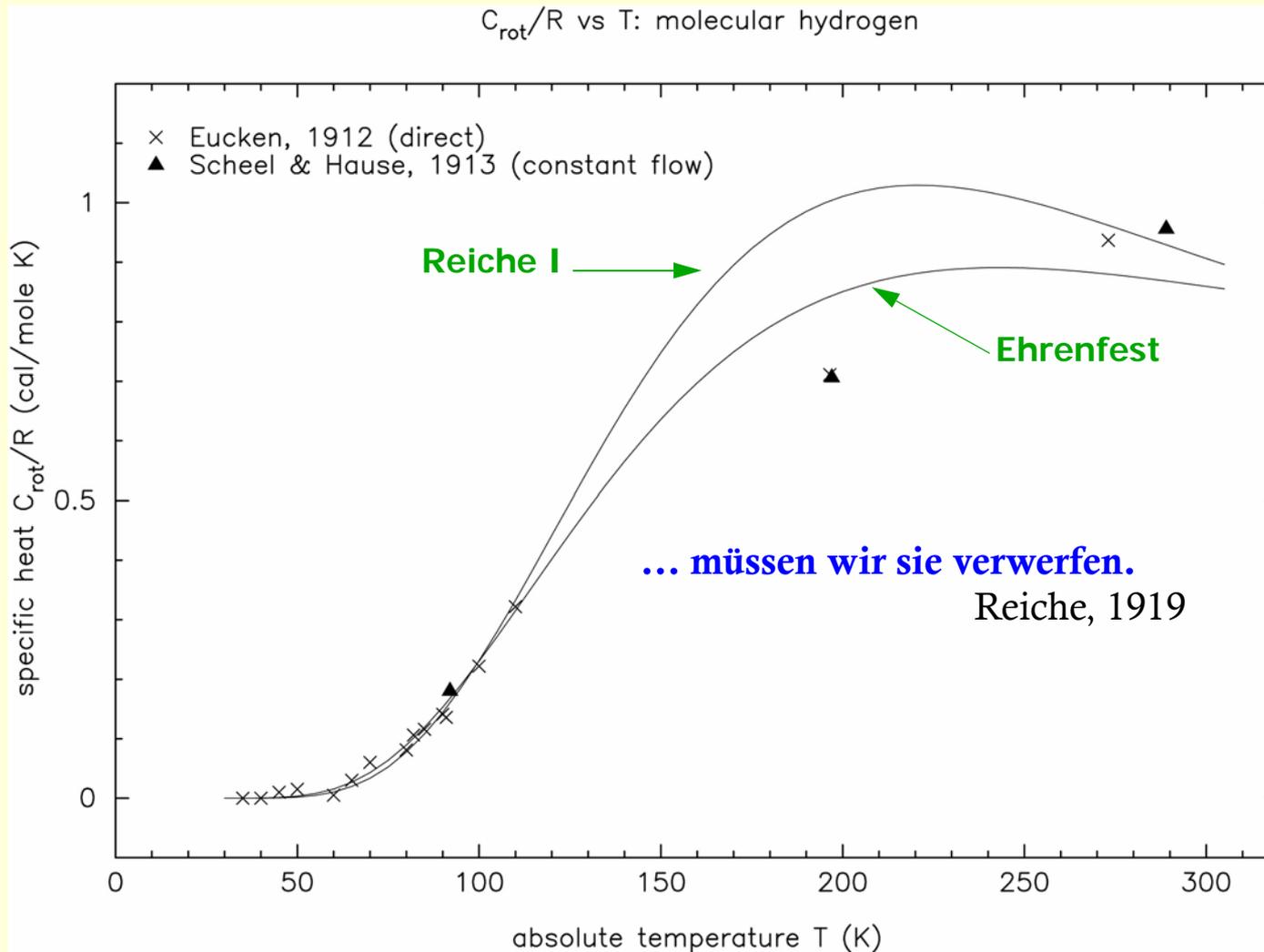
$$f(x) = 3x + 80x^4 + 135x^5 + 567x^9 + 1344x^{10} + 875x^{13} \\ + 2034x^{16} + 6075x^{17} + 9962x^{25} + \dots$$

$$g(x) = 1 + 6x + 9x^2 + 10x^4 + 30x^5 + 25x^8 + 14x^9 + 42x^{10} \\ + 70x^{13} + 18x^{16} + 54x^{17} + 90x^{20} + 148x^{25} \dots$$

Reiche used these results to calculate a numerical table:

**HOW DID HE DO THE CALCULATIONS?**

# REICHE CURVE I



# WHAT WAS WRONG?

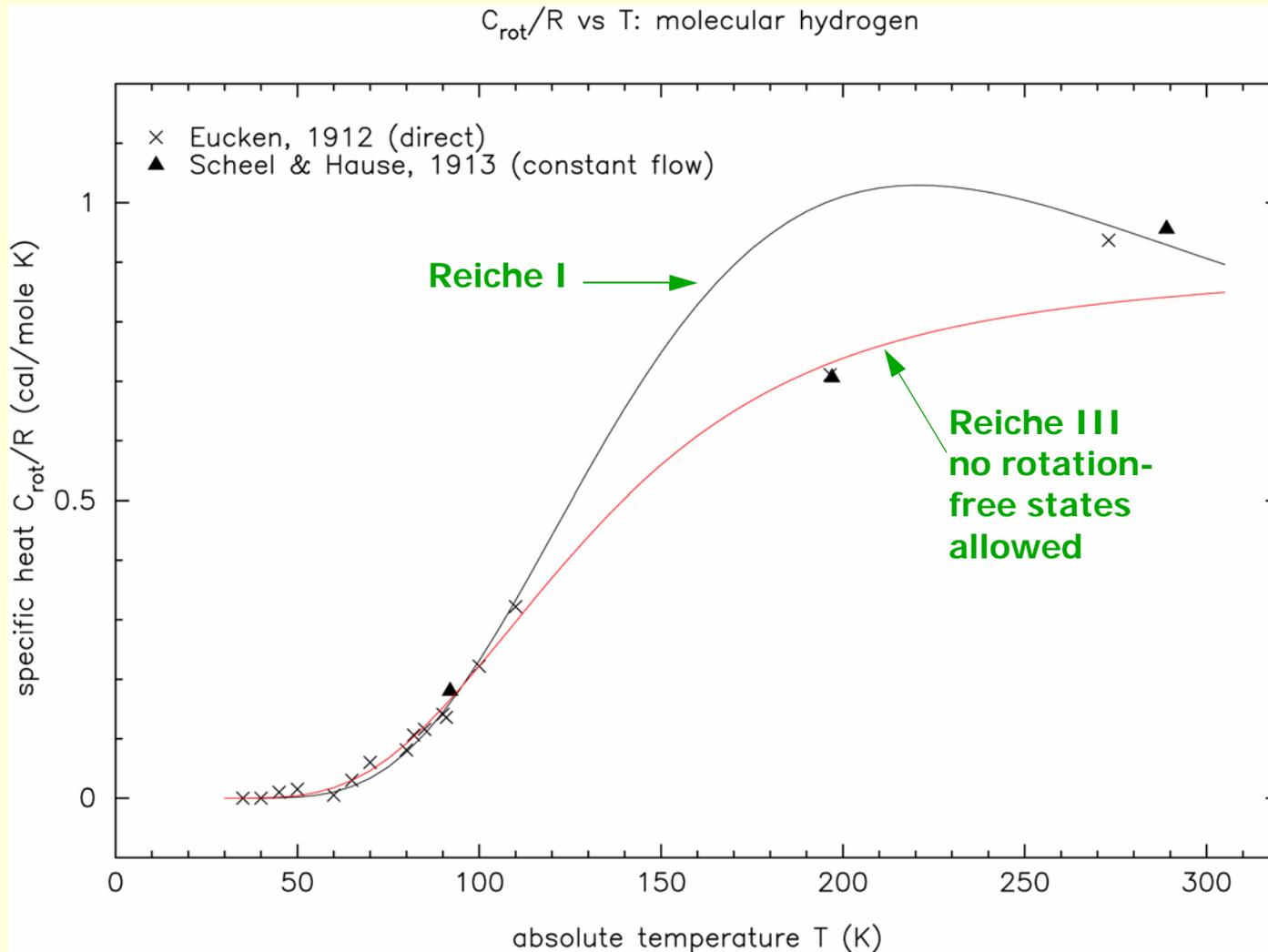
- Perhaps the degeneracy levels are wrong?
- Or perhaps one should investigate other assumptions in calculation of  $Q$ ?

**One might therefore make the hypothesis, that the rotationless state ... does not exist, that is, one forbids the quantum state  $n = n_1 + n_2 = 0$**

Zero-point energies thus appear in the context of Planck's "*first* theory"!

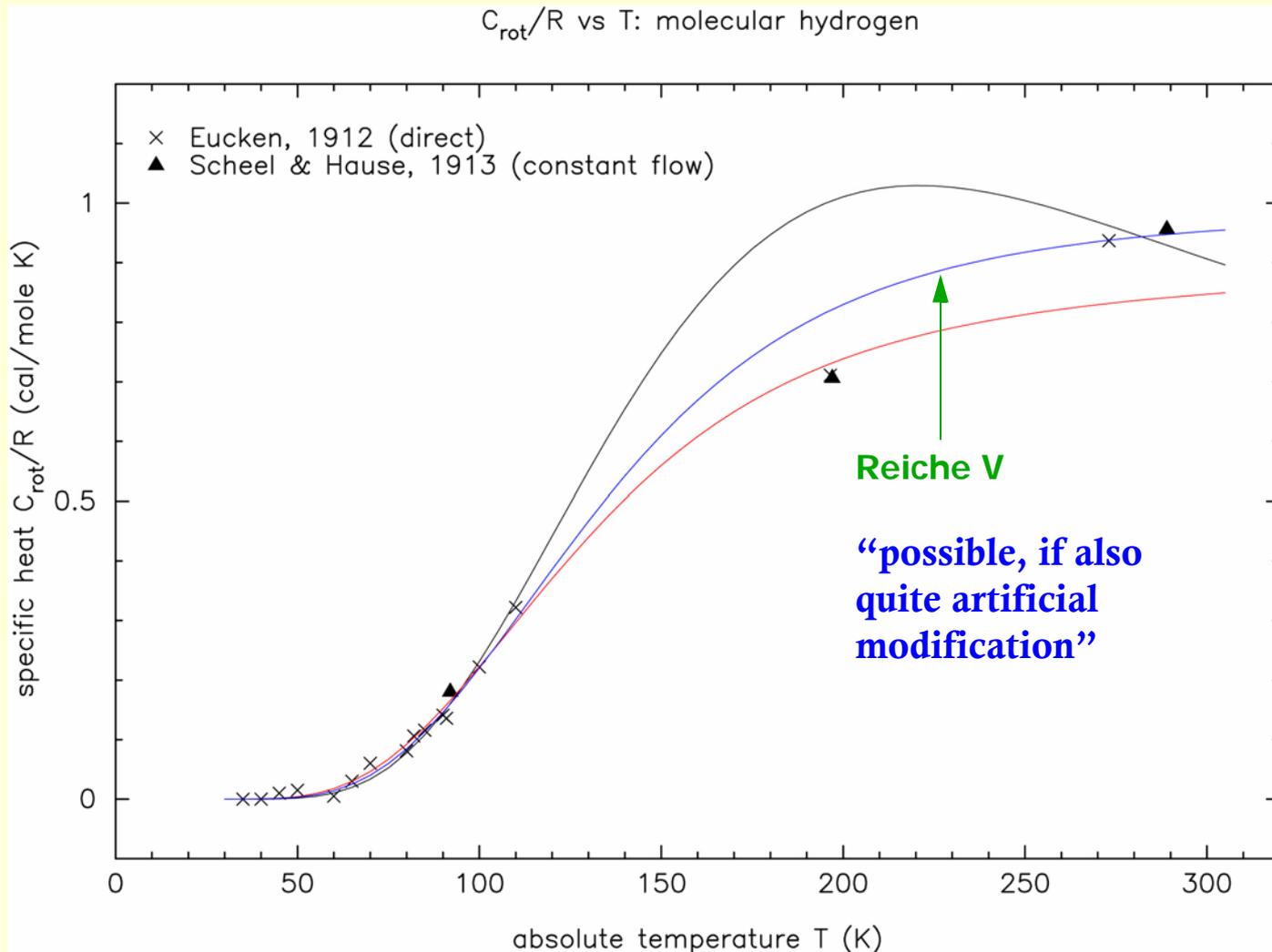
- Reiche explored four such possibilities, and then investigated Planck's "*second* theory"!

# REICHE CURVE III



# REICHE CURVE V

Consider a possible, if also quite artificial, modification. It consists therein, that one forbids not only the quantum state  $n = n_1 + n_2 = 0$ , but also all states for which  $n_2 = 0$



(same curve as Rotsajn) This condition places a seemingly arbitrary restriction on the plane of rotation. Reiche does not discuss; but see Tolman, Herzfeld.

# PLANCK'S SECOND THEORY

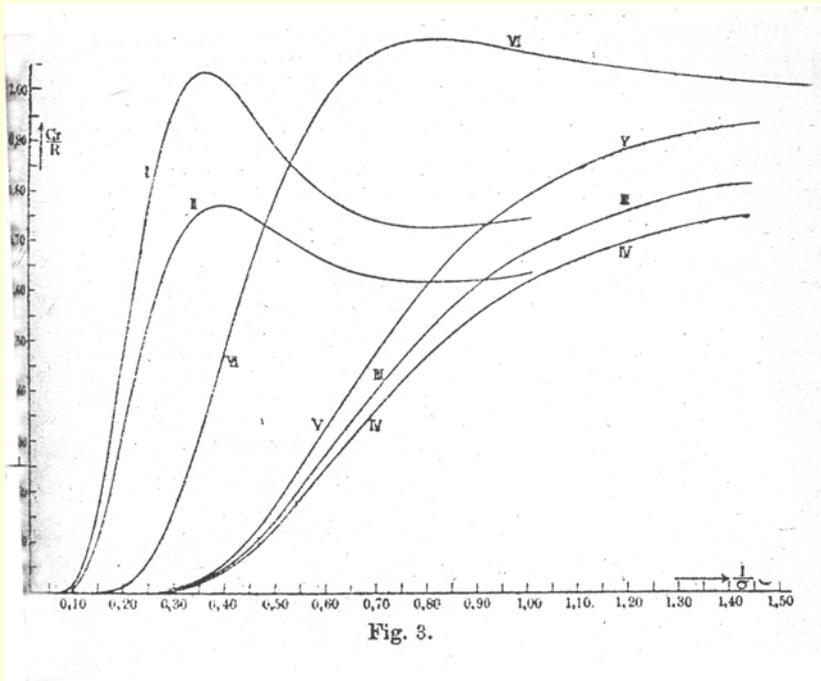
Reiche also discussed the predictions of Planck's "second theory" with two degrees of freedom—continuous absorption of energies, but quantized emission.

- "coherent" rotational degrees of freedom lead to an even higher "hump" than Reiche's Curve I (as far as I know, Reiche gave the first published graph of Planck's "coherent" theory)
- "incoherent" degrees of freedom lead to the same result as Reiche's Curve V (as previously shown by Sophie Rotszajn, another student of Simon Ratnowsky in Zurich).

The calculations of the specific heat of hydrogen are therefore of no help in determining

**... one of the most fundamental questions of the whole quantum theory, whether, namely, Plank's first or second theory is correct. (Reiche 1921)**

# MOMENTS OF INERTIA



from Reiche 1919: plot of

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

By early 1920s, spectroscopic measurements began to give independent values for  $J$ .

This graph from Reiche (1919) shows the effect of the moment of inertia. Reiche and others fit these curves to the data by finding a value of  $J$  that gave good agreement at low temperatures.

Even though  $J$  is the only free parameter, the different choices of models correspond to strikingly different values; for example,

	$J$ (in gm-cm <sup>2</sup> )
Einstein-Stern	$1.47 \times 10^{-41}$
Ehrenfest	$6.9 \times 10^{-41}$
Holm	$1.36 \times 10^{-41}$
Reiche I	
Reiche III	$2.214 \times 10^{-41}$
Reiche V	$2.293 \times 10^{-41}$
Planck	
Schrödinger (1924)	$1.43 \text{ to } 1.48 \times 10^{-41}$

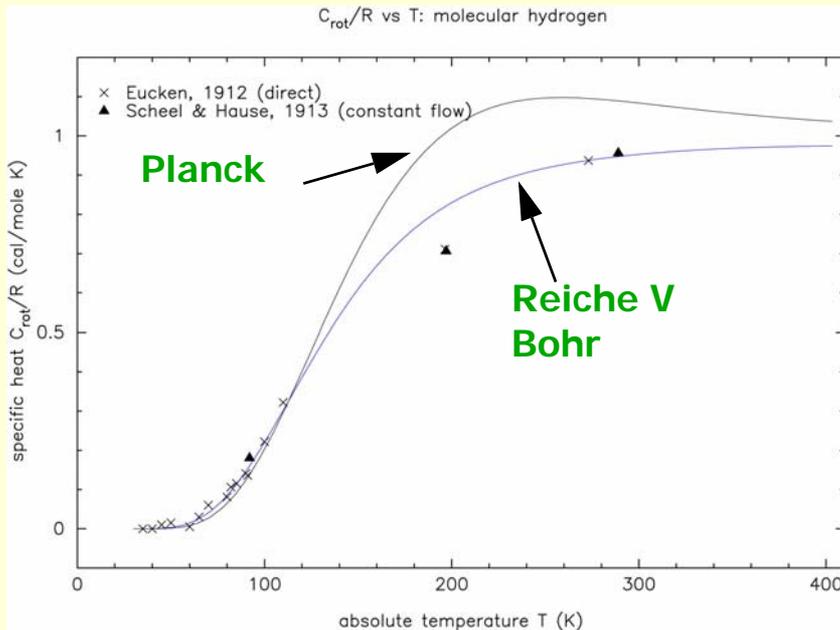
# NIELS BOHR AND THE SPECIFIC HEAT OF HYDROGEN

## ON THE APPLICATION OF THE QUANTUM THEORY TO PERIODIC SYSTEMS



Niels Bohr had found the Reiche V result about 3 years earlier in a paper ALMOST published in 1916

- withdrawn at last moment from the *Philosophical Magazine*
- used quantized energy states
- treated systems with several degrees of freedom
- developed, less formally, a theory of phase space surfaces similar to Planck's 1915 theory to find "weights"
- Bohr's theory likewise implied **no rotation-free states!**
- led to specific heat identical to that found by Reiche in 1919
- Bohr knew about Planck's 1915 theory, and seems to have been the first to make a graph!



# NIELS BOHR AND THE SPECIFIC HEAT OF HYDROGEN

- assumed quantized energy levels
- showed that the volume of phase space for periodic systems with one degree of freedom is  $Q = nh$
- for systems with more than one degree of freedom, **it is not possible ... to obtain a general expression for the volume  $Q$  limited by such a surface; but from a simple consideration of dimensions it follows that ...**

$$Q = C (nh)^r \quad C = \text{constant}, r = \text{no. of degrees of freedom}$$

note similarity to Planck's result

- By an analogy with classical statistical mechanics, Bohr argued that the probability  $P_n$  of a system being in the  $n$ th quantum state was

$$\frac{dQ}{dn} \propto P_n = n^{r-1} = n \text{ for two degrees of freedom}$$

note difference from Planck

As a result, the probability of a system existing in the  $n = 0$  state is zero. Bohr observes that

**This so-called zero-point energy has here an origin quite distinct from that in Planck's theory. In the present theory it arises simply from the fact that ... there is no probability of a periodic system of several degrees of freedom being in the state corresponding to  $n = 0$ ; or in other words, there is no extension in phase corresponding to such a state.**

Quite recently, and after the theory given in this section was worked out, Planck has published a paper which gives a generalization of his second theory to systems with several degrees of freedom ...

# EDWIN C. KEMBLE (1889–1984)



In October 1917, at a meeting of the American Physical Society, Edwin C. Kemble reported his own work—part of his Harvard Ph.D. thesis—in which he had also calculated the specific heat of hydrogen, taking both degrees of freedom into account.

- specific heat work not published until 1923, in a paper written with John Van Vleck, Kemble's first Ph.D. student
- assumed quantized energy states, but found “weights” using Planck's phase-space theory.
- concluded that **no rotation-free states** could exist.
- primary interest was not specific heat, but rotation-vibration spectra of diatomic molecules.

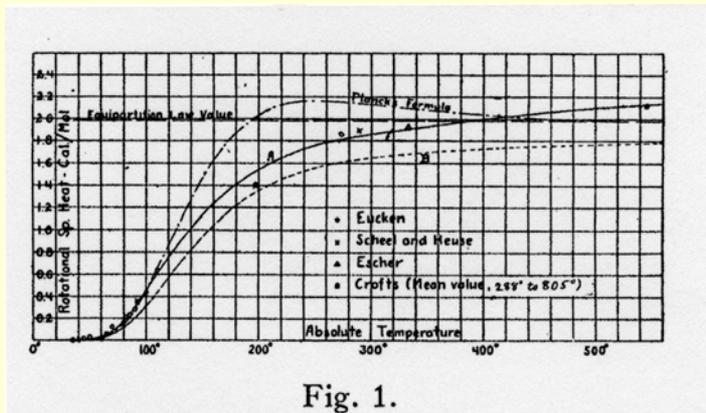


Fig. 1.

Note high upper temperature range

In order to bring the theory into complete harmony with the observed structure of the infrared bands of HCl and at the same time to derive a formula ... which would reproduce the observed values in the case of hydrogen, it was necessary to introduce the zero point hypothesis ... by excluding zero from the list of the possible values of the energy of rotation

Kemble, 1917

# KEMBLE'S SPECIFIC HEAT CALCULATIONS

When Kemble did this work in his 1917 Ph.D. thesis,

- he was familiar with Planck's 1915 phase space theory; referred to "... **Planck's recent extension of the quantum theory to systems having more than one degree of freedom.**" (p. 2)
- he had not seen Sommerfeld's theory (*Annalen* delivery had been interrupted by the war).

Like Reiche, Kemble explored several possible variations:

- Summarized Planck's theory for two degrees of freedom, and like Bohr, did a graph.

**Planck did not plot the specific heat curve to which the above formula leads. The writer has taken the trouble to do so. ... The theoretical curve is in obvious and complete disagreement with experimental values.**

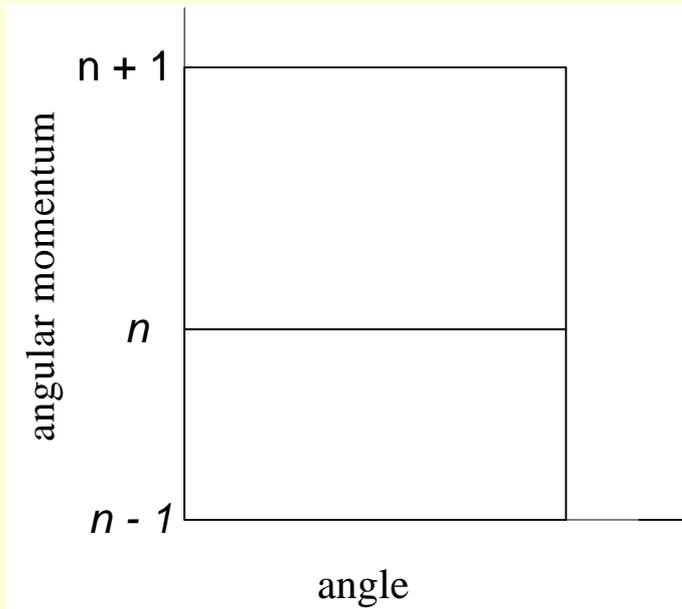
- Argued Planck's second theory couldn't be right, and therefore only Planck's first theory should be used, but with a zero-point energy.
- Vibration-rotation spectra led to same conclusions.

Having refuted Planck's theory, Kemble proceeded to use quantized energy levels, but found the weights using Planck's phase space theory:

# KEMBLE'S SPECIFIC HEAT CALCULATION

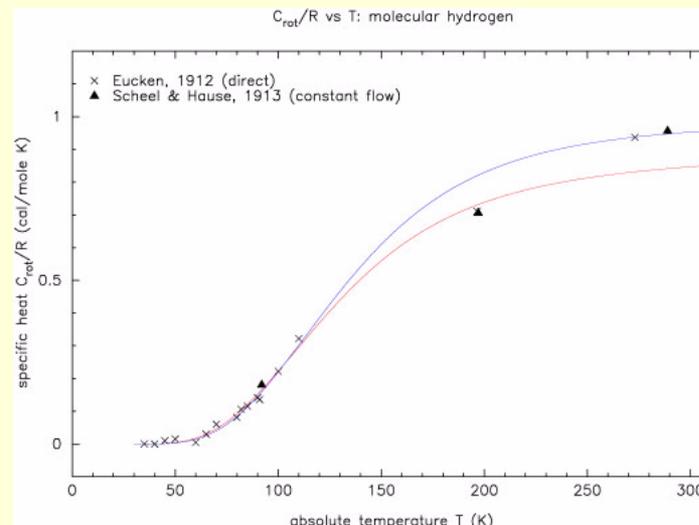
1. Kemble calculated the partition function for quantized energies, but assuming no zero point energy. The phase space element above the energy gave the weight. He found the same partition function and specific heat as Reiche I.
2. Then, considered zero point motion (i.e., eliminated  $n = 0$  term). Now he argued, there was an **ambiguity in the choice of phase space cell**.

... when the zero point hypothesis is introduced it becomes equally plausible to assume that the probability of each condensation surface [i.e., hypersurface] is proportional to the volume of the region element just outside it, or the volume of the element just inside it, or to the mean volume of the two adjacent region elements. (p. 22)

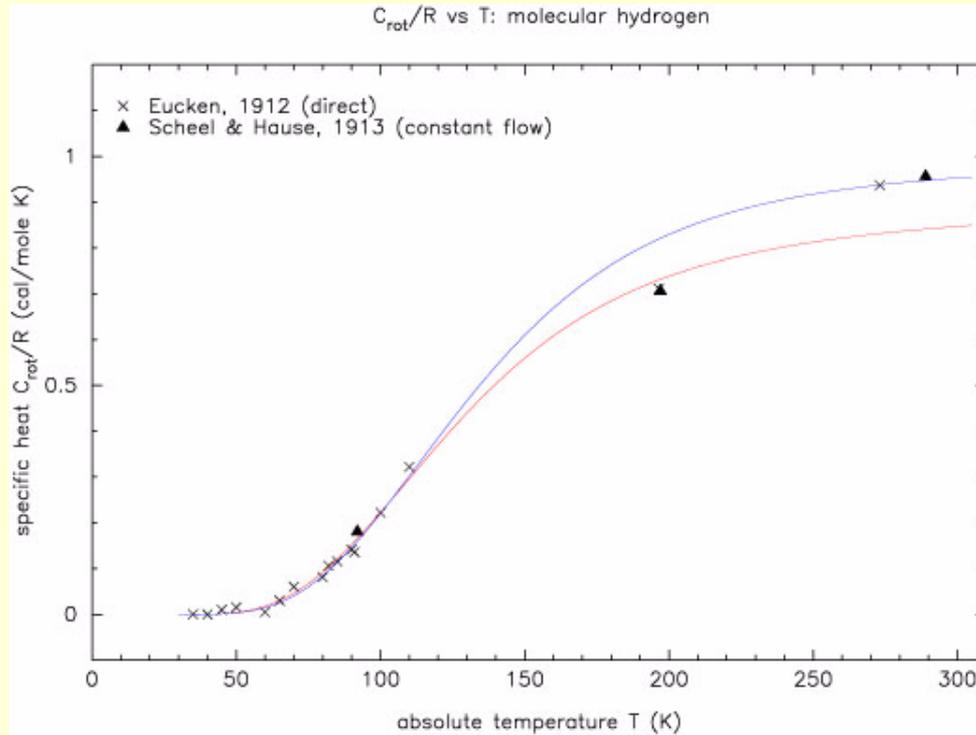


The second choice led to an absurd curve. The first and third led to the same results as Reiche III (red) and Reiche V (blue).

Kemble found it difficult to decide.



# KEMBLE'S SPECIFIC HEAT CALCULATION



In his thesis, Kemble thought that the blue curve (Reiche 5) was the more likely, although for the red curve, the discrepancy

... may be explained as the result of the vibrational specific heat. ... Of course, neither of these formulas may prove to be correct, but they are so much better than [Planck's] as to afford substantial confirmation of the zero-point hypothesis.

Then for a while around 1917, thought red curve (Reiche 3) preferable—tangled thicket

Note: As a molecule rotates faster

- centrifugal expansion increases moment of inertia, thus shifts rotational energies
- anharmonic potential likewise stretches molecule, increases moment of inertia, at higher vibrational energies
- Both effects could have effect of shifting Reiche's curve 3 upwards (Kemble and Van Vleck, and occasionally others, thought these effects might be important).
- Both effects also affect molecular spectra—Here, as we shall see, Kendall's main interest—molecular spectra—was asserting itself.

# REICHE, KEMBLE, AND VAN VLECK

## Reiche

- deeply interested in comparing models, understanding assumptions
- could models distinguish between first and second Planck theories?
- satisfied with *rigid* rotator model
- seemed perplexed by the need to assume that a molecule could not be in a rotation-free state (zero-point energy)
- took discrepancies with data seriously

**...the best still was the curve, number five. But even this was not very good. ...there was one experimental point terribly below, terribly far off. ... I'm pretty sure that ... I asked [Eucken] about the reliability of that point.**

Reiche, AHQP interview, 1962

## Kemble and John Van Vleck

Van Vleck was Kemble's first Ph.D. student. They published a joint paper on hydrogen in 1923, **correcting** and extending the results of Kemble's thesis.

- deeply concerned to extend theory to high temperatures, and to take **anharmonic** vibrations into account.
- led, in 1923, to complex (and non-separable equation for rotator energy.
- In 1923, assumed a zero-point energy almost without comment.
- found the agreement of their theory (essentially Reiche V) satisfactory.

**As I remember, our results gave us a specific heat curve that didn't have a hump in it. That was the important thing.**

Kemble, AHQP interview, 1962

# MOLECULAR SPECTRA

## THEMES:

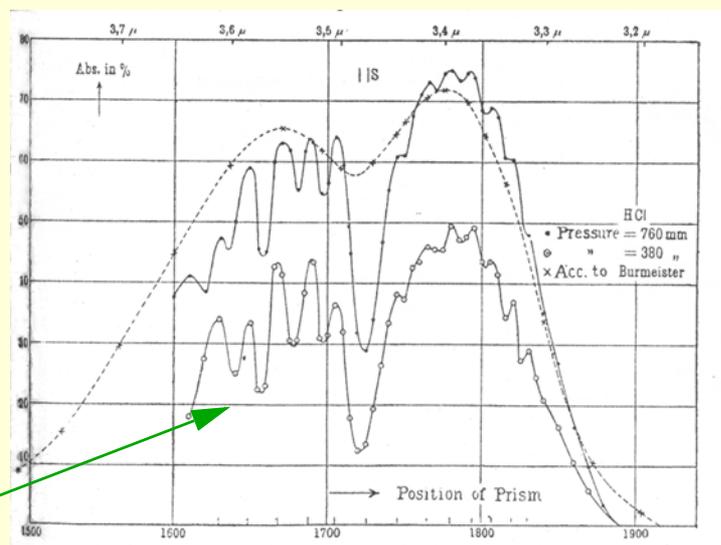
- improving experimental techniques for measuring infra-red molecular spectra
- Lord Rayleigh's prediction (1892): vibrational absorption spectra should show rotation-induced peaks on either side of vibrational peak; should see

$$\nu_{vib} - \nu_{rot} \quad \nu_{vib} \quad \nu_{vib} + \nu_{rot}$$

- **Nernst's Laboratory** again:
  - **Niels Bjerrum** — worked out early quantum theory of molecular absorption spectra in 1911—14
  - **Eva von Bahr** — first experiments showing evidence of quantized absorption peaks in HCl (1913)

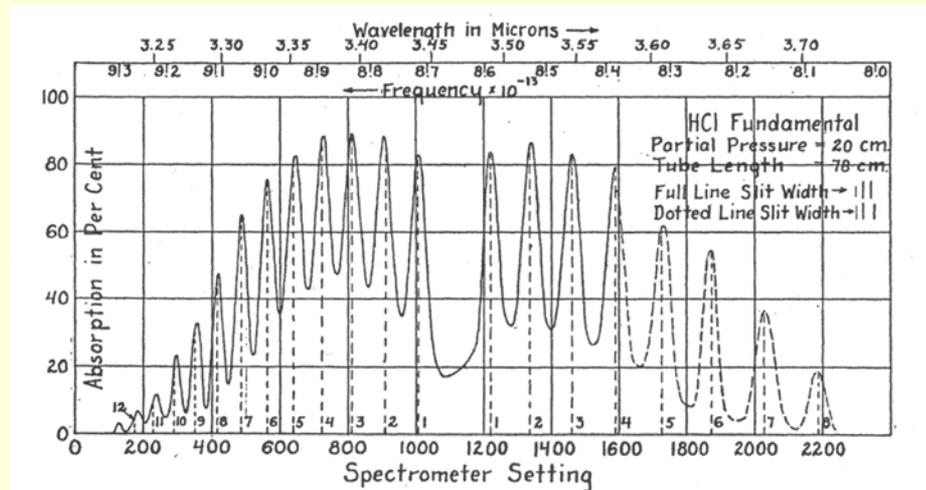
Peaks were interpreted as quantized rotational states (NOT transitions).

data of Eva von Bahr, 1913  
(in *Philosophical Magazine*)



# VIBRATION-ROTATION DATA FOR HCL

Kemble and Brinsmade (1917)



Imes (1919)

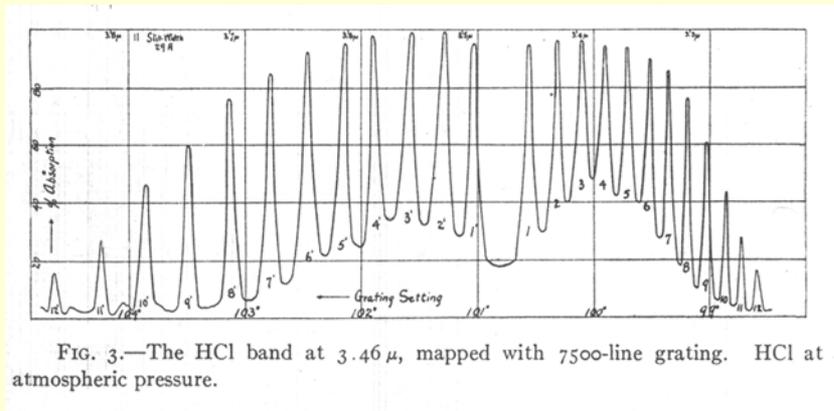


FIG. 3.—The HCl band at 3.46  $\mu$ , mapped with 7500-line grating. HCl at atmospheric pressure.

- How to explain the gap?
- How to explain the closer spacings at higher frequencies? (same **centrifugal and anharmonic effects** Kemble considered in specific heats)

Reiche was primarily interested in the first, Kemble with the second.

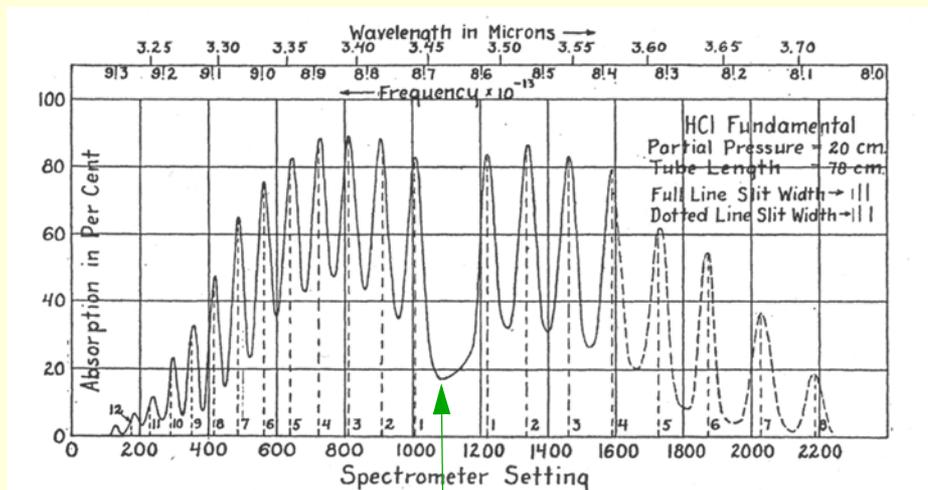
Both agreed that the gap  $\Rightarrow$  zero rotation states were forbidden.

**The extreme sensitivity of the galvanometer used in this work to the slightest mechanical or magnetic disturbance is a source of regret. Many times it was not possible to obtain consistent deflections even during the favorable hours, between midnight and dawn, chosen for observation.**

Elmer Imes, *Astrophysical Journal*, 1919

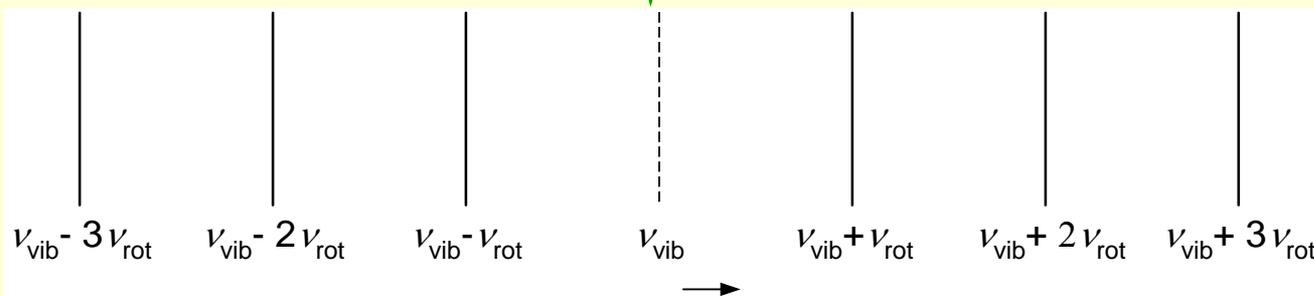
# THEORY: BEFORE ABOUT 1920

Bjerrum interpreted the peaks in von Bahr's data as representing quantized rotational states (that is, radiation corresponding to the rotational frequency of the molecule), **NOT** transitions between states. So, initially, did Kemble and others.



This picture persuaded Kemble and others that Planck's second theory could not be right—the peaks meant that rotational states must be quantized.

In this interpretation, the gap means that rotation-free states cannot exist!

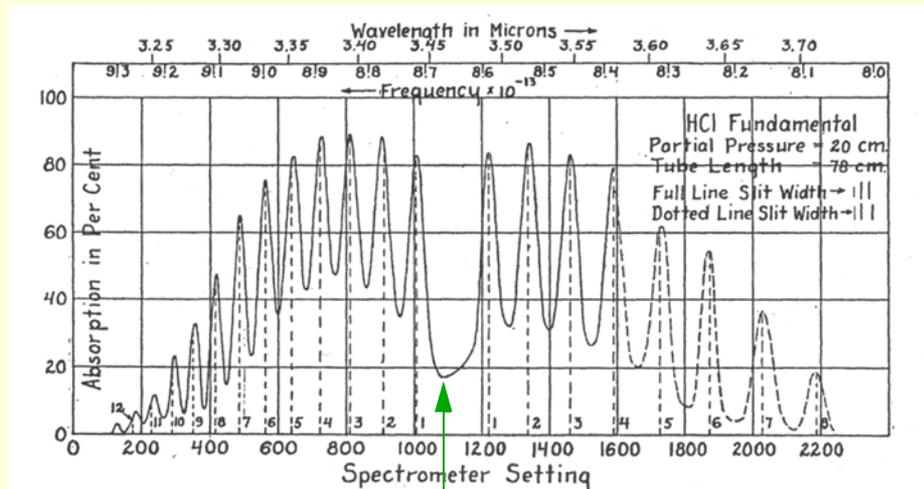


Kemble (1920) seems to have thought the lines represented rotational states, even though by this time he interpreted the vibrational frequency as  $\Delta E/h$ —that is, the frequency represented the transition between states, not the frequency at which the molecule was vibrating! Schwartzchild in 1916 (see Assmus) made a similar distinction between electronic transitions and rotational state.

# THEORY

The theory of vibration-rotation spectra is a moving target around 1920, with several threads, and contributions from a number of theorists, including Bjerrum, Kemble, Torsten Heurlinger, Wilhelm Lenz, and **Adolf Kratzer** (student of Sommerfeld).

Here I describe a thread starting with Reiche and Einstein in 1920 that lead (indirectly) to further specific heat calculations by Richard Tolman, Erwin Schrödinger, Van Vleck, and others.



Gap

## Interpretation (Reiche, 1920)

- Each peak corresponds to the absorption of one vibrational quantum, and either absorption or emission of one rotational quantum.
- Selection rule (from Correspondence Principle) showed rotational state could change by only one quantum.
- In this interpretation, **the gap is a problem.**

# THE GAP

Recall that the rotator energy is given by

$$E_m = m^2 \frac{h^2}{8\pi^2 J}$$

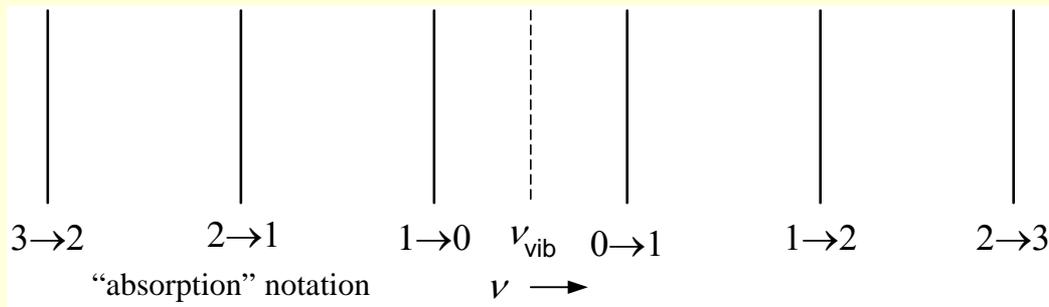
Energy difference between rotational levels is

$$\begin{aligned} E_m - E_{m-1} &= \left[ m^2 - (m-1)^2 \right] \frac{h^2}{8\pi^2 J} \\ &= \left( m + \frac{1}{2} \right) \frac{h^2}{4\pi^2 J} \quad m = 0, 1, 2, \dots \end{aligned}$$

frequency of rotation-vibration transition is

$$\nu = \nu_{vib} \pm \left( m + \frac{1}{2} \right) \frac{h}{4\pi^2 J} \quad m = 0, 1, 2, \dots$$

**There is no gap!** This equation yields equally spaced lines!



The earliest such diagrams I have seen are from 1920 (Reiche and Kratzer). Notation (absorption or emission) is not consistent.

# REICHE AND HALF-QUANTA

Reiche, after conversations  
with Einstein, proposed instead

$$E_m = \left(m + \frac{1}{2}\right)^2 \frac{h^2}{8\pi^2 J}$$

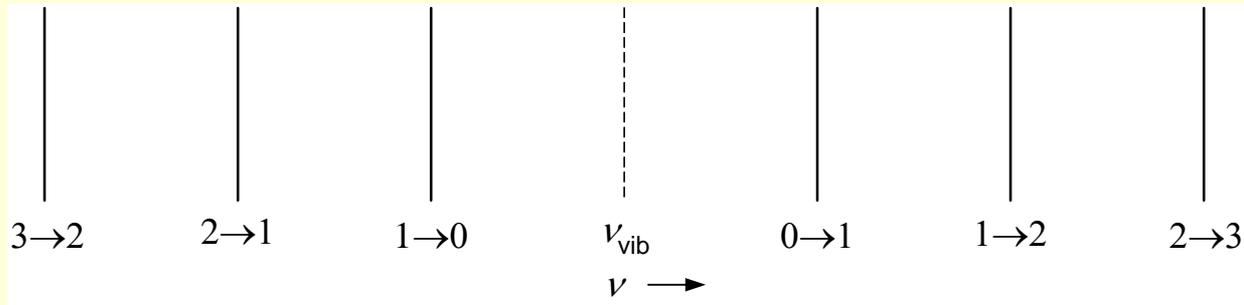
Energy difference between  
rotational levels is

$$\begin{aligned} E_m - E_{m-1} &= \left[ \left(m + \frac{3}{2}\right)^2 - \left(m + \frac{1}{2}\right)^2 \right] \frac{h^2}{8\pi^2 J} \\ &= (m + 1) \frac{h^2}{4\pi^2 J} \quad m = 0, 1, 2, \dots \end{aligned}$$

frequency of rotation-  
vibration transition is

$$\nu = \nu_{vib} \pm (m + 1) \frac{h}{4\pi^2 J} \quad m = 0, 1, 2, \dots$$

**Now there is a gap!** Moreover, there is no possibility of a rotation-free state.



labels often given in half-quanta format, for example:  $1/2 \rightarrow 3/2$

# REICHE AND HALF-QUANTA

Reiche proposed this solution in 1920, in the *Zeitschrift für Physik*, after seeing Imes' HCl spectra, and after discussions with Einstein. (Aside: Reiche and Einstein apparently got to know each other fairly well around this time.)

- Reiche's suggestion did not catch on.
- It was succeeded by another suggestion of Adolf Kratzer that avoided the necessity of half-quanta. Sommerfeld adopted it, and Reiche did so himself, in his 1921 text.
- But then, half-quanta were proposed again,
  - by Kratzer in 1922, and
  - by Hendrik Kramers and Wolfgang Pauli in 1923.

No one remembered Reiche!

Adolph Kratzer: student of Sommerfeld. Developed theory of rotation-vibration spectra along the same lines as Kemble, in a series of papers starting around 1920.

- And this time, they were applied to the specific heat of hydrogen, initially by Richard Chace Tolman in 1923.

## **ASIDE: EINSTEIN AND REICHE**

Reiche and Einstein apparently got to know each other fairly well around this time.

When my sister and I were children, we used to play a game which we called *Professor*, and where we acted as the professors. Each time Einstein visited my father, we used to run to the wastepaper basket afterwards and fish out all the thrown-away handwritten notes and papers Einstein and my father had prepared. We used to play with these papers and we would have lengthy discussions about them — of course, without having the faintest idea what it was all about. Once, Einstein came into our playroom, saw us sitting on the floor discussing these papers, and heard one of us making the remark that all this was not correct and there were some errors in the notes. Einstein listened to our professor-like conversation, asked us to show him the papers, and then said he must agree there was something wrong with the writings. He thanked us for telling him.

He was known to us as *Uncle Albert*, and we liked him because he always brought a box of chocolate for us.

Hans Reiche (1990)

# ASIDE: EINSTEIN CONTINUED TO BE INTERESTED

65

## SITZUNGSBERICHTE DER PREUSSISCHEN AKADEMIE DER WISSENSCHAFTEN. 1920

II. Sitzung der physikalisch-mathematischen Klasse. 15. Januar.

Vorsitzender Sekretar: Hr. PLANCK.

\*1. Hr. EINSTEIN sprach über Das Trägheitsmoment des Wasserstoff-Moleküls.

Wendet man die TERNODESche Theorie der Entropiekonstante auf den Freiheitsgrad der Rotation des Wasserstoffes an, so erhält man eine Formel, welche aus der Kurve der spezifischen Wärme das Trägheitsmoment  $J$  ohne Quantentheorie exakt zu berechnen gestattet. Man erhält so den Wert  $J = 0.96 \cdot 10^{-41}$ . Die Publikation erfolgt später.

Correspondence:

- Einstein to Ehrenfest, 1 March 1920 (CP 9)

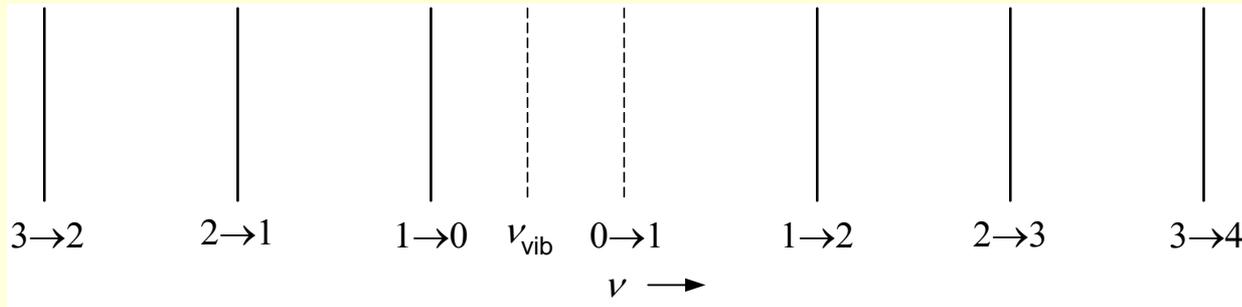
The vanishing of absorption at zero is the extraordinary thing. It lends support to the argument that, in rotation, the permissible motions lie not with the quantum numbers  $n$  but rather with  $n + 1/2$ .

- Einstein to Fritz Haber, 6 October 1920.

But the specific heat function of hydrogen as well as the Bjerrum spectrum of HCl speak for a zero-point energy of rotation.

# ADOLPH KRATZER'S 1920 PROPOSAL FOR THE GAP

No half quanta, and no mention of half quanta (in *Zeitschrift für Physik* a few months after Reiche).



The absorption transition in which the molecule absorbs one vibrational quantum, and goes from the  $m = 0$  to  $m = 1$  rotational state, does not appear. But the one in which the molecule falls from  $m = 1$  to  $m = 0$  does show up!

**In order to understand this fact, we may assume that the rotation-free state is by no means an impossible state. The theory of specific heats and the absence of the zero line reveal merely that the probability for the existence of the rotation-free state is vanishingly small. On the possibility of the occurrence of the null state will hereby nothing be claimed. This improbable state can rather be produced through external influences, but then exists only a very short time ...**

Kratzer 1920

adopted by Sommerfeld (3rd [1922] ed

**This deduction is surprising at first sight, and is excellently confirmed by the behavior of the specific heat of rotation ... of hydrogen**

**The reverse transition, 1 to 0 absorption, is present—a fact very difficult to reconcile with the possibility of thermal equilibrium. This was an annoying difficulty for some time ...**

Walter F. Colby (NRC Report, 1926)

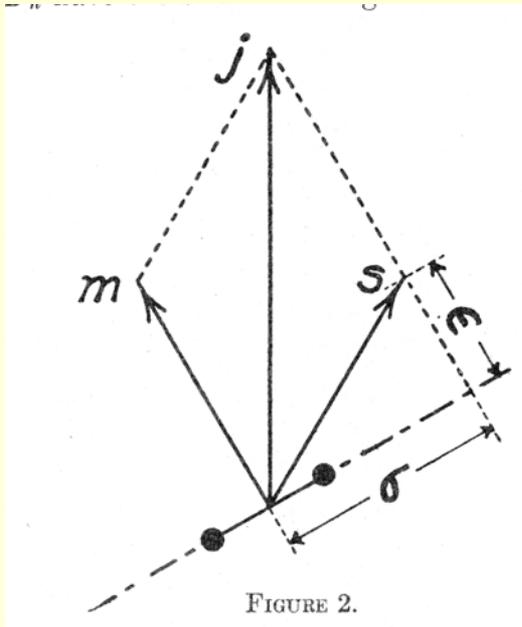
**Kratzer himself proposed half-quanta in 1922, followed shortly thereafter by ...**

# KRAMERS-PAULI THEORY AND HALF-QUANTA (1923)

Molecular hydrogen and the hydrogen halides can be described using the rigid rotator (“non-gyroscopic”—that is, assuming zero angular momentum about the axis of symmetry).

However, it turned out during the 20s that some diatomic molecules (and of course, more complex molecules) had to be treated with “gyroscopic” models, in which three rotational degrees of freedom were present.

Kramers and Pauli, in a 1923 paper, developed the following model:



from Kemble (NRC) (1926)

- $m$ : rotational angular momentum associated with rotation of nuclei about center of mass—and thus, perpendicular to the line joining the nuclei.
- $s$ : electronic angular momentum. The vector  $s$  is rigidly oriented at a fixed angle to the line joining the two nuclei. Note the components  $\epsilon$  and  $\sigma$  respectively parallel with and perpendicular to the direction of  $m$
- $j$ : total angular momentum, quantized in integral units

Assumption:  $j$  and  $s$  are quantized,  $m$  is not.

# KRAMERS-PAULI THEORY (1923)

from Ruark and Urey (1930)

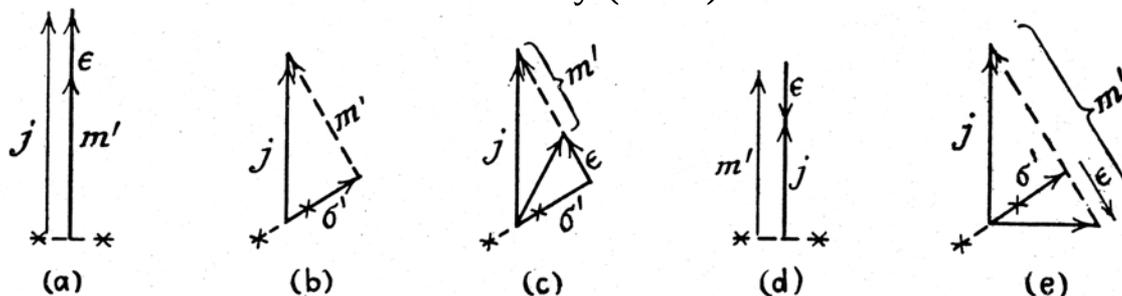


FIG. 18.—Vector combinations of the gyroscopic diatomic molecule—Kramers-Pauli model.

Kramers and Pauli assumed that a diatomic molecule may have a resultant electronic angular momentum vector, rigidly oriented with respect to the line of nuclei at an arbitrary angle, which is supposed to be the same for all rotational states. The components of this angular momentum parallel and perpendicular to this line are represented by  $\sigma'h/2\pi$  and  $\epsilon h/2\pi$ , respectively. It is assumed that the electronic angular momentum  $s$ , which is equal to  $(\sigma'^2 + \epsilon^2)^{1/2}$  in quantum units, and the total angular momentum of the molecule  $j$ , are quantized. In the rotation of this molecule, the vector  $s$  lies in a plane determined by the line of nuclei and the direction of  $j$ .

The arrangement of vectors shown in Fig. 18de were excluded by Kramers and Pauli, since they are dynamically unstable... They were included by Kratzer, however, because they are necessary to account for the number of observed energy levels.

In view of the uncertainty regarding the importance of dynamical stability for quantized motions this objection seems not to be crucial.

Ruark and Urey, 1930

Kemble, NRC, 1926

# KRAMERS-PAULI THEORY (1923)

Ruark and Urey, 1930

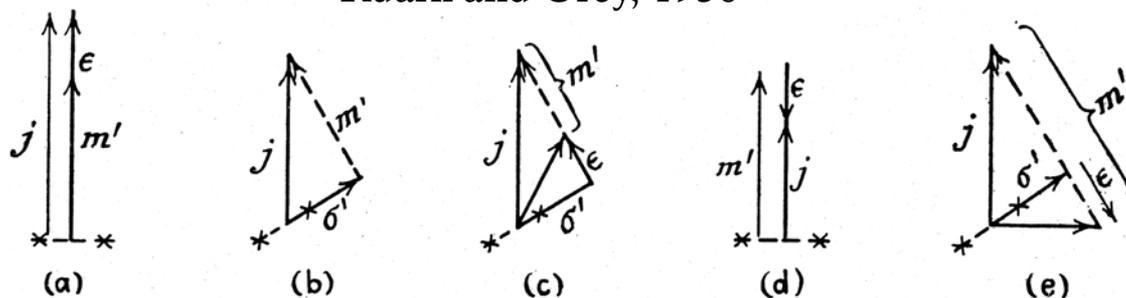


FIG. 18.—Vector combinations of the gyroscopic diatomic molecule—Kramers-Pauli model.

Fig. 18(a) shows the configuration for both HCl and H<sub>2</sub>. If one assumes

$$\epsilon = \frac{1}{2}, \quad j = \text{integer} \Rightarrow \text{total angular momentum} = j \frac{h}{2\pi}$$

Then the rotational quantum number and energy are given by

$$m = j - \frac{1}{2}$$

$$E_{rot} = \frac{1}{2J} \left( \left\{ j - \frac{1}{2} \right\} \frac{h}{2\pi} \right)^2$$

**This [result] would mean that no rotation-free state of the molecule exists.**

Kramers and Pauli, 1923

# RICHARD TOLMAN AND HALF-QUANTA

## ROTATIONAL SPECIFIC HEAT AND HALF QUANTUM NUMBERS

Physical Review 1923



Tolman based his argument for half-quanta on molecular spectra (citing Kratzer, but not Kramers and Pauli), and then turned to the specific heat of hydrogen.

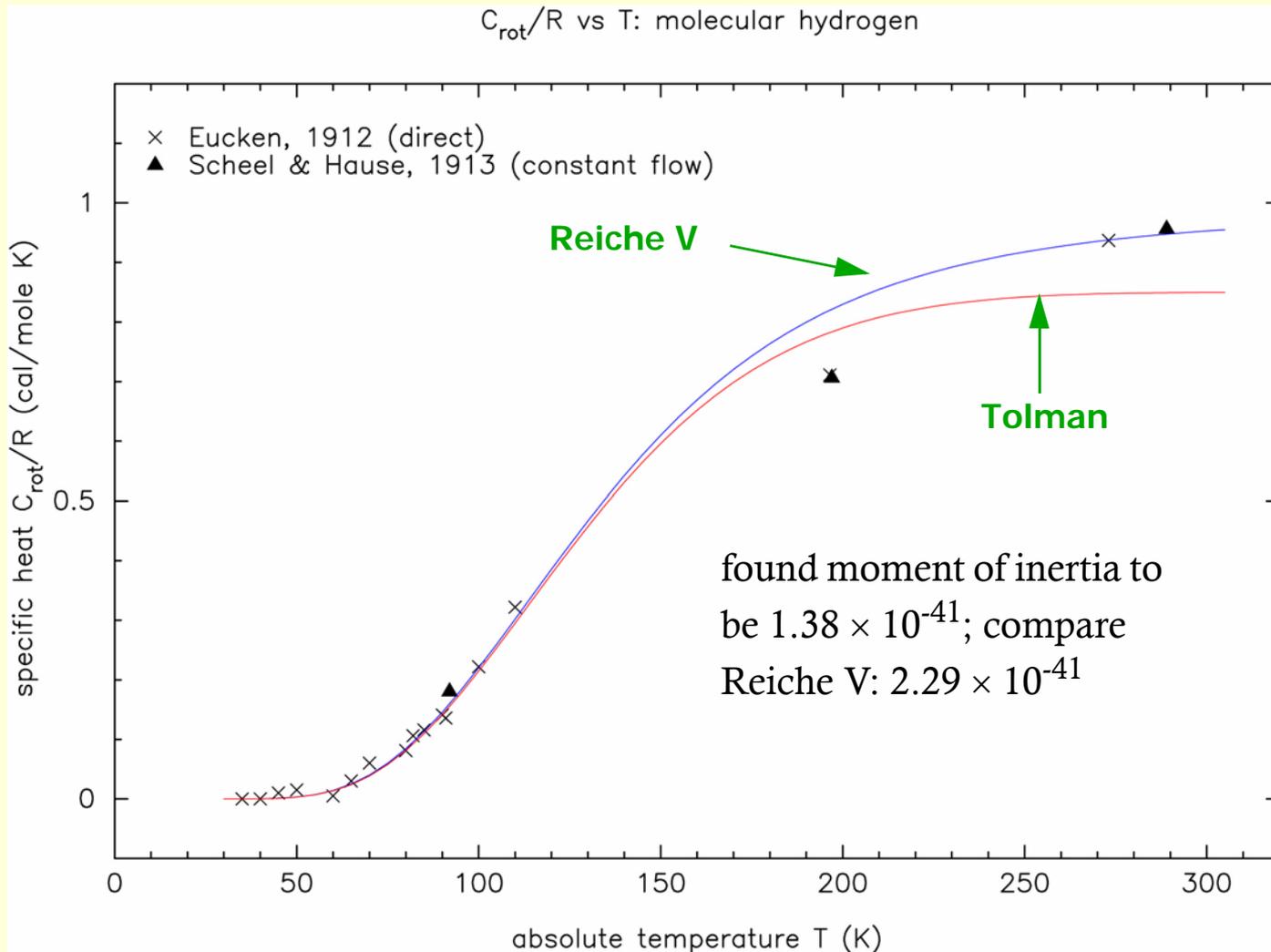
He started with

$$Q = \sum_1^{\infty} 2ne^{-(n-\frac{1}{2})^2\sigma} \quad \text{and proceeded in much the same way as Reiche.}$$

**... it should be noted how simply we have arrived at the ...a priori probabilities of the successive energy levels ... without resorting to any artificial rejection of the states of no rotation ...**

Tolman 1923

# TOLMAN'S RESULT FOR THE SPECIFIC HEAT



- comments that moment of inertia is significant since it is in better agreement with the “many lined spectrum of hydrogen” than the Reiche V result.
- suggested that vibrational effects might improve agreement at high temperatures

# SCHRÖDINGER, HALF-QUANTA, AND MOMENTS OF INERTIA



## ON THE ROTATIONAL HEATS OF HYDROGEN

*Zeitschrift für Physik* 1924

## SPECIFIC HEATS (THEORETICAL PART)

*Handbuch der Physik*, 1925

- In a 1917 review article in *Naturwissenschaften*, Schrödinger had shown some skepticism towards the early theories for the specific heat of hydrogen
- He sounded no less skeptical in 1924!
- Like Tolman, Schrödinger used “half-quanta,” and cited Kramers and Pauli in the *Handbuch* article; but he also introduced *arbitrary* weights

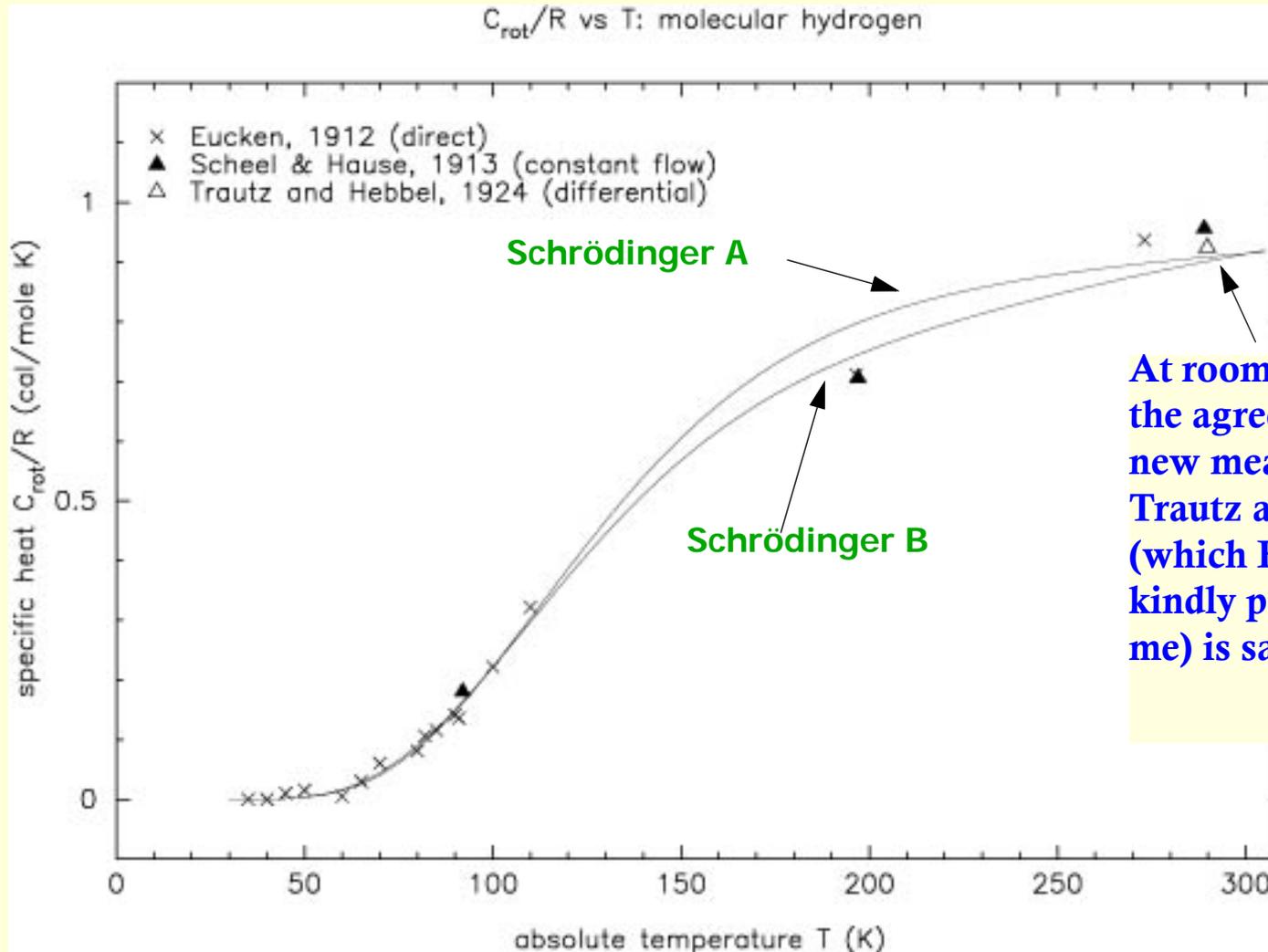
**The requirements of the theory are so uncertain that one might do better to match the weight ratios to the observations as well as possible.**

$$Q = \sum_1^{\infty} g_n e^{-(n-\frac{1}{2})^2 \sigma}$$

$$g_1 : g_2 : g_3 = 1 : 2 : 4 \quad \text{Schrödinger A}$$

$$g_1 : g_2 : g_3 = 4 : 7 : 17 \quad \text{Schrödinger B}$$

# SCHRÖDINGER, HALF-QUANTA, AND MOMENTS OF INERTIA



# SCHRÖDINGER, HALF-QUANTA, AND MOMENTS OF INERTIA

## WHY HALF-QUANTA?

Schrödinger first appealed to the evidence from band spectra:

**The approach first introduced into band spectra by Kratzer not only made the absence of rotation-free states understandable without special assumptions ...**

But as he also said,

**Without doubt, better agreement with the simple dumbbell model [whole quanta] would be attained if one liberalized the choice of weights.**

- He then pointed out that the **moment of inertia** calculated from his half-quanta theory agreed better with results from **electronic** band spectra of molecular hydrogen than did Reiche's "whole quanta" theory!

**EARLIER: VIBRATION-ROTATION SPECTRA OF HCL HAD REINFORCED THE APPARENT ABSENCE OF ROTATION-FREE STATES IN MOLECULAR HYDROGEN**

**WITH TOLMAN AND SCHRÖDINGER: ELECTRONIC BAND SPECTRA OF MOLECULAR HYDROGEN NOW BEGAN TO INFLUENCE THE SPECIFIC HEAT THEORIES!**

# JOHN VAN VLECK AND ELMER HUTCHISSON

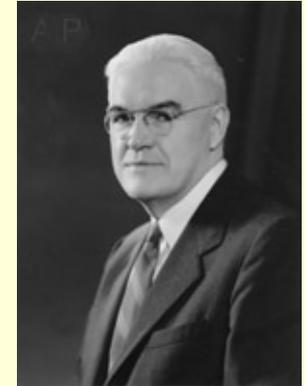
## ON THE QUANTUM THEORY OF THE SPECIFIC HEAT OF HYDROGEN

Physical Review, 1926



John Van Vleck

Late in 1926, Van Vleck and Hutchisson (his first Ph.D. student at the University of Minnesota) published back-to-back articles in the *Physical Review*, summarizing the theoretical and experimental status of the specific heat of hydrogen:



Elmer Hutchisson

### Context:

- considerably more data had been published
- implications of hydrogen band spectra for specific heats even more apparent
- quarter quanta?
- new quantum mechanics introduced: “half quanta” fit naturally into the new scheme

... the quantum theory has been revolutionized by the new mechanics developed by Born, Heisenberg, Jordan, and Schrödinger.

Van Vleck 1926

$$\left\{ \left( m + \frac{1}{2} \right)^2 - \frac{1}{4} \right\} \frac{h^2}{8\pi^2 J} = m(m+1) \frac{h^2}{8\pi^2 J}$$

half quanta      energy of a rigid rotator      modern QM

# VAN VLECK AND HUTCHISSON

Themes:

- detailed discussion of possible theoretical models, including whole quanta, half quanta, “weak” quantization, exclusion of every other state, gyroscopic models, quarter quanta, ...
- detailed discussion of electronic transitions in hydrogen (which include vibrational and rotational levels), implications for moment of inertia.

**At any rate the hydrogen secondary spectrum is so complicated and difficult to interpret that it does not as yet appear to furnish any conclusive evidence against any of the various specific heat curves ...**

- discusses nuclear vibration frequency—important in determining importance of vibrational contribution to the specific heat at higher temperatures (puzzling)
- alternately weak and strong band intensities
- absolute entropies and entropy constant (Sakur-Tetrode);—another way of getting at the moment of inertia

**Existing dissociation data does not appear adequate to warrant any definite conclusions ... In short the correlation of experimental and theoretical chemical constants is at present in a decidedly chaotic state.**

- (Hutchisson) discussion of the current state of experiment, how well the various theories compare with the data. The calculations were once again involved and difficult!

# VAN VLECK AND HUTCHISSON

## RESULTS

Unfortunately, an impossible specific heat curve is obtained ... from the simple theory of the rotator in the new mechanics.

...

The failure of the simple theory is doubtless due to the non-polar character of the hydrogen molecule and is probably intimately connected with the alternating intensities found in the band spectra of certain non-polar molecules.

...

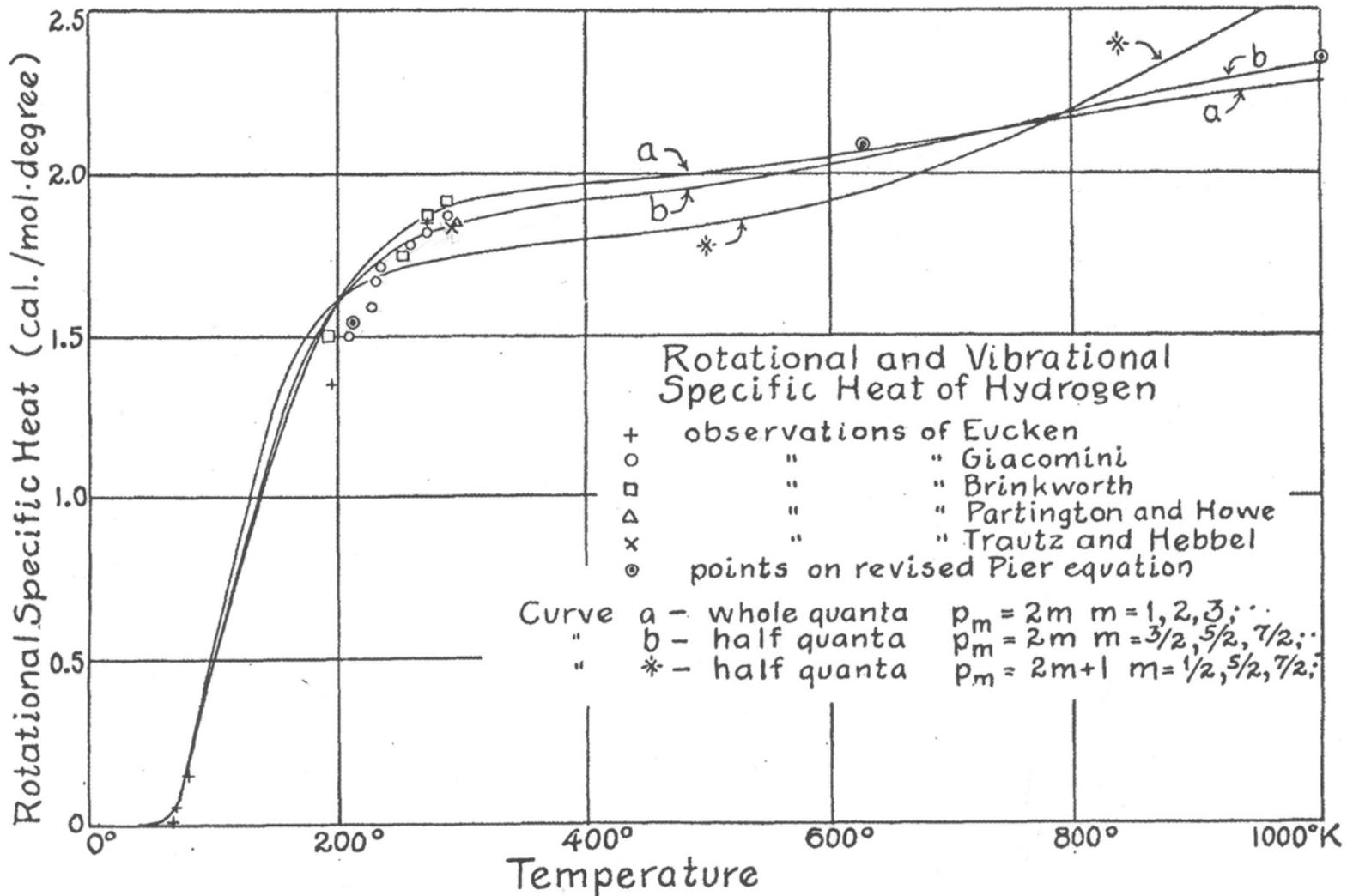
We shall list below several specific ways of crawling out of the specific heat dilemma by assuming more or less empirically a different quantization than in the simple polar rotator. Most of the suggestions appear rather artificial and are frankly only conjectures

...

--Van Vleck 1926

- “whole quanta” are excluded by new quantum theory
- best result: **eliminate from consideration the lowest energy state** of the quantized rotator (!!)

# VAN VLECK AND HUTCHISSON 1926

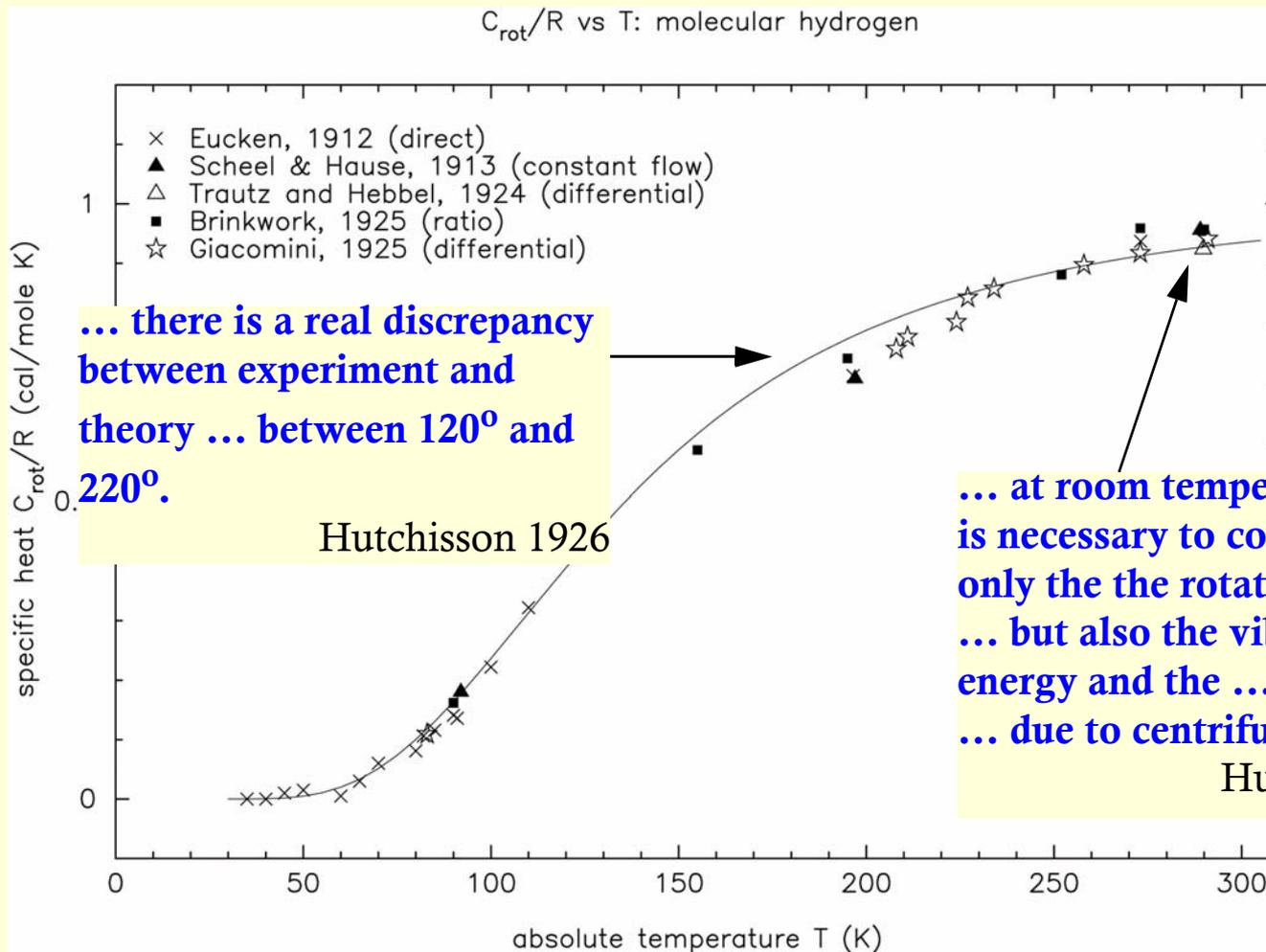


Hutchisson, Physical Review, 1926

# VAN VLECK AND HUTCHISSON 1926

Most of the suggestions appear rather artificial... one must at the same time realize that observed specific heats furnish fairly definite evidence as to ... a priori probabilities and ranges of quantum numbers. For this reason, it does not appear altogether unlikely that the true specific heat curve is of the form (b) given below.

Van Vleck 1926

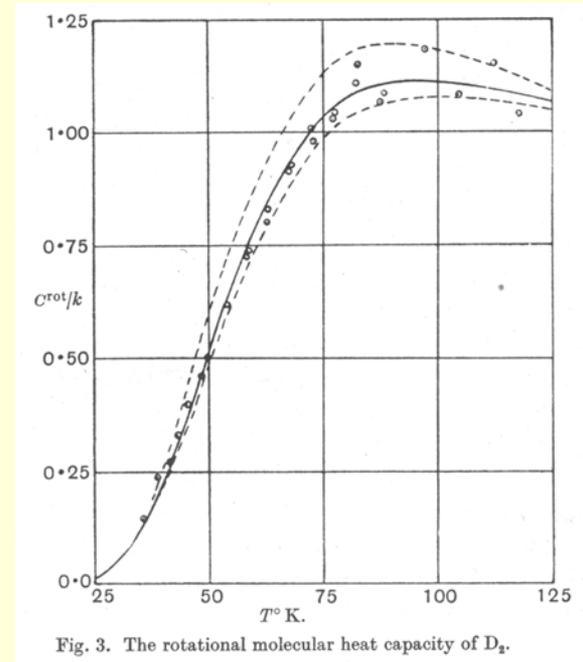


# “ASTONISHING SUCCESSES” “BITTER DISAPPOINTMENT”

- No fully accurate description of the specific heat of hydrogen ever emerged in the old quantum theory.
- The same theory did fairly well in explaining molecular vibration-rotation spectra.
- **Both** specific heats and molecular spectra  $\Rightarrow$  molecules cannot be in rotation-free states!

Subsequent developments include:

- Friederich Hund (1927)
- **David Dennison (1927)** (modern solution)  
**central:** new value of  $J$  from band spectra measurements of  $4.64 \times 10^{-41}$  — more than double Reiche  $V$  value, triple Tolman's.
- experimental work continued through 1930s (Eucken, Paul Harteck, Karl Clusius, others) and included measurements of the specific heat of HD and  $D_2$



from Fowler & Guggenheim,  
*Statistical Thermodynamics*, 1939

## A FEW REFERENCES

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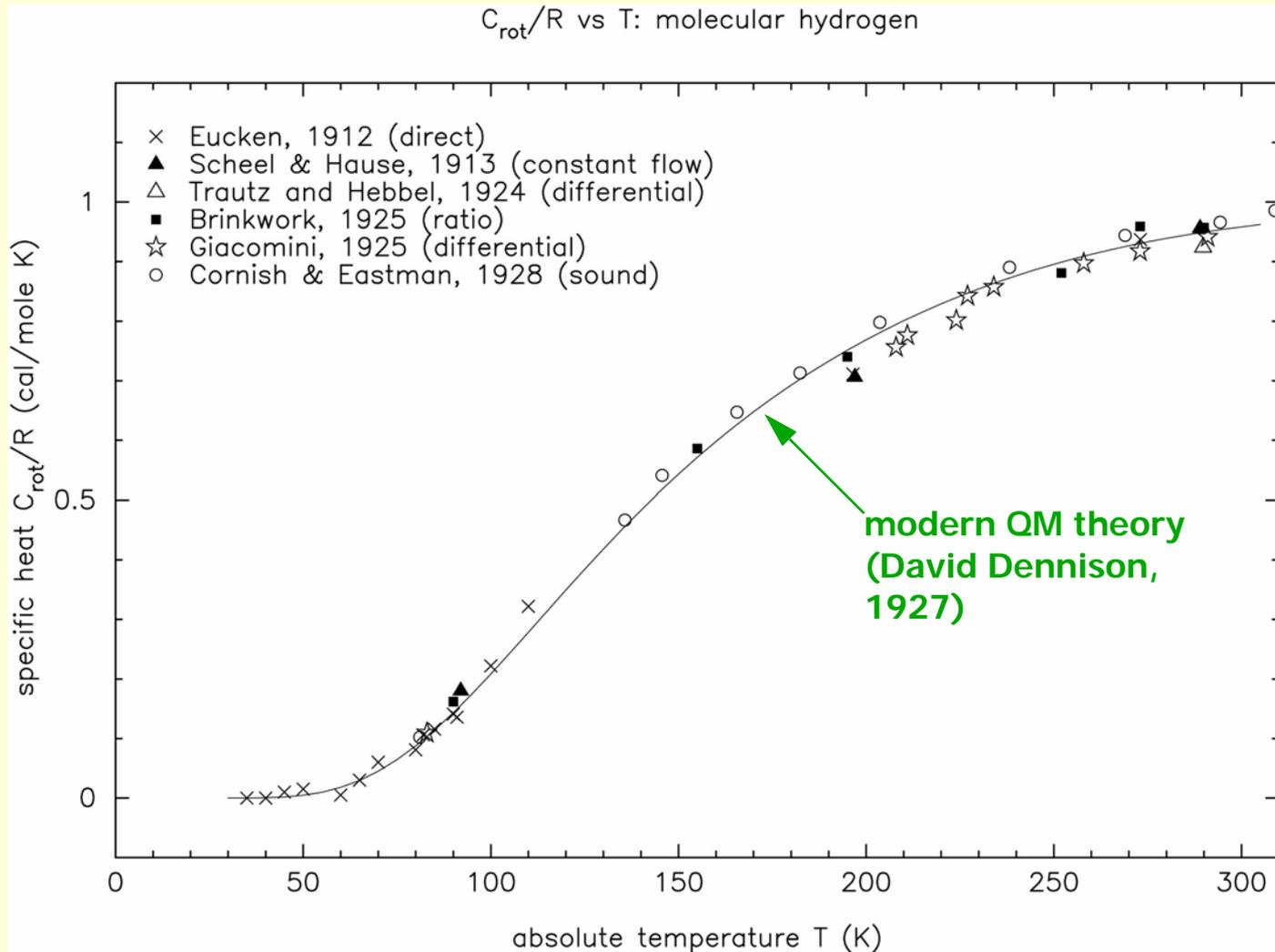
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Chiyoko Fujisaki, "From Delandres to Kratzer—Development of the understanding of the origin of infrared band spectra I & II," *Historia scientarum* **24**, 53–75 and **25**, 57–86 (1983)

Martin J. Klein, *Paul Ehrenfest: Vol 1, The Making of a Theoretical Physicist* (North Holland, New York, 1970)

Sin-itiro Tomonaga, *The Story of Spin* (University of Chicago, Chicago, 1997)

# THEORY AND EXPERIMENT BY THE LATE 1920S



# MODERN QUANTUM MECHANICS

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

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

where  $J$  is the moment of inertia 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)  $\Leftrightarrow$  symmetric rotational state ( $n$  even)

## ORTHOHYDROGEN

triplet nuclear state (symmetric)  $\Leftrightarrow$  antisymmetric rotational state ( $n$  odd)

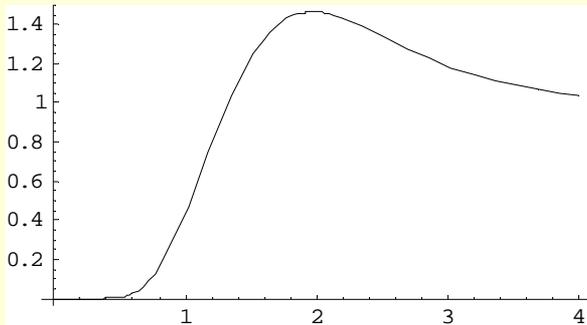
orthohydrogen  $\Leftrightarrow$  parahydrogen transition is slow

# MODERN QUANTUM MECHANICS

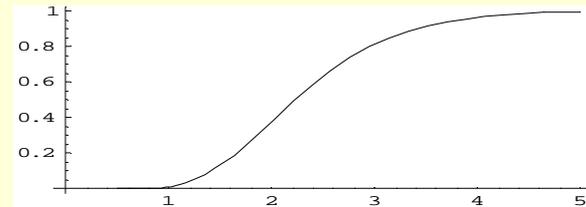
To calculate the specific heat of molecular hydrogen:

- Assume  $H_2$  molecule is a quantized rotator
- Treat nuclei as **identical particles** (anti-symmetric wave function).
- Result: hydrogen is a (weakly interacting) mixture of para- and ortho-hydrogen, in the ratio 1:3 at room temperature.

specific heats of para- and orthohydrogen at low temperatures



**PARAHYDROGEN**



ortho-hydrogen

If one combines these two curves in the ratio 1 part para to 3 parts ortho, one obtains a smoothly decreasing curve that agrees well with experiment.