Franck, Hertz, and the Nature of ionization

Experimentalists in search of a theory

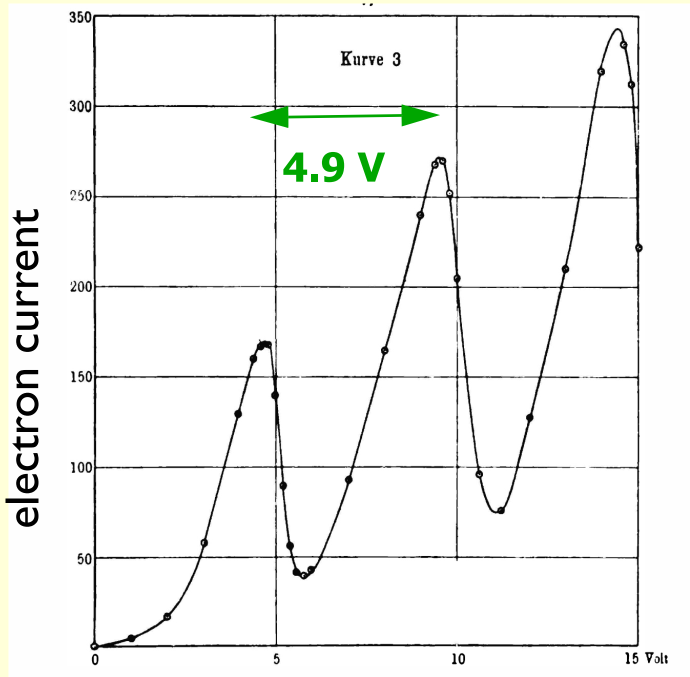
James Franck

Gustav Hertz

Clayton Gearhart
St. John's University (Minnesota)

American Physical Society
Denver
April 2013

Franck and Hertz on ionization: 1914



Accelerating voltage

In 1914, Franck and Hertz bombarded mercury vapor atoms with slow electrons.

- Peaks $\Rightarrow$ the onset of inelastic collisions, in which energy is transferred to the mercury atom.
- Franck and Hertz thought (**incorrectly**) that the 4.9 Volts between peaks represented the **ionization potential** of mercury—that is, the collisions produced mercury ions. (It was what we would call today an excited state.)
- But they also noticed that 4.9 volts corresponded to 2536 Å, the wavelength of a prominent uv **resonance line** in the spectrum of mercury.
- A second experiment, with a borrowed ultraviolet spectrometer, confirmed the presence of this line.

They concluded:

The transferred energy will in part be used for ionization, in part emitted as light radiation of frequency ν.

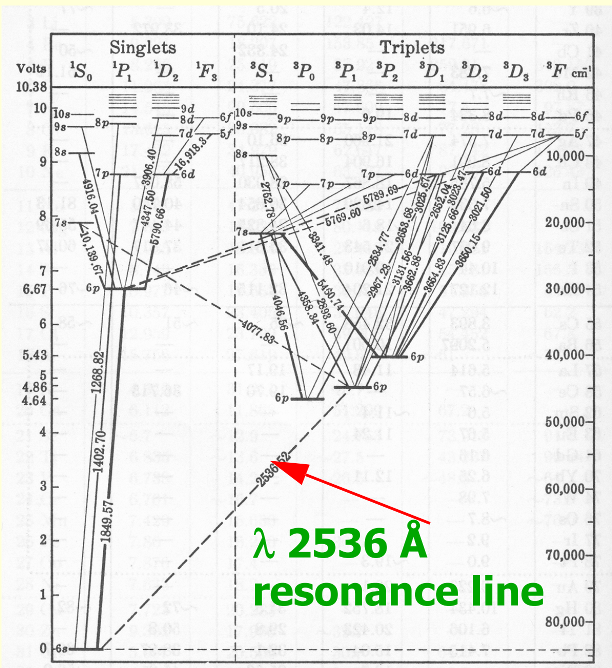
Spectral lines and ionization before Bohr

... in every mercury atom an electron is present that can oscillate with a frequency corresponding to the wavelength 253.6 μμ. ...

The transferred energy will in part be used for ionization, in part emitted as light radiation of frequency *ν*.

Franck and Hertz, May 1914

Before Bohr, spectral lines were interpreted as term differences, but **not** as energy level differences!



So where did Franck and Hertz's interpretation come from?

- not from Bohr!
- but also, not from the widespread assumption that **ionization must precede radiation**.

The Physics Institute, University of Berlin

James Franck
Ph.D. 1906
gas discharge;
then ion mobility

Physics in Berlin, early in the 20th century:

- quantum theory (Planck, Nernst, Einstein ...)
- close-knit group of young, enthusiastic experimentalists

Gustav Hertz
Ph.D. 1911
ir absorption in CO_2

Franck and Hertz, October 1911

"On a Connection between the Quantum Hypothesis and the Ionization Potential"

ionization energy = $h\nu$

But what is the frequency ν ?

Franck and Hertz suggested the "**selective photoelectric effect**" in alkali metals (Robert Pohl and Peter Pringsheim) might apply to gases. (spurious "resonance" effect; don't ask)

A theory by Friedrick Lindemann related the selective photoeffect frequency to atomic radius.

Pohl, Pringsheim, and Lindemann were all at the University of Berlin,

calculate or measure $\nu_{selective\ photoeffect}$, measure ionization potential, see if

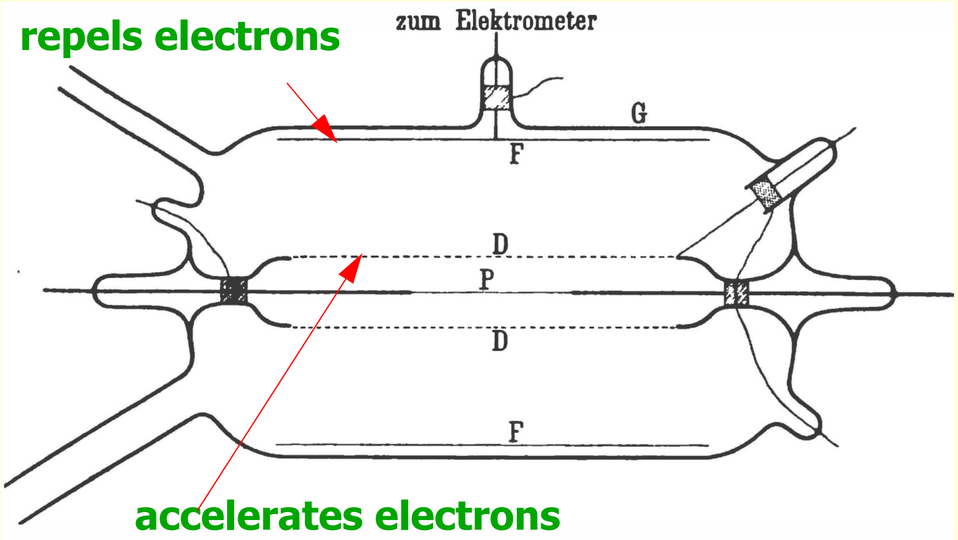
ionization energy = $h\nu_{selective\ photoeffect}$

In the near future, we will attempt to determine the ionization potential of a series of gases directly ... , and hope thus to contribute to an experimental clarification of the question.

For strongly electronegative gases, ... it can also be the case that one quantum is insufficient for ionization, so that only radiation results from the absorption of a quantum, and a collision that delivers two quanta first produces ionization.

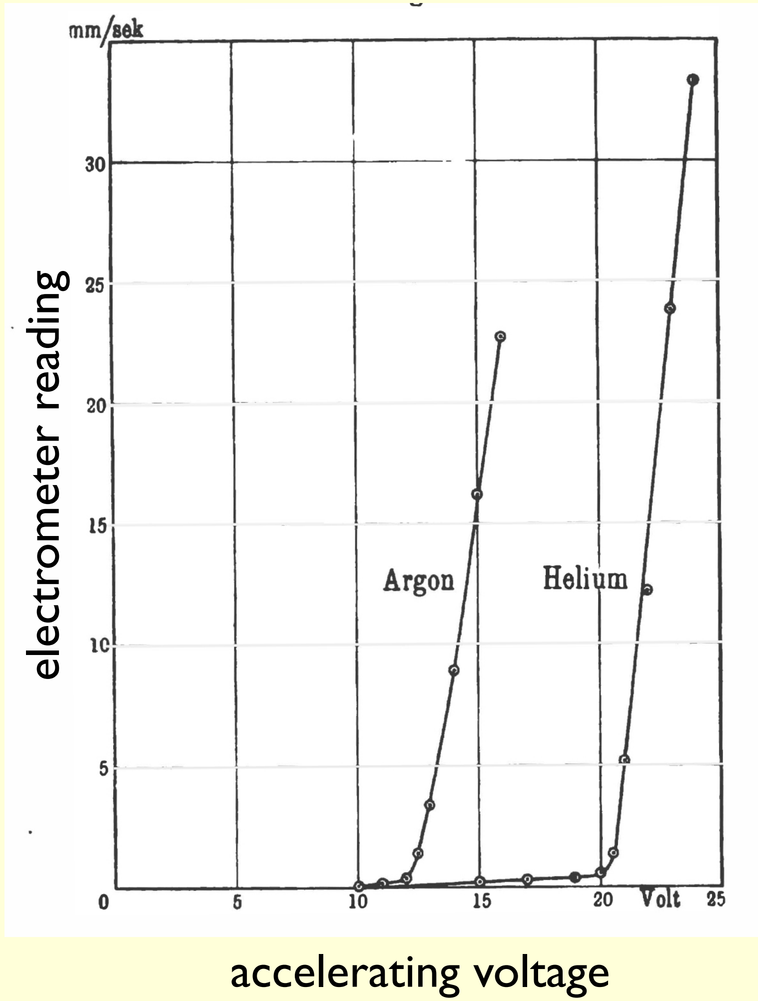
Franck and Hertz, January 1913

"Measurement of the Ionization Potential in different Gases"



The experiment was designed to measure the ionization potentials of helium, argon, and several other gases by detecting (**what they thought were**) positively charged ions.

- test of Pohl/Pringsheim/Lindemann theory (and two others) were inconclusive



Above all the monatomic metal vapors of mercury and the alkalis should be investigated, since Pohl and Pringsheim found the frequency of the selective photoeffect for them.

Nature of the collisions: 1913–1914

"On Collisions between Gas Molecules and Slow Electrons"(April 1913)"

"On Collisions between Gas Molecules and Slow Electrons. II."((July 1913)

"On the Connection between Ionization by Collision and Electron Affinity." (September 1913)

"Towards a Theory of Ionization by Collision" (December 1913)

Before moving on to mercury, F&H published four papers measuring **electron mean free paths** and **elasticity of electron-molecule collisions**.

- This work challenged **John S. Townsend**'s prevailing theory of how current increases as a stream of accelerated electrons collides with gas molecules.
- Townsend: student of J. J. Thomson; since 1900, professor at Oxford
- His experiments (from about 1900) were among the first to establish order of magnitude estimates of the ionization potential.
- His values for ionization potentials disagreed with those of F&H (1913)

As early as 1911, Franck and Hertz sounded doubtful about the "**not always certain hypotheses and simplfications**" involved.

NATURE OF THE COLLISIONS: 1913–1914

John Townsend (Oxford)

Townsend's theory, as understood by F&H, assumed

- Electrons lose **all** kinetic energy in a collision, even if the electron energy is less than the ionization potential.
- **If the electron energy is greater than or equal to the ionization potential, a collision always results in ionization.**

F &H argued that these assumptions lead to systematic errors in i.p.

By contrast,

- For energies below the i.p., Franck and Hertz found that for noble gases (and later, for mercury vapor), collisions were completely elastic — electrons lost no KE in collisions.
- **They cited other experiments, "above all, β radiation," to argue that**

James Franck

... by no means every collision for which the electron has the necessary energy … results in ionization. It appears that a predisposition of the molecule as well as the place where the molecule is struck plays a part.

Franck and Hertz, 1914

Gustav Hertz

leaves open the possibilty of radiation w/o ionization

Frank and Wilhelm Westphal, January 1912

"On the influence of ionization collision by fluorescence"

F&H illuminated iodine vapor in a discharge tube, causing the iodine to fluoresce, in order to see if fluorescence increased the discharge current. It did. But they did NOT assume that ionization accompanied illumination, **unlike** F&H's conclusions in 1914.

The presumption is expressed, that electrons oscillating under the influence of light will be split off more easily than the same electron without illumination.

If one assumes that the probabilities [of fluorescence and ionization] **are independent of one another, then it follows that the probability that a molecule will be ionized during fluorescence is for all practical purposes zero. ...**

The second possibility is that the probability that a molecule fluoresces /shines [*leuchtet*] and that it will be ionized, are not independent of one another, but depend on the same predisposition. ...

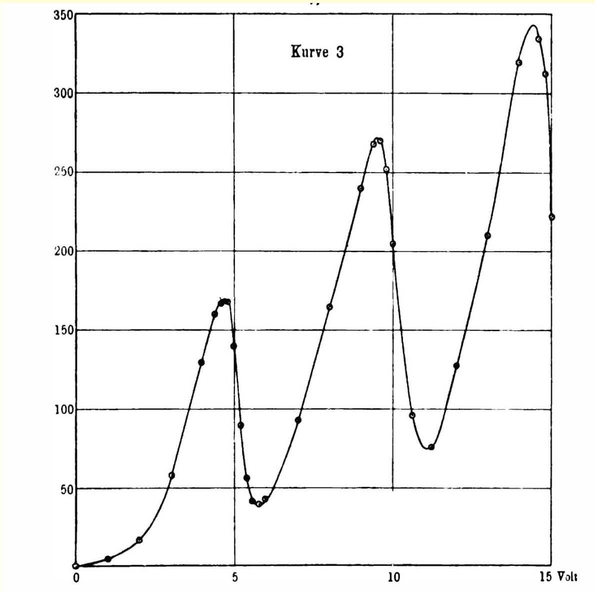
Franck and Westphal, 1912

On the other hand, the paper with Franck and Westphal makes much more sense, because we see there a difference between ionization and resonance of an electron in an atom or a molecule. ... How can one say the one thing and the other together, at the same date? That I don't understand at all, because this really makes a lot of sense, and that was before Bohr's paper and so on, and I was astonished that we had that much intelligence in writing this paper.

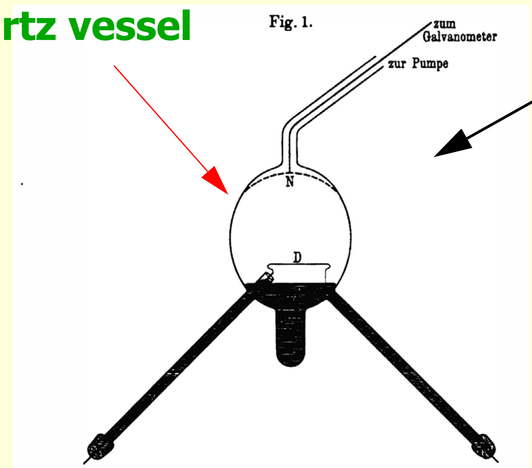
Franck, 1962

Franck and Hertz, April and May, 1914

"On Collisions between Electrons and Mercury Molecules and the Ionization Potential of the same"



quartz vessel



Based on their work the previous year, Franck and Hertz **significantly redesigned their apparatus** (persistent theme!):

- peaks represent onset of inelastic collisions, and hence (**they thought**) ionization
- noticed that the 4.9 volt peak spacing is equivalent to the λ 2536 resonance line of mercury
- confirmed the presence of this uv line specroscopically, in a second experiment
- calculated Planck's constant *h*
- selective ~~photoeffect~~ gone

The transferred energy will in part be used for ionization, in part emitted as light radiation of frequency ν.

Franck and Einstein

Kuhn:
Back now before the Bohr atom, you don't remember now particular conversations about the quantum?

Franck
I remember one with Einstein. And he shook his head and said, "In the principle of relativity, everything is so clear. But in quantum theory it is horrible. What a mess it is in." … Anyway, he said this, and my answer was. "You are certainly right. But you see, as an experimentalist, I am of the opinion that it pays to fish in muddy water."

Franck, 1962

A Few References

K. T. Compton, "Critical Potentials. Part I. Critical Potential Methods" Bulletin of the National Research Council **9**, 3–60 (1924).

John L. Heilbron, "A History Of The Problem Of Atomic Structure From The Discovery Of The Electron To The Beginning Of Quantum Mechanics." Ph.D. Dissertation, University of California (Berkeley) 1964.

Gustav Hertz, "Zur Geschichte unserer Versuche über den Energieaustausch zwischen langsamen Elektronen und Atomen." (Unpublished, 1966; in James Franck Papers, University of Chicago Library).

Helge Kragh, *Niels Bohr and the Quantum Atom* (Oxford U. Press, Oxford, 2012)

Jost Lemmerich, *Aufrecht im Sturm der Zeit: Der Physiker James Franck, 1882-1964* (GNT-Vlg, , 2007); translated in Jost Lemmerich, *Science and Conscience. The Life of James Franck* (transl. Ann M. Hentschel), Stanford University Press , (2011)

Henry Gilbert Small, "The Helium Atom in the Old Quantum Theory" (Ph.D. dissertation, University of Wisconsin, 1971)