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# James Franck, the ionization potential of helium, and the experimental discovery of metastable states



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#### ABSTRACT

In 1920, James Franck together with Fritz Reiche and Paul Knipping found strong experimental evidence that the lowest-lying triplet state in helium is metastable—an atom in this state cannot make a spontaneous transition to the ground state. Even though their evidence was entirely experimental, they tied their results almost inextricably to Alfred Landé's 1919 model of the helium atom, and in the process, misunderstood the new theoretical selection rules of Adalbert Rubinowicz and Niels Bohr. In an additional complication, experiments of the English physicists Frank Horton and Ann Catherine Davies contradicted Franck's. Although Franck's result has held up, the reasons for the discrepancies remain unclear.

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#### 1. Introduction

Helium has always been a troublesome element. First discovered in spectroscopic observations of the sun, it displays two noncombining spectral series, one consisting of singlet terms, the other of triplets (thought to be doublets before 1927).<sup>1</sup> Spectroscopists at first suspected that the two series might belong to separate elements, dubbed "parhelium" (singlets) and "orthohelium" ("doublets"). The two names are still employed.<sup>2</sup>

Our story begins in 1911 with the work of James Franck (1882–1964) and Gustav Hertz (1887–1975), who used collisions of

slow electrons with gas molecules, including helium, to understand the nature of ionization by collision and to measure the ionization potentials and other properties of those gases.<sup>3</sup> By this time, spectroscopists had measured spectral wavelengths of helium and many other elements. They inferred series terms from these measured spectral lines, and understood that all spectral lines could be calculated from the differences between the wave numbers of the series terms.<sup>4</sup> Indeed, terms came to be thought of as more fundamental.<sup>5</sup>

For helium, the terms and wavelengths were well known and tabulated (Fig. 1), with one important exception: no one had the slightest idea of the location of the lowest ("normal" or ground

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<sup>&</sup>lt;sup>1</sup> I will usually refer to "doublets" in quotation marks to remind readers that they are triplets. See Appendix A.1 for a short introduction to spectroscopic terminology and notation.

<sup>&</sup>lt;sup>2</sup> Kragh (2009) gives a full account of this history. Parhelium is often called parahelium, and occasionally helium and orthohelium are used interchangeably.

<sup>&</sup>lt;sup>3</sup> See Gearhart (2014) for discussion and bibliography of the Franck-Hertz experiments and their immediate aftermath.

<sup>&</sup>lt;sup>4</sup> See Fig. 1 for a partial term diagram of helium. For a more complete diagram, see e.g. Herzberg (1937, 1944).

<sup>&</sup>lt;sup>5</sup> For an early example, see Dunz (1911). See also Brand (1995, ch. 7).



**Fig. 1.** Partial term diagram for helium, showing a few S and P terms and a few lines of the principal series stemming from the singlet and triplet 2S states, the first lines of which Paschen investigated in 1914 (see text). Note also the 0.8 V difference between the 2 <sup>1</sup>S and 2 <sup>3</sup>S states. The splitting of the triplet states cannot be seen on the scale of this drawing. See Appendix A.1.



Fig. 2. Frank and Hertz's 1913 apparatus for measuring ionization potentials, from Franck and Hertz (1913). See Gearhart (2014).

state) term. Did it belong to the singlet or "doublet" series? Or to neither? Or might both series have normal terms? Transitions to the normal state were widely believed to be in the far ultraviolet, but were not seen optically until the early 1920s, when Theodore Lyman (1874–1954), a pioneer of far ultraviolet spectroscopy, finally detected them (Lyman & Fricke, 1921; Lyman, 1922a, 1922b; see also Lyman, 1914, 1928).

Initially, these spectral terms had nothing to do with energy levels. They became such only after the advent of Niels Bohr's (1885–1962) new atomic theory in 1913. Even in 1914, Franck and Hertz thought in terms of a Thomson-like model in which electrons oscillated within an extended positive charge, each spectral line corresponding to the oscillation of an atomic electron.

When Franck and Hertz began their experiments, the energy needed to ionize helium was unknown. In 1913, they attempted to measure it, adopting a method developed by Philipp Lenard (1862–1947) and designed to detect positive ions produced in collisions with slow electrons (Fig. 2). The apparatus worked as follows: a mesh electrode D accelerates electrons emitted by a hot filament P. These electrons collide with gas molecules in the region between D and a collecting electrode F connected to an electrometer. The collector F is biased to repel electrons but attract positive ions, so that an increase in the electrometer reading should signal the presence of the latter.

For helium, they saw a sharp jump in their electrometer reading at about 20.5 V.<sup>6</sup> They assumed that they were seeing positive ions produced by electron collisions, and that they had therefore measured the ionization potential. In fact, they had measured only the excitation potential of the lowest "doublet" state—to use the conceptual scheme that emerged only after Bohr. As the helium atom returned to the normal state, it emitted ultraviolet light. This light in turn led to the emission of photoelectrons from the collecting electrode (Fig. 2); and of course, photoelectrons leaving the collecting electrode and positive ions arriving were electrically equivalent.

In 1914, Franck and Hertz turned to mercury, and again attempted to measure the ionization potential. This time they used a different experimental technique, detecting the onset of inelastic collisions as electrons struck gas atoms. They also repeated their measurements on helium, and found the same 20.5 V result they had recorded a year earlier, increasing their confidence both in this new technique, and in their earlier result. But once again, what they thought was ionization turned out to be excitation.

Shortly thereafter, Franck and Hertz found themselves in the German army, and their experimental collaboration came to an end. Neither resumed research until after the Great War. Nevertheless, their work inspired widespread emulation, particularly in North America. A crucial experiment came in 1917 from Bergen Davis (1869–1958) and his student Frederick Goucher (1888–1973) at Columbia University. Goucher contrived an extension of Franck and Hertz's 1913 apparatus by adding a new mesh electrode—imagine it placed close to the collecting electrode *F* in Fig. 2—that could be biased either positively or negatively with respect to the collector, thus allowing them to distinguish between positive ions and photoelectrons. Their results were unambiguous: In mercury, Franck and Hertz had seen photoelectrons, not positive ions. Moreover, Davis and Goucher detected positive ions at the higher voltage (about 10.3 V) corresponding to the principal series

<sup>&</sup>lt;sup>6</sup> It turned out that this value and most of the other early measurements of excited states and ionization energies in helium by Franck and others were systematically high by about 0.8 V. See Section 8 below. The values of excitation and ionization voltages measured by Franck and others were often slightly different, as will be apparent below. For example, different experiments gave values for the excitation potential in the range 20.4–20.5 V (not taking the systematic error described above into account). There is a similar small range for the ionization potential. Error estimates were not always given, but when given, were generally a fraction of a volt, and authors often said that their reported results were consistent with the slightly different results of other experiments.

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