Franck, Hertz, and the Nature of ionization

Experimentalists in search of a theory

James Franck

Gustav Hertz

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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:

\[
\text{The transferred energy will in part be used for ionization, in part emitted as light radiation of frequency } \nu.
\]
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.
Physics in Berlin, early in the 20th century:

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

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

Gustav Hertz  
Ph.D. 1911  
ir absorption in CO₂
ionization energy = $h\nu$

But what is the frequency $\nu$?

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 Friedrich 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.
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.
“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 simplifications” involved.
Nature of the collisions: 1913–1914

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

... 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

leaves open the possibility 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”

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 $\lambda 2536$ resonance line of mercury
- confirmed the presence of this uv line spectroscopically, 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 $\nu$. 
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


