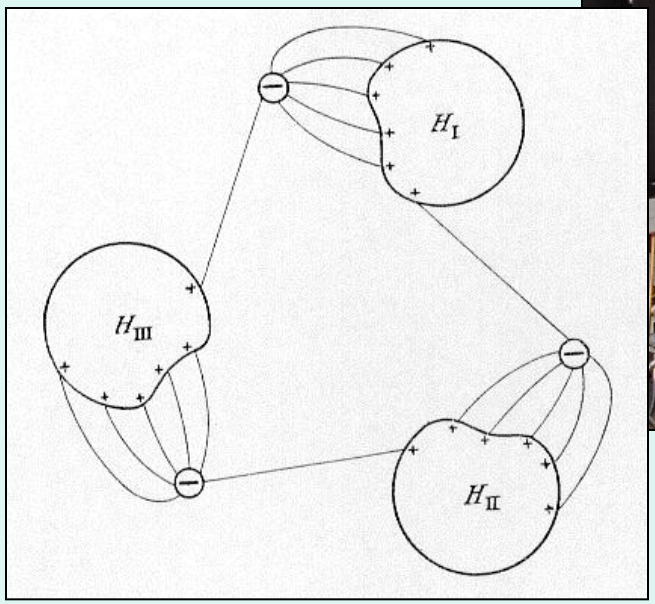
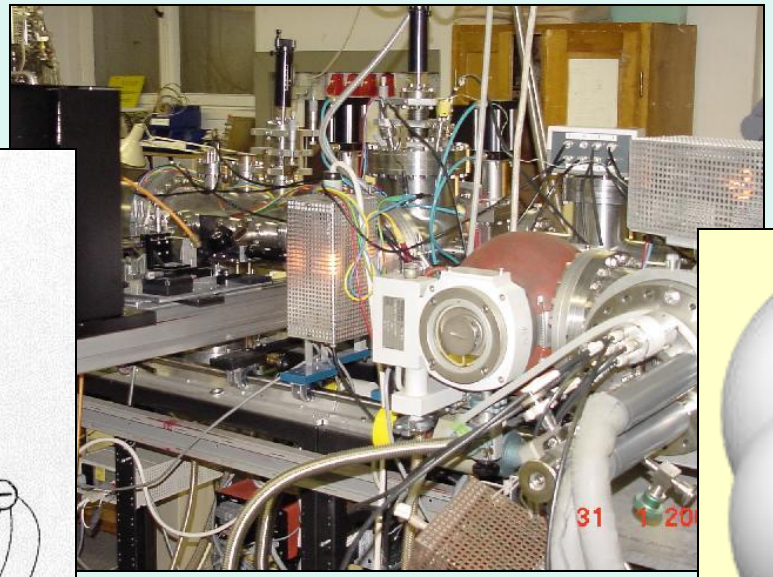
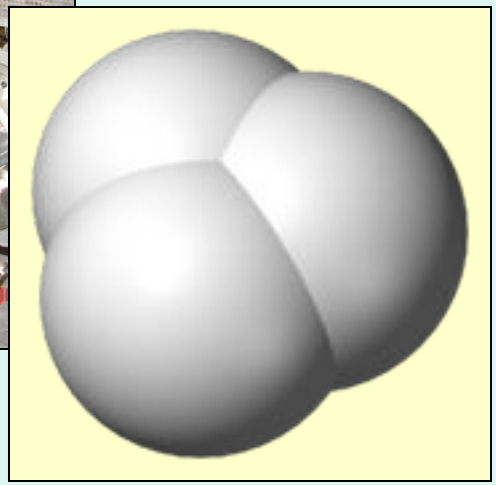
A Controversial Molecule:

The Early History of H_3^+ and H_3







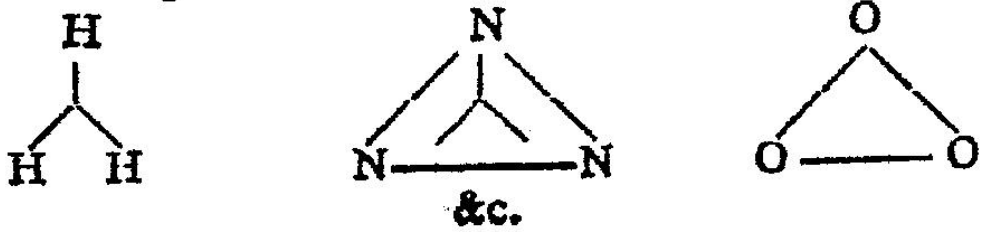
H. Kragh, Centre for Science Studies, Aarhus University, Denmark

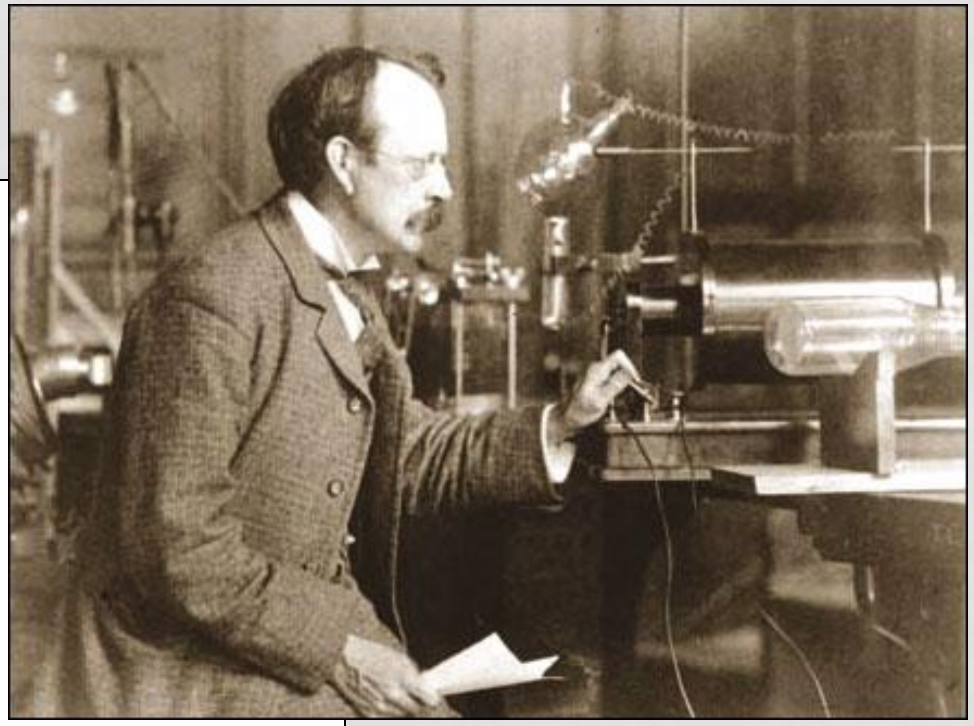
The first appearance of triatomic hydrogen (1895)

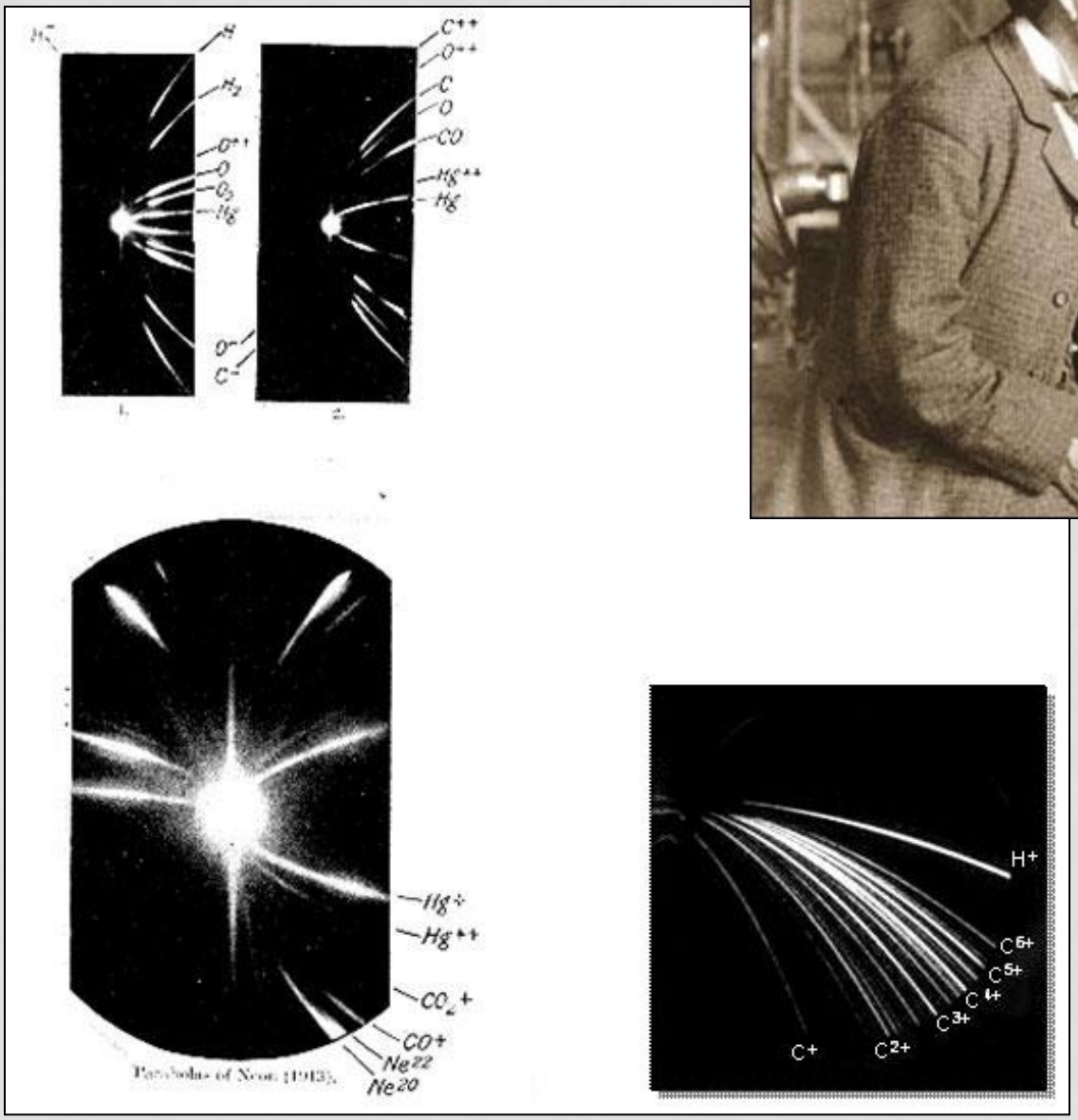
He = H_3 ?

B. Brauner (1855-1935)

If it should be possible to prove that helium and argon are peculiarly condensed hydrogen and nitrogen we shall have to expect a similar mode of condensation for oxygen (the group O_3 differing essentially from ozone, a peroxide of oxygen, O=O=O), and probably for fluorine. The constitution of the gases would then be something like the following :—







positive rays

(*Kanalstrahlen*)

RAYS OF POSITIVE ELECTRICITY

AND THEIR APPLICATION TO

CHEMICAL ANALYSES

BY

SIR J. J. THOMSON, O.M., F.R.S.

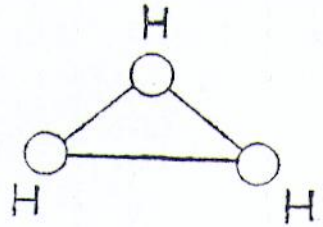
MASTER OF TRINITY COLLEGE, CAMBRIDGE
PROFESSOR OF EXPERIMENTAL PHYSICS, CAMBRIDGE

WITH ILLUSTRATIONS

SECOND EDITION

LONGMANS, GREEN AND CO.
39 PATERNOSTER ROW, LONDON
FOURTH AVENUE & 30TH STREET, NEW YORK
BOMBAY, CALCUTTA, AND MADRAS
1921

An example or two may make this clearer. On the new view H_3 is a possible valency compound, even when hydrogen is monovalent, as the following diagram shows. Each atom



in H_3 is the origin and also the termination of a tube of

J.J. Thomson, ”The forces between atoms and chemical affinity,” *Phil. Mag. 27* (1914), 757-789.

MEDDELANDEN

FRÅN

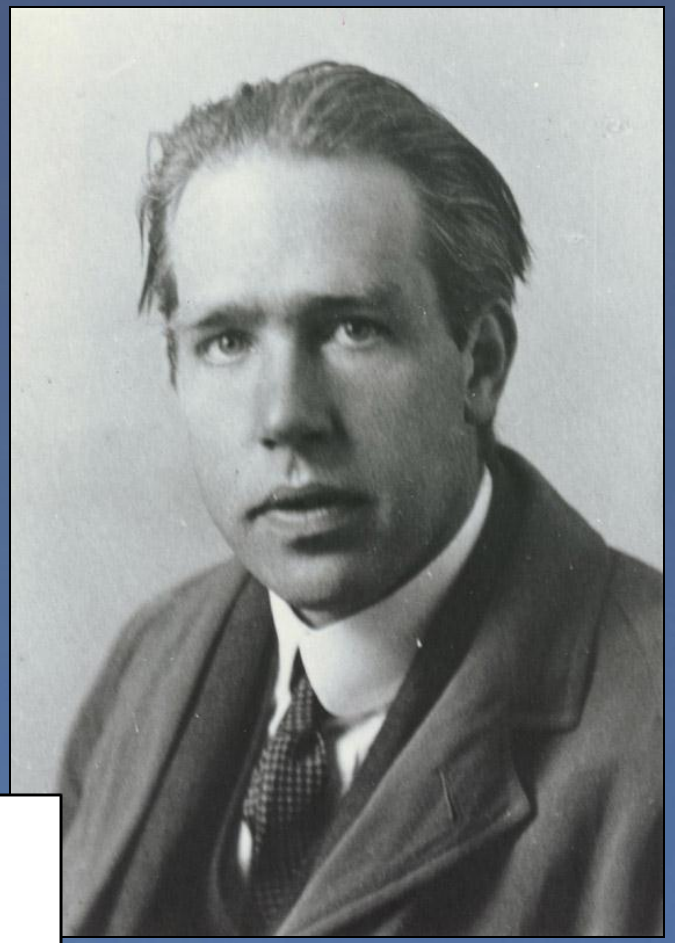
K. VETENSKAPSAKADEMIENS NOBELINSTITUT

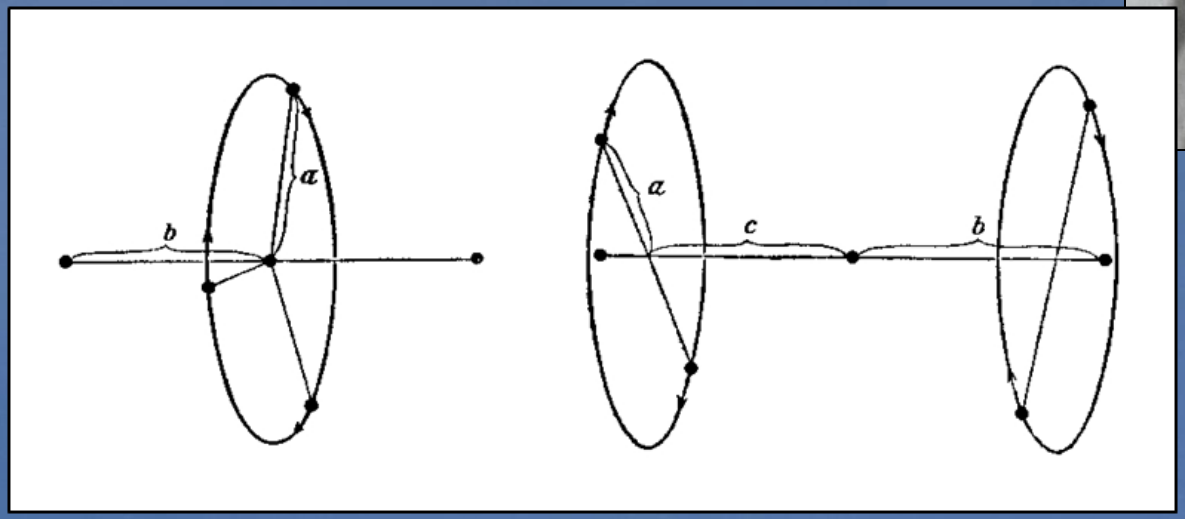
BAND 5. N:o 28.

On the model of a triatomic hydrogen molecule.

By

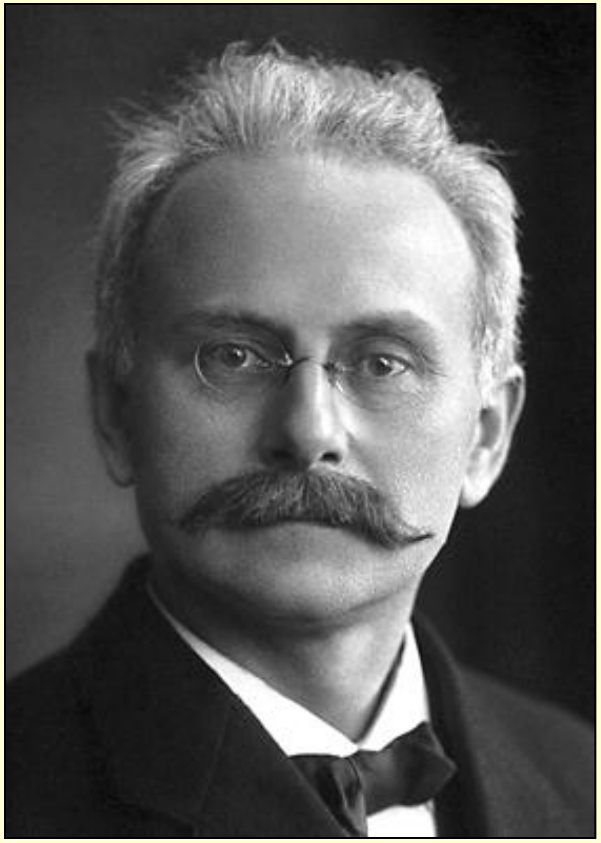
N. BOHR.

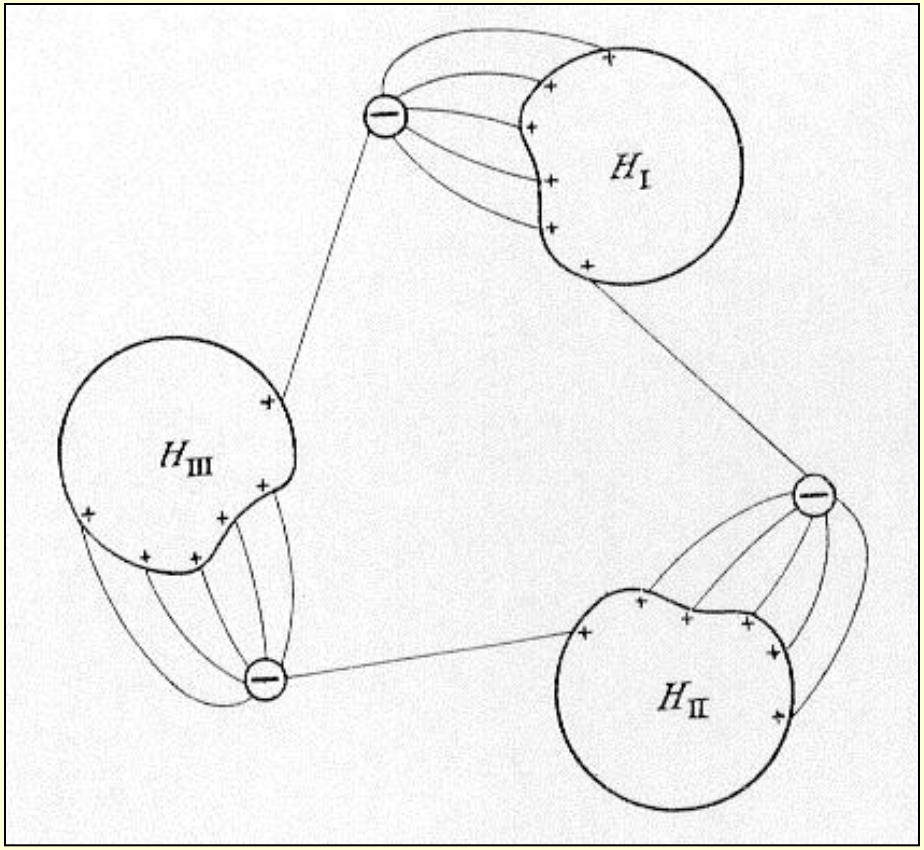




Bohr's models of

H_3 and H_3^-

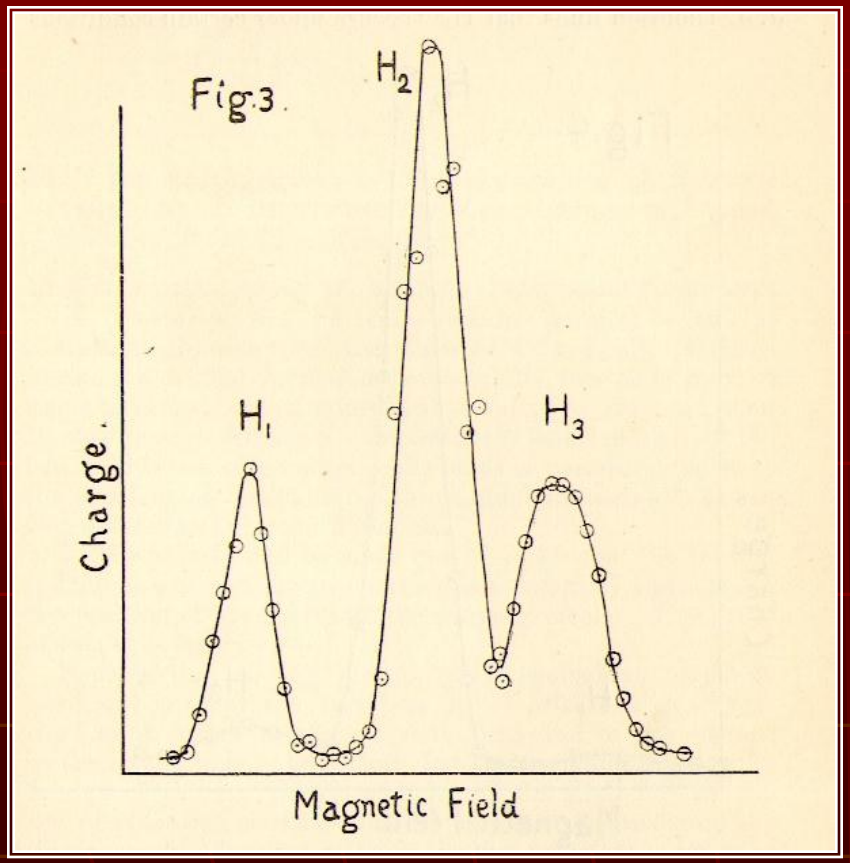


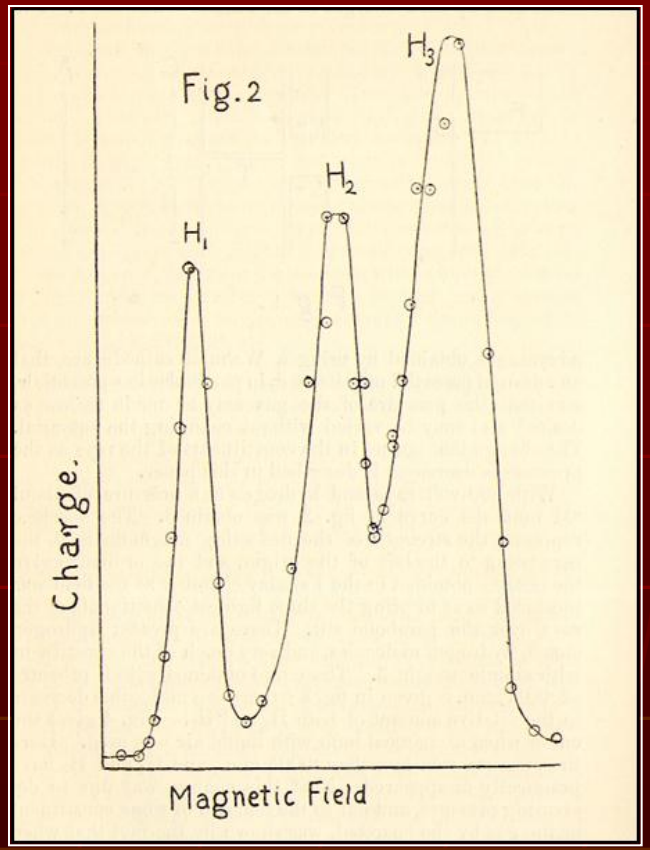


J. Stark, ”Über das dreiatomige Wasserstoffmolekül,” *Zs. Elektrochemie 19* (1913), 862-863.

J. Stark, *Prinzipien der Atomdynamik III* (Leipzig, 1915).

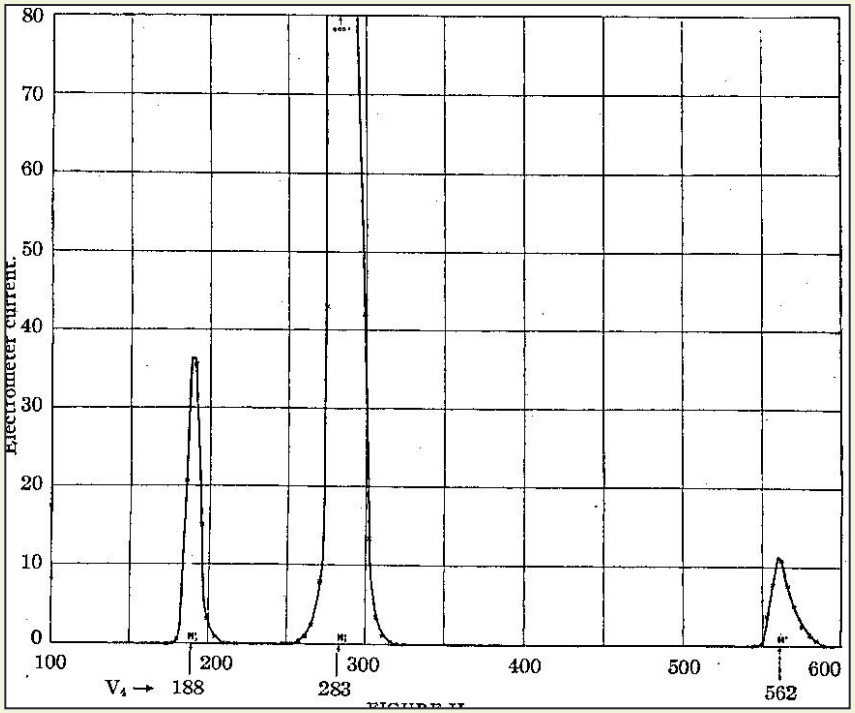
Early positive-ray recordings, showing the existence of H^+, H_2^+ and H_3^+

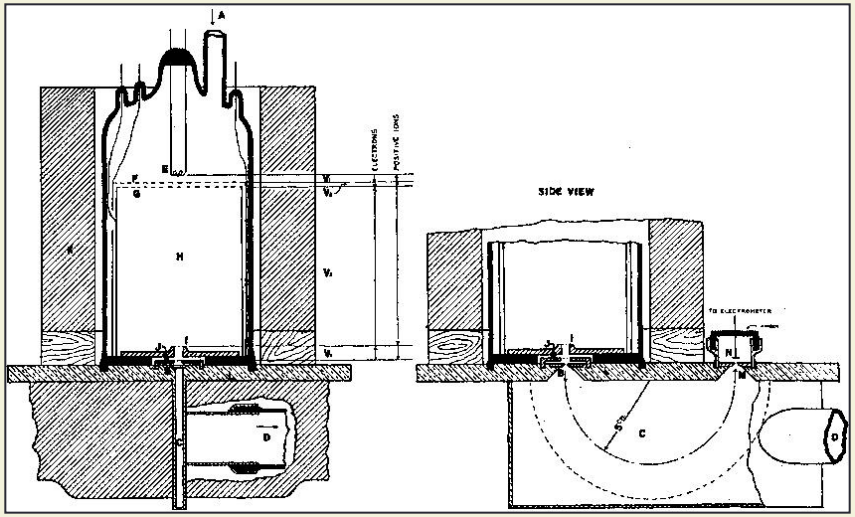




A.J. Dempster, "Ionization of hydrogen molecules and the formation of H_3," *Phil. Mag. 31* (1916), 438-443.

H_3^+ H_2^+ H^+



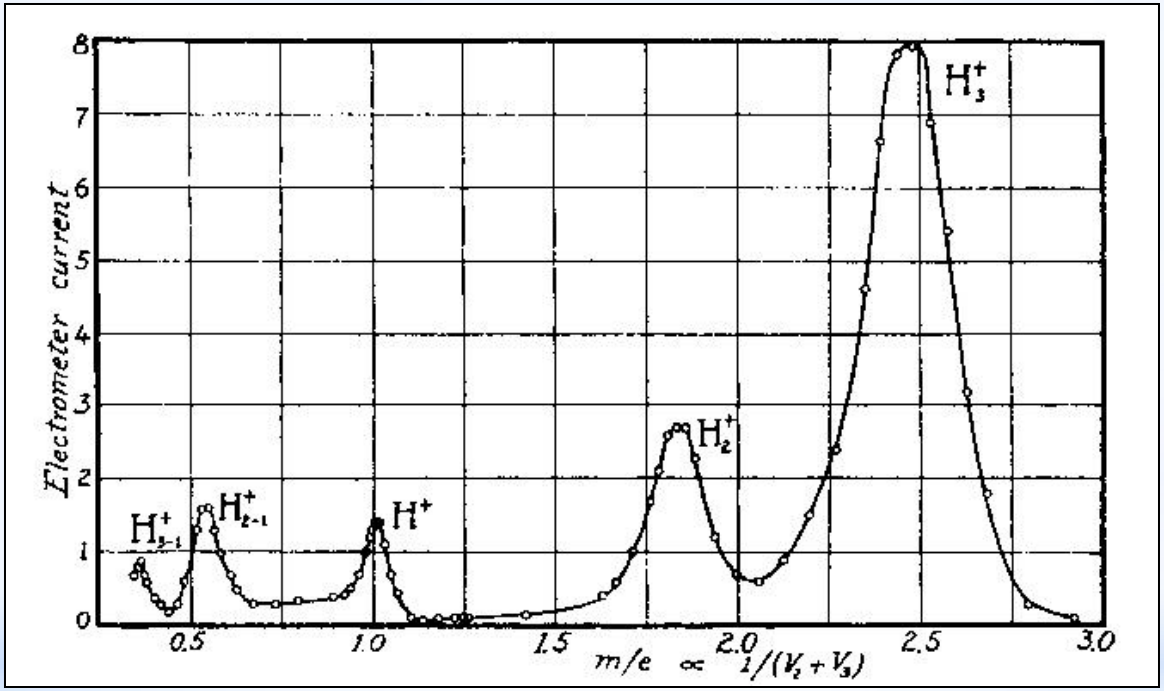


T.R. Hogness & E.G. Lunn, 1924-25

$$H_2^+ + H_2 \rightarrow H_3^+ + H$$

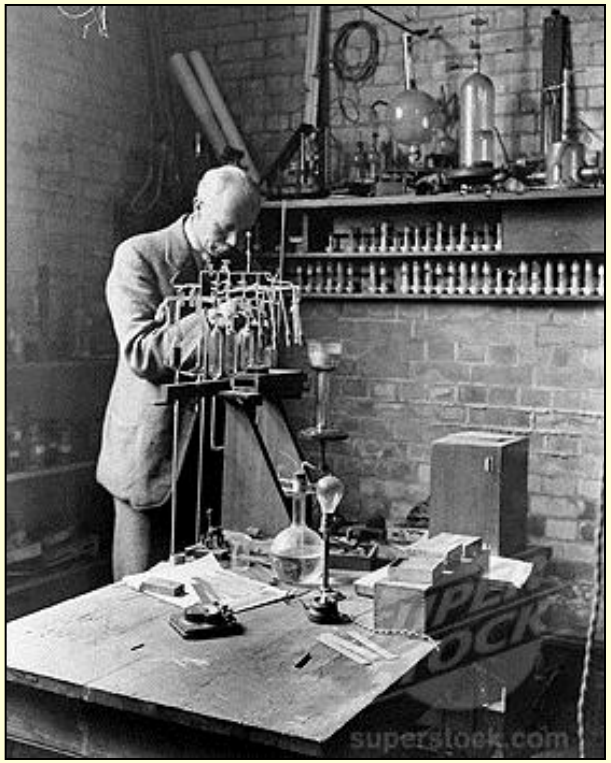
Reaction process for the formation of H_3^+

H_3^+ *is real*

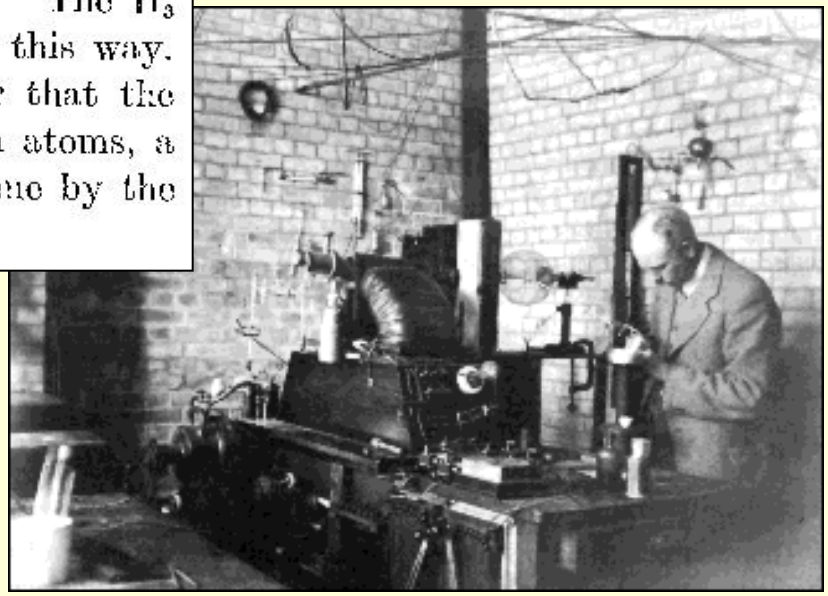


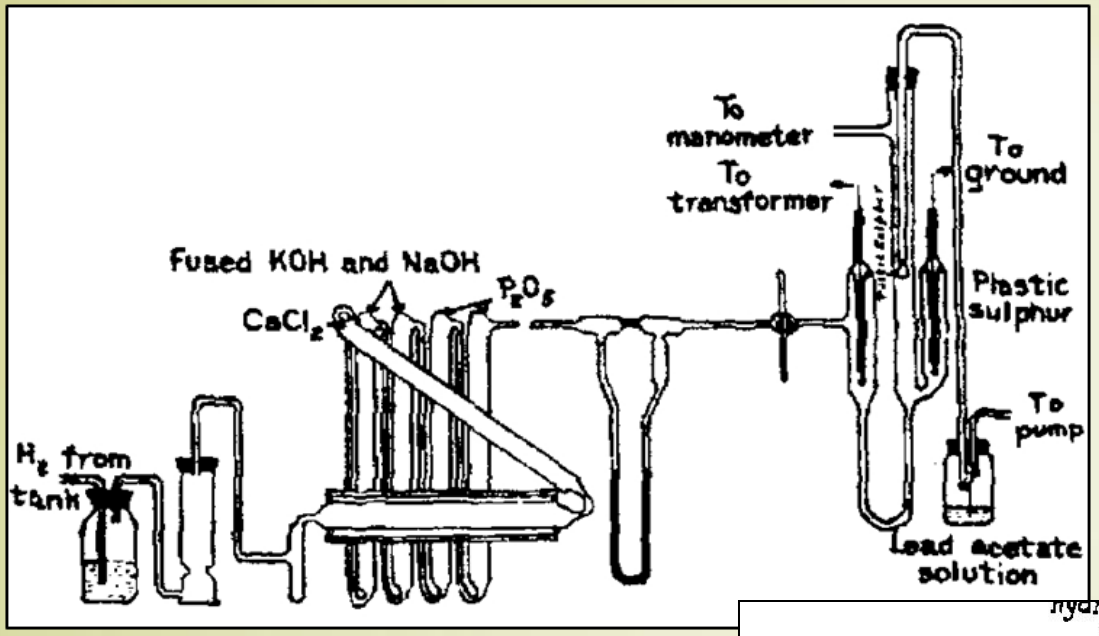
H.D. Smyth, ”Primary and secondary products of ionization in hydrogen,” *Phys. Rev. 25* (1925), 452-468.

Francis W. Aston, *Isotopes* (London, 1923)



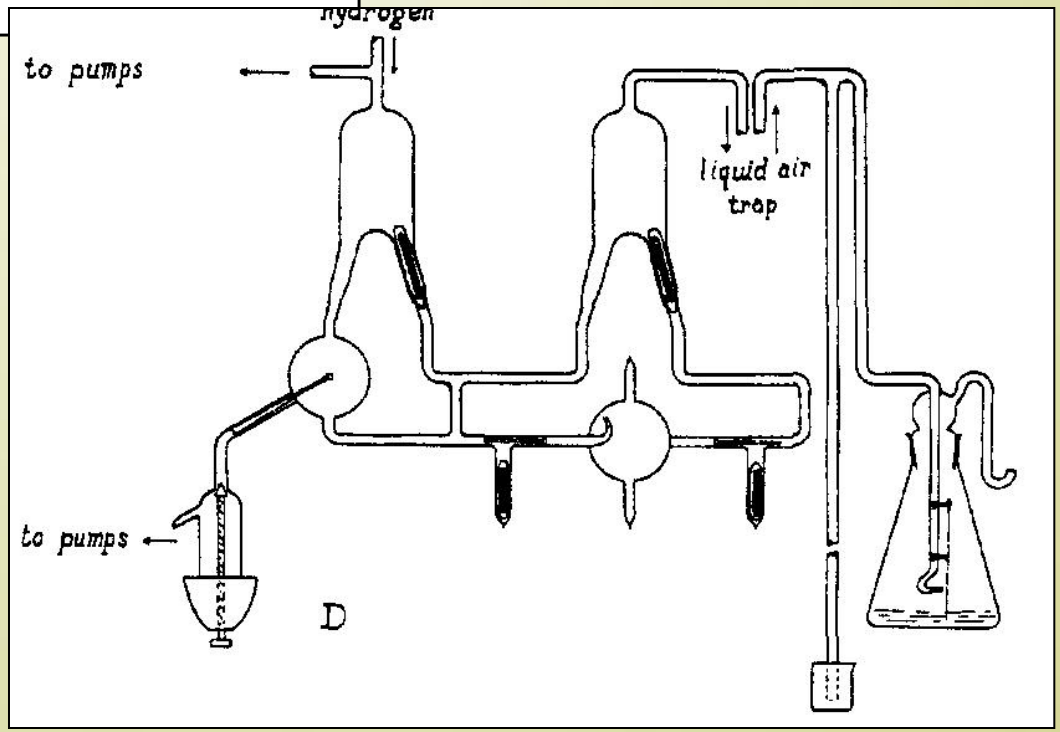
59. Triatomic Hydrogen H_3.—The occurrence of a parabola corresponding to a mass 3 was first observed and investigated by Sir J. J. Thomson.[2] He came to the conclusion that it was probably due to triatomic hydrogen. The simplest way of obtaining this substance is to bombard KOH with cathode rays and pump off the gases so produced. The H_3 used for the above measurements was obtained in this way. The mass deduced proves in a conclusive manner that the particle causing it is a molecule of three hydrogen atoms, a result independently established about the same time by the chemical work of Wendt and Landauer.[3]





"Active hydrogen"

(= H_3 ?)



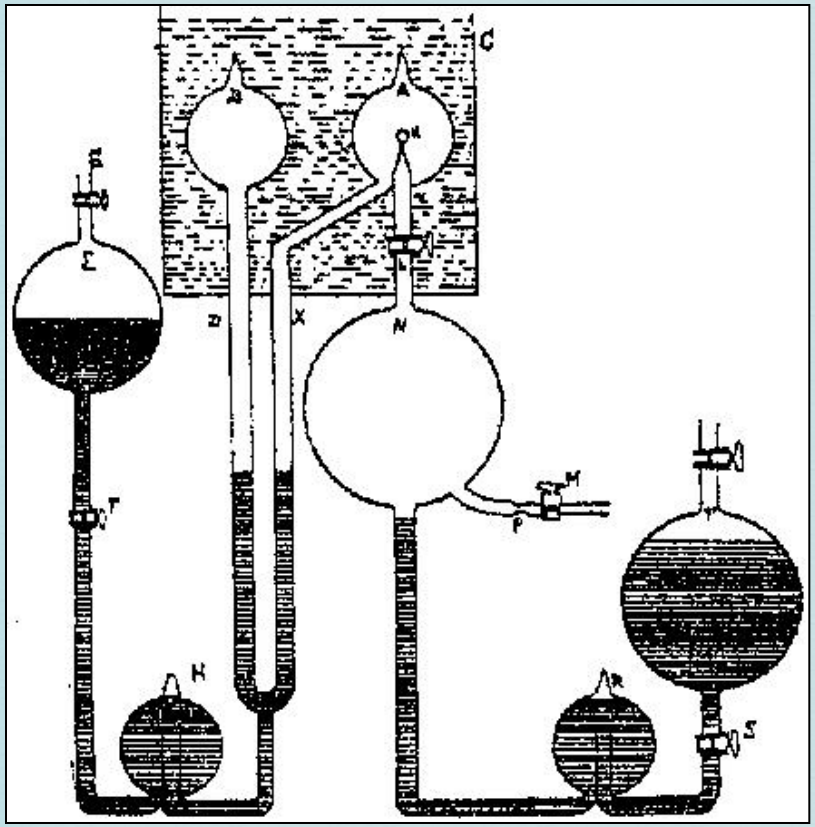
Active hydrogen reacts readily with

nitrogen ($\rightarrow NH_3$)

sulfur ($\rightarrow H_2S$)

… which can easily be tested.

Contraction effect



Some chemists found a marked contraction in volume when pure H_2 was exposed to α rays, which they suggested was due to

$$3\ H_2 \rightarrow 2\ H_3$$

They also found that the boiling point of the new active hydrogen was markedly higher than ordinary hydrogen.

W. Duane & G.L. Wendt, "A reactive modification of hydrogen by alpha-radiation," *Phys. Rev. 10* (1917), 116-128.
G.L. Wendt & R. Landauer, "Triatomic hydrogen," *J. Am. Chem. Soc. 42* (1920), 930-946.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

AN ATTEMPT TO PREPARE TRIATOMIC HYDROGEN[1]

BY HUGH M. SMALLWOOD[2] AND H. C. UREY

RECEIVED JUNE 9, 1927 PUBLISHED MARCH 7, 1928

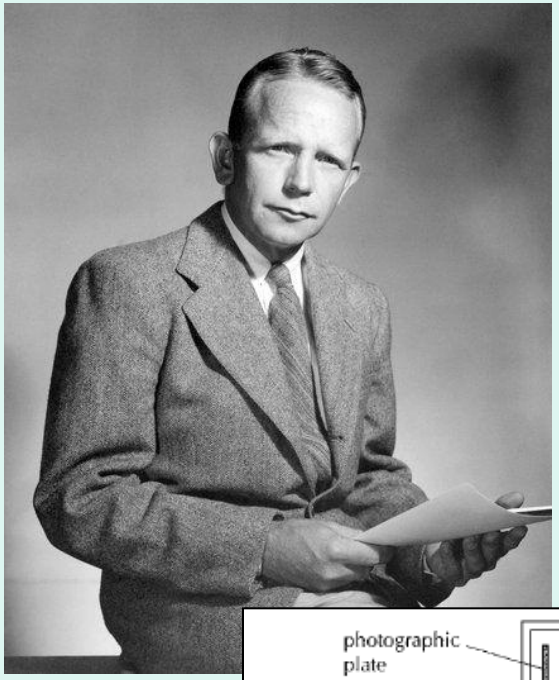
Introduction

The preparation and properties of an active modification of hydrogen, supposed to be triatomic, have been described by a number of investigators.[3] According to their papers, whenever hydrogen is ionized or dissociated a small amount of active product is formed. The activating agents that have been used with success include α-particles, the Siemens ozonizer, the vacuum discharge and the corona discharge. It ha
been stated that if oxygen is burned in an atmosphere of hydrog
if hydrogen-oxygen mixtures containing deficiency of oxygen are deto
part of the hydrogen remaining after the combustion is activated.
furthermore been reported that hydrogen is activated by passag

J. Am. Chem. Soc. *50* (1928), 620-626.

Harold C. Urey (1893-1981)

Nobel Prize in chemistry 1934 for the discovery of deuterium (^{2}H)



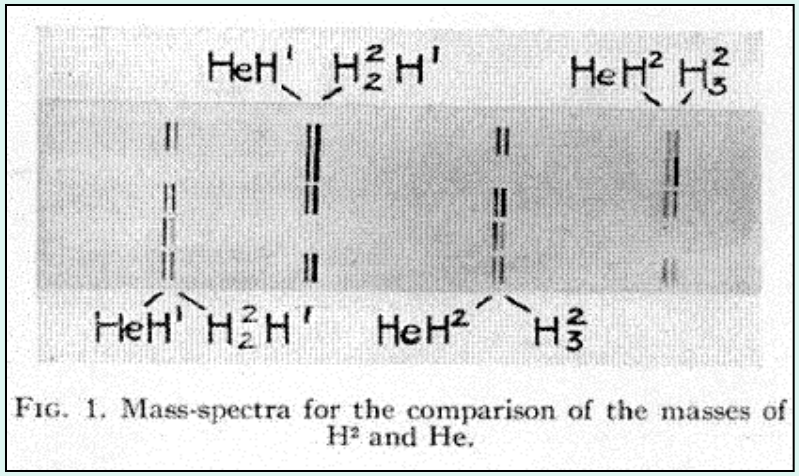
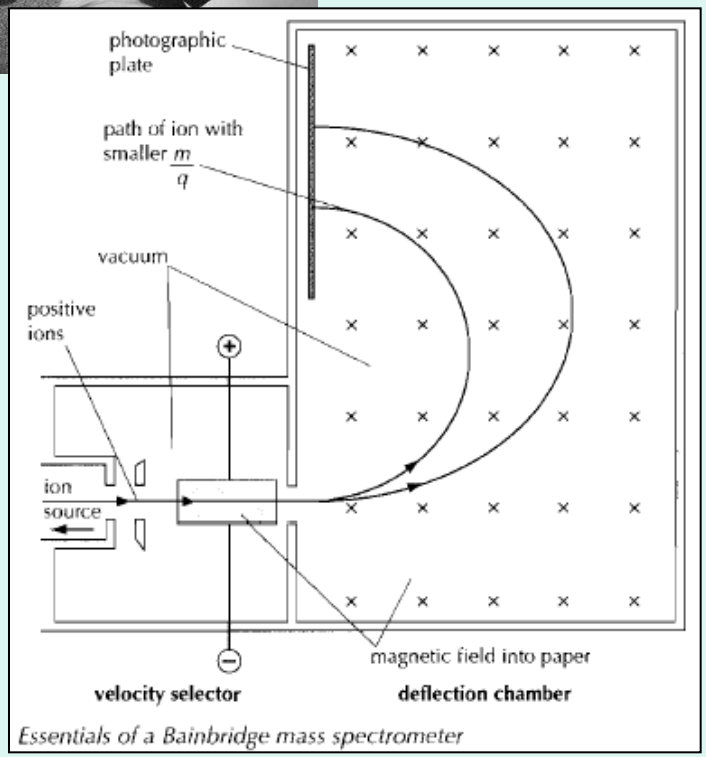


FIG. 1. Mass-spectra for the comparison of the masses of H^2 and He.

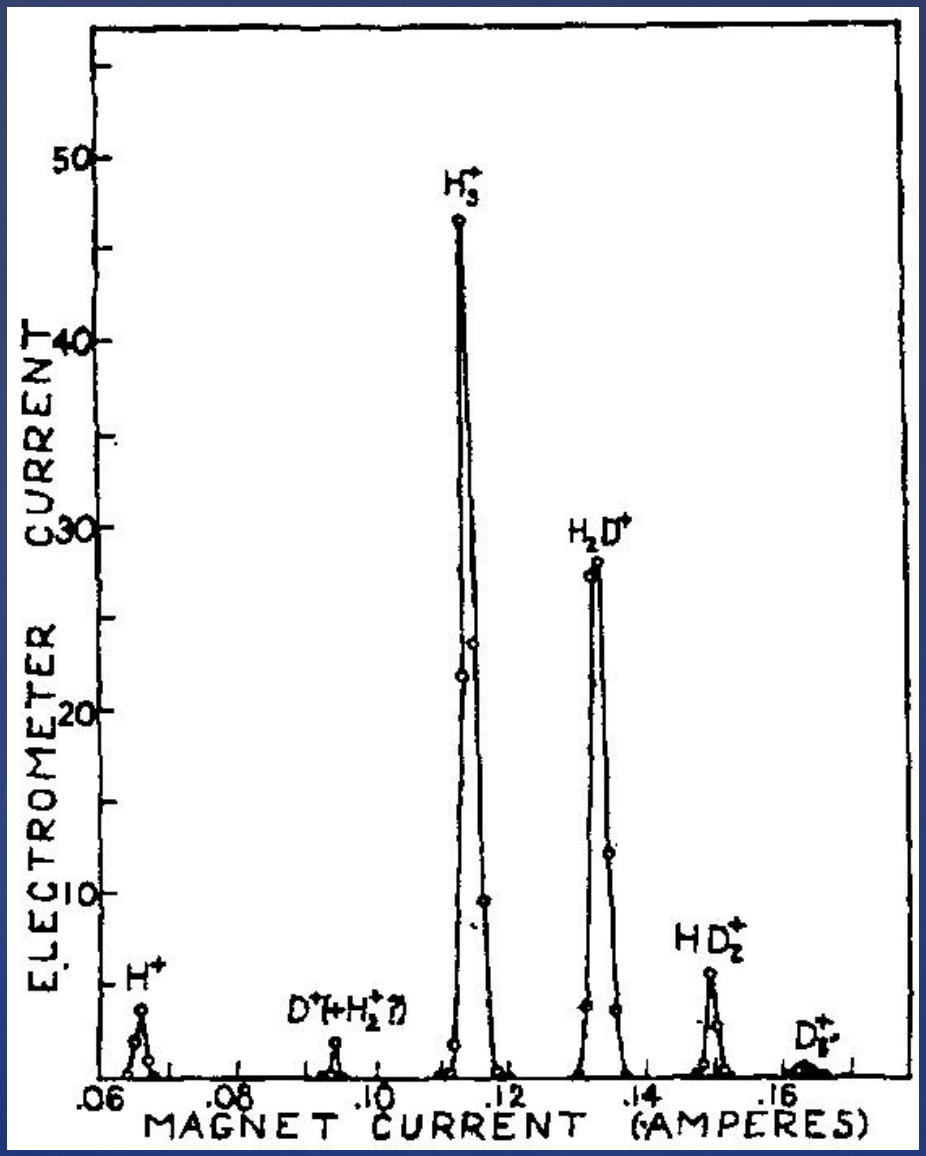


Essentials of a Bainbridge mass spectrometer

Mass spectrometry, isotopes, and hydrogen molecular ions.

K. Bainbridge et al., 1932+

Triatomic hydrogen isotope ions

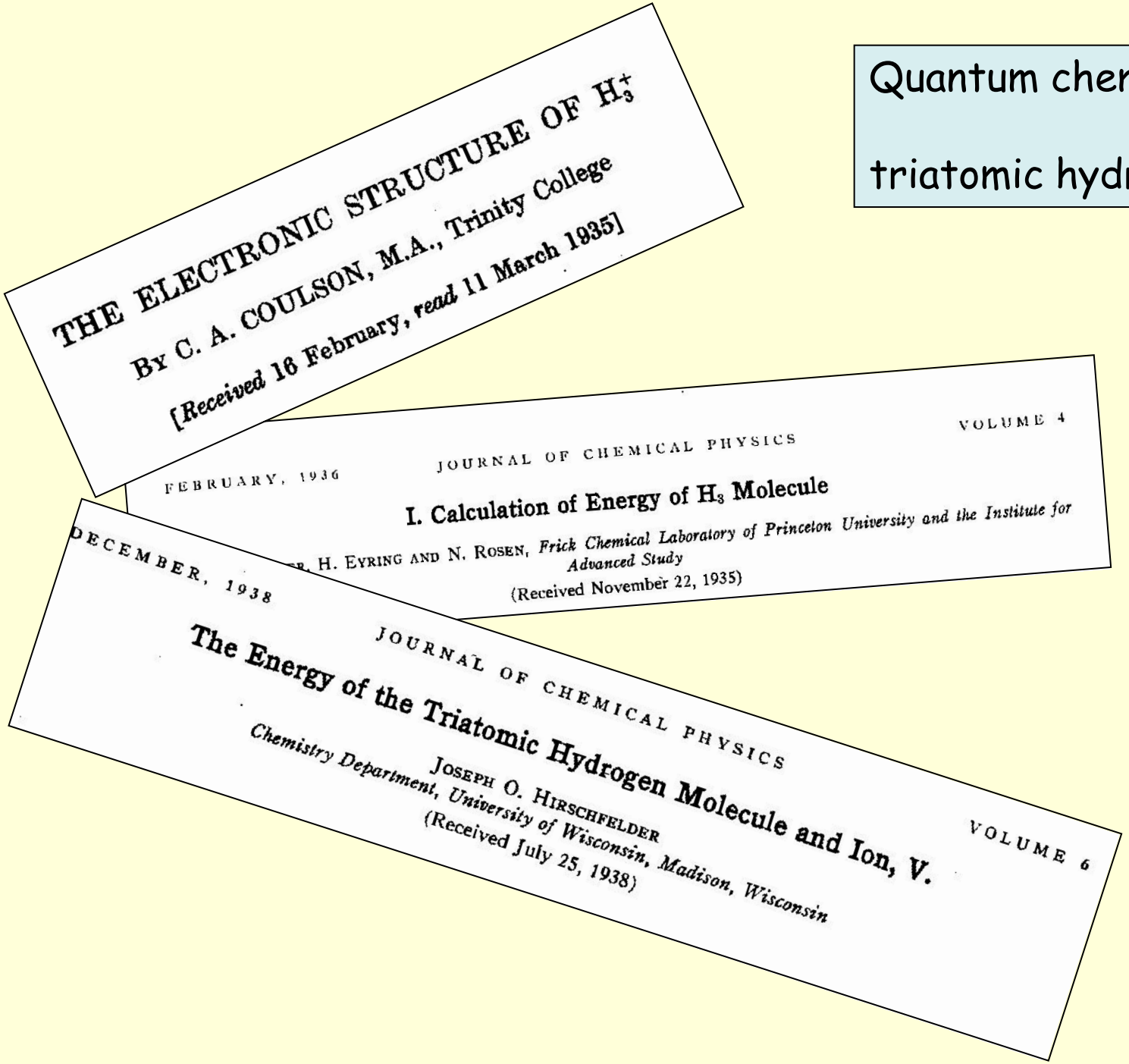


O. Luhr,

J. Chem. Phys. 3 (1935), 146.

Quantum chemistry and

triatomic hydrogen



THE ELECTRONIC STRUCTURE OF H_3^+

By C. A. COULSON, M.A., Trinity College

[*Received* 16 February, *read* 11 March 1935]

FEBRUARY, 1936 JOURNAL OF CHEMICAL PHYSICS VOLUME 4

I. Calculation of Energy of H_3 Molecule

H. EYRING AND N. ROSEN, *Frick Chemical Laboratory of Princeton University and the Institute for Advanced Study*

(Received November 22, 1935)

DECEMBER, 1938 JOURNAL OF CHEMICAL PHYSICS VOLUME 6

The Energy of the Triatomic Hydrogen Molecule and Ion, V.

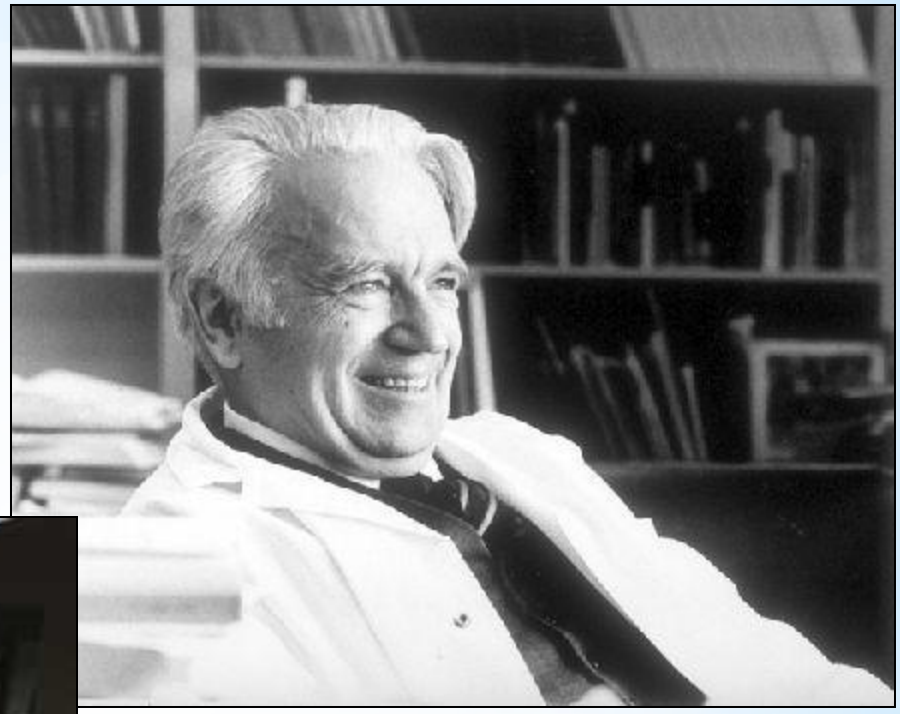
JOSEPH O. HIRSCHFELDER

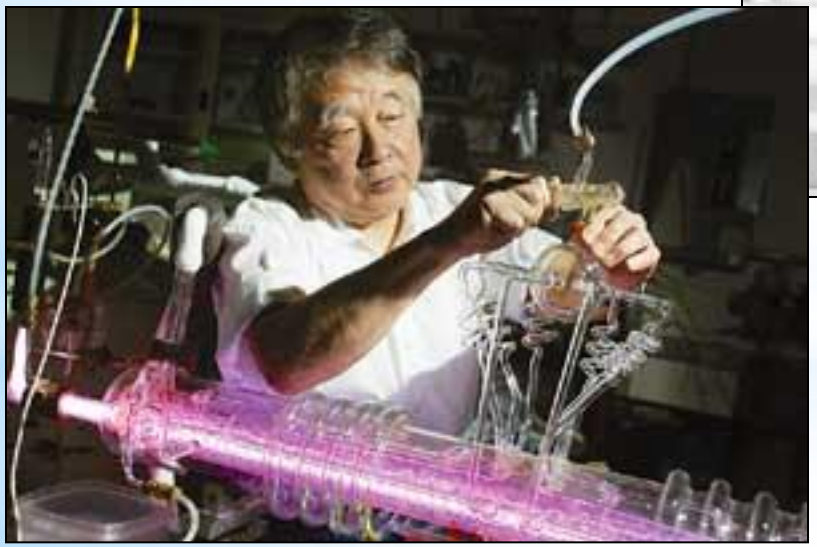
Chemistry Department, University of Wisconsin, Madison, Wisconsin

(Received July 25, 1938)

Triatomic hydrogen vindicated

G. Herzberg, ”A spectrum of triatomic hydrogen,” *J. Chem. Phys. 70* (1979), 4806-4807.





T. Oka, ”Observation of the infrared spectrum of H_3^+ ,” *Phys. Rev. Let. 45* (1980), 531-534.

Some lessons from the H_3 / H_3^+ case

- Illustrates the evidential nature of (much) scientific knowledge.

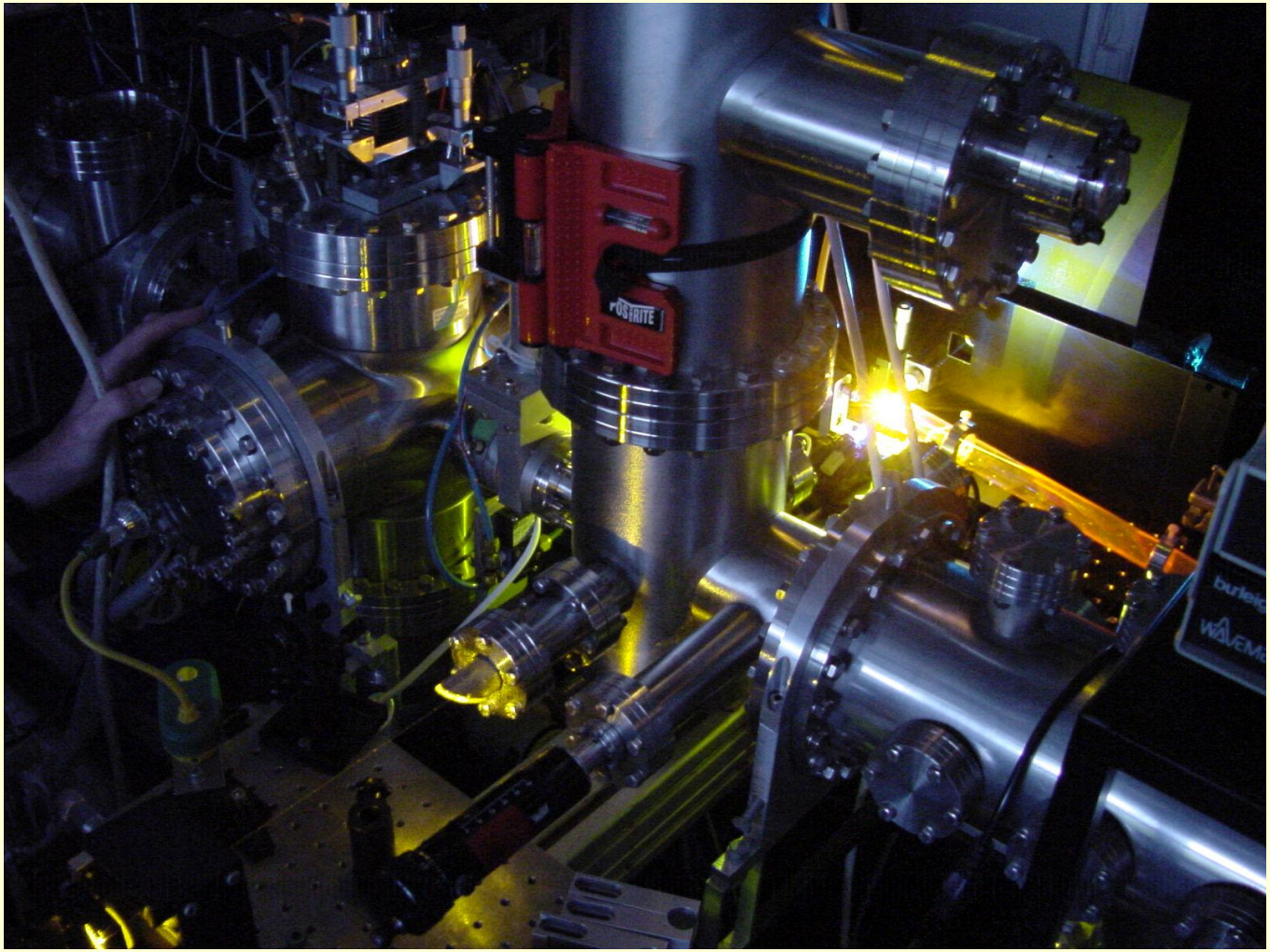
- Evidence claims can always be questioned or contradicted by counterevidence.

- Even though there is very good reasons to suspect the non-existence of *X*, *X* may still turn our to exist.

- Comparison with other cases of maybe-discoveries, e.g., anomalous water ("polywater") in the 1960s and 1970s.

- Interdisciplinarity: shifts between physics and chemistry (and later astronomy).

- The notion of discovery: Who discovered H_3? Was H_3^+ discovered twice?


POSITIVE