

through the gas under investigation. The photographic plate shows a set of unexposed lines that result from the absorption by the gas of distinct wavelengths of the continuous spectrum.

- For every line in the absorption spectrum of a given gas there is a corresponding line in the emission spectrum; however, the reverse is not true. The lines in the absorption spectrum represent transitions to excited states that all originate in the ground state. The lines in the emission spectrum, on the other hand, represent not only transitions to the ground state but also transitions between various excited states. The number of lines in an emission spectrum will thus exceed the number of lines in the corresponding absorption spectrum.

3.3.2 Moseley Experiment

Henry Moseley in 1913 carried out a systematic study of K_α x rays produced by all then-known elements from aluminum to gold using the Bragg technique of x-ray scattering from a crystalline lattice of a potassium ferrocyanide crystal. The characteristic K_α x rays (electronic transition from $n_i = 2$ to $n_f = 1$) were produced by bombardment of targets with energetic electrons. The results of Moseley's experiments serve as an excellent confirmation of the Bohr atomic theory.

From the relationship between the measured scattering angle ϕ and the known crystalline lattice spacing d (the Bragg law: $2d \sin \phi = m\lambda$, where m is an integer) Moseley determined the wavelengths λ of K_α x rays for various elements and observed that the $\sqrt{\nu}$ where ν is the frequency ($\nu = c/\lambda$) of the K_α x rays was linearly proportional to the atomic number Z . He then showed that all x-ray data could be fitted by the following relationship

$$\sqrt{\nu} = \sqrt{a}(Z - b), \quad (3.41)$$

where a and b are constants.

The same $\sqrt{\nu}$ versus Z behavior also follows from the Hartree-type approximation that in general predicts the following relationship for the wave number k

$$k = \frac{1}{\lambda} = \frac{\nu}{c} = R_\infty Z_{\text{eff}}^2 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \quad (3.42)$$

or

$$\sqrt{\nu} = \sqrt{cR_\infty \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)} Z_{\text{eff}}. \quad (3.43)$$

For K_α characteristic x rays, where $n_i = 2$ and $n_f = 1$, the Hartree expression gives

$$k(K_\alpha) = \frac{3}{4}R_\infty Z_{\text{eff}}^2 = \frac{3}{4}R_\infty (Z - 1)^2. \quad (3.44)$$

Note that in the K_α emission $Z_{\text{eff}} = Z - 1$ rather than $Z_{\text{eff}} = Z - 2$ which is the Z_{eff} predicted by Hartree for neutral multi-electron atoms. In the K_α

emission there is a vacancy in the K shell and the L-shell electron making the K_α transition actually sees an effective charge $(Z - 1)e$ rather than an effective charge $(Z - 2)e$, as is the case for K-shell electrons in neutral atoms.

Moseley also measured several lines belonging to the L characteristic radiation series for various elements and found similar regularities. This result, now referred to as the Moseley law, has been of great importance in substantiating the Rutherford–Bohr atomic theory and highlighted the significance of the atomic number Z of elements as indicator of nuclear charge.

3.3.3 Franck–Hertz Experiment

Direct confirmation that the internal energy states of an atom are quantized came from an experiment carried out by *James Franck* and *Gustav Hertz* in 1914. The experimental set up is shown schematically in Fig. 3.7a.

An evacuated vessel containing three electrodes (cathode, anode, and plate) is filled with low pressure mercury vapor. Electrons are emitted thermionically from the heated cathode and accelerated toward the perforated anode by a potential U applied between cathode and anode. Some of the electrons pass through the perforated anode and travel to the plate, provided their kinetic energy upon passing through the perforated anode is sufficiently high to overcome a small retarding potential U_{ret} that is applied between the anode and the plate.

The experiment involves measuring the electron current reaching the plate as a function of the accelerating voltage U . With an increasing potential U the current at the plate increases with U until, at a potential of 4.9 V, it abruptly drops, indicating that some interaction between the electrons and mercury atoms suddenly appears when the electrons attain a kinetic energy of 4.9 eV. The interaction was interpreted as an excitation of mercury atoms with a discrete energy of 4.9 eV; the electron raising an outer shell mercury electron from its ground state to its first excited state and in doing so losing a 4.9 eV portion of its kinetic energy and its ability to overcome the retarding potential U_{ret} between the anode and the plate.

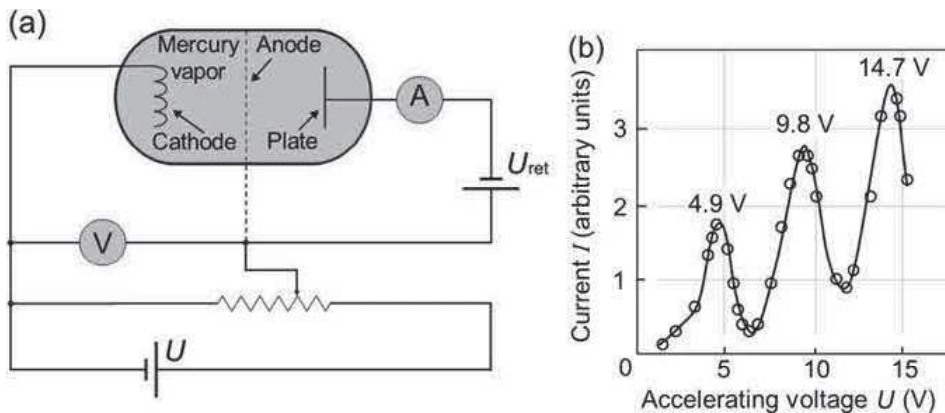


Fig. 3.7. (a) Schematic diagram of the Franck–Hertz experiment; (b) Typical result of the Franck–Hertz experiment using mercury vapor