FRANCK and HERTZ

Collisions between Electrons and Mercury Vapor Molecules and the Ionization Potential of Such Molecules [1]

IN A PREVIOUS PAPER WE were able to show that the ionization potential, that is, the potential through which an electron must fall freely in order to ionize a gas molecule by collision, is a

[1] James Franck and Gustav Hertz, *Verhand. Deut. Physik, Ges.*, 16 (1914), 457–467—trans. editors.

characteristic quantity for each gas, and we have measured this parameter for He, Ne, Ar, H, O, and N. The method we used is similar to that used by Lenard and by V. Baeyer, and consists of the direct determination of the moment that the colliding electrons induce ionization. It required a great deal of precaution to avoid false results arising from electric double layers and from the initial velocities of the electrons emitted by the glowing wire. Moreover, we had to be especially careful to avoid an apparent ionization limit simulated when the observed ionization lying below a certain velocity of the primary electrons sank below the sensitivity threshold of the apparatus. Such an error, not present in our work, cannot be excluded from the ionization potentials recently published by F. Mayer and may account for the difference between our and F. Mayer's value for the ionization potential of nitrogen. By carefully avoiding this error, we arrived at exactly one volt for this ionization potential. Later attempts to extend this procedure to metallic vapors were unsuccessful because it was impossible to eliminate disturbances arising from heating the apparatus.

To test the relationship between the magnitude of the ionization potential and the other atomic constants, especially radius and proper frequency, which are obtained from quantum theory on the one hand and from atomic models on the other hand, it appeared to us desirable to develop a method whose accuracy exceeds that of the previous method and which can also be applied to metallic vapors. We have succeeded in doing this, as the results of our investigations of collisions between gas molecules and slow electrons show. The new procedure which was first developed only for the case of gases that have no affinity for electrons but which can also probably be applied to other gases is based on the following facts which we discovered in our previous work:

1. In the collision between a gas molecule and an electron whose kinetic energy is smaller than the ionization energy of the molecule, the electron is reflected, in general, but it also suffers a loss of energy which is smaller, the smaller the electron affinity of the gas is. For gases with no electron affinity, this loss is immeasurably small.

2. In a collision between an electron and a gas molecule that results in ionization, the electron loses all its kinetic energy.

3. If the kinetic energy of the electron is equal to or larger than the ionization energy, the probability that the collision will lead to ionization is not small compared to [unity] 1.

The new method of measuring the ionization potential rests on the fact that the ionization energy is the maximum kinetic energy that electrons can have and still be reflected without energy loss after numerous collisions with gas molecules.

Since we wanted to apply this method to measure the ionization potentials of metallic vapors, we first had to convince ourselves that such

vapors, insofar as collisions are concerned, really behave like gases without electron affinity, as one may expect from a consideration of their behavior in electrical discharges, and above all, because of the incidence of self-sustaining electrical discharges at large vapor densities and small field intensities. The apparatus used in this investigation and in the final measurement of the ionization potential is shown in [Fig. 46–1].

D is a platinum wire with a thin central section which can be brought to incandescence by a current. N is a fine cylindrical platinum wire mesh with a 4-cm radius surrounding D, and G is a cylindrical platinum foil, which is separated from N by 1 to 2 mm. G was grounded through a galvanometer. Rings of platinum foil were embedded in the glass covering to prevent any current from flowing to the galvanometer from parts of the wire carrying the voltage. Besides glass and platinum, the apparatus contained no fixed parts. All leads were fused into the glass.

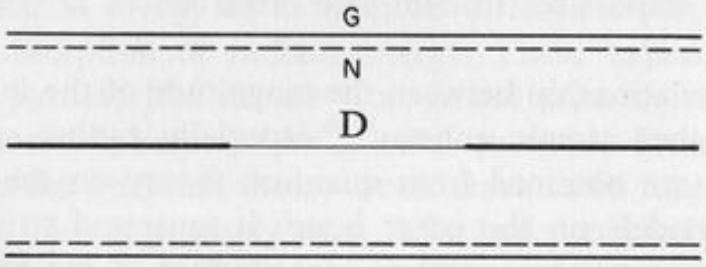

Fig. 46–1.

During the measurements the apparatus was enclosed in an electrically heated paraffin bath. The apparatus was connected to a continuously operating pump through a narrow U-tube which was also in the heat bath and which had a mercury-filled section at its lowest point. Since, in addition to this, a drop of mercury was present at the bottom part of the apparatus itself, the pressure of the mercury vapor could not have been essentially lower than that corresponding to the saturation pressure for the given temperature. The precise value of the pressure is of no consequence. Since most of the measurements were made at temperatures between 110° and 115°, the pressure of the mercury vapor was about 1 mm.

The preliminary investigations, which were to show that the mercury vapor behaves like a gas with no electron affinity during collisions between electrons and gas molecules, correspond throughout to those which were carried out earlier on helium. It was found that the electrons are reflected without energy loss from the mercury atoms as long as their velocities correspond to a drop through less than 5 volts. The curves 1 and 2 in [Fig. 46–2] show the energy distribution for two cases, which, just as in the previous investigations, are obtained by graphical differentiation of those curves which give the current measured by the galvanometer

as a function of the retarding potential between the wire mesh N and the collecting cylinder.

For curve 1 the accelerating potential between D and N was 4 volts, for curve 2 it was 7.5 volts. We see that throughout, the measurements correspond to those [previously] obtained for helium. The difference in the curve shapes arises from the difference in the geometry of the apparatus that was used. We see from these measurements that the sudden onset of the inelastic collisions in mercury vapor occurs when the electron beam falls through 5 volts; this means that the ionization potential of mercury vapor is 5 volts. To establish this point still more accurately, we then proceeded as follows: For constant retarding voltage between N and G we measured the current flowing through the galvanometer as a function

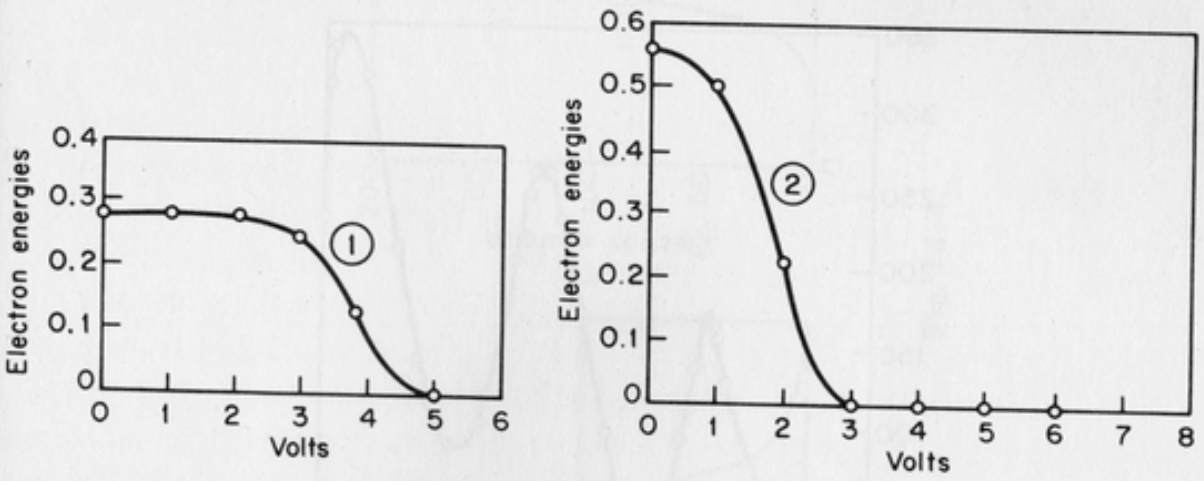

Fig. 46–2.

of the accelerating potential between N and D. The following phenomena are to be expected: As long as the accelerating potential is smaller than the retarding potential, the current is zero. After that it rises until the accelerating potential equals the ionization potential. At that moment the electrons in the neighborhood of the wire mesh suffer inelastic collisions and induce ionization. Since these electrons themselves and those released by ionization have but a very small additional potential to fall through before they reach the mesh, they pass through the mesh with hardly any detectable speed and are thus in no position to move against the retarding potential. The galvanometer current thus falls to zero as soon as the accelerating potential exceeds the ionization potential. If we now increase the accelerating potential still further, the region where the electrons suffer inelastic collisions moves inwardly away from the mesh. The electrons that are present after the inelastic collisions, thus, on their way to the mesh, fall through a potential that is equal to the difference between the accelerating and ionization potentials. As soon as this difference exceeds the

retarding potential between N and G, electrons can move against the retarding field and the galvanometer current begins to rise again. Since the total number of electrons is increased by the ionization, this current rises more than it did originally. As soon, however, as the accelerating potential equals twice the ionization potential, the electrons in the neighborhood of the wire mesh suffer inelastic collisions the second time. Since, in these collisions, the electrons lose all their energy and the newly appearing electrons also have no measurable speed, electrons can no longer move against the retarding potential. Hence, as soon as the accelerating potential exceeds twice the ionization potential, the galvanometer current again sinks to zero. Since this same phenomenon recurs whenever the accelerating potential is an integral multiple of the ionization potential, we may expect

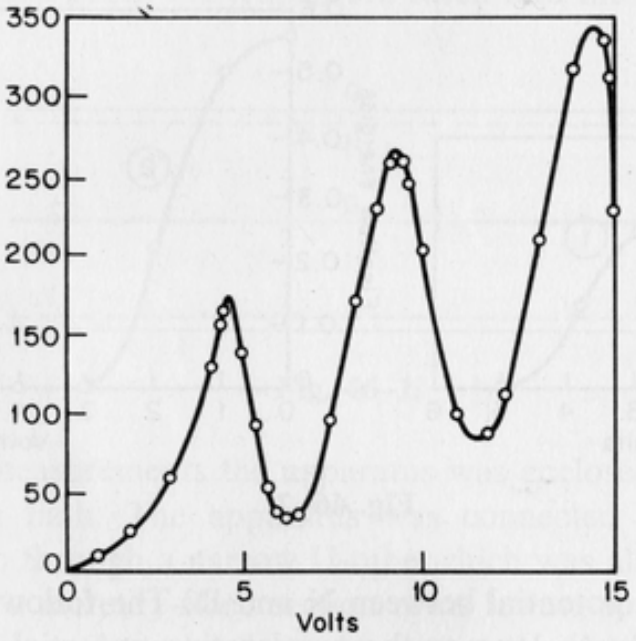

Fig. 46–3.

to obtain a curve which has maxima of increasing size which are spaced at just the ionization potential. The shape of the curves is also actually affected by the fact that there was a potential drop of 1.3 volts between the ends of the glowing wire which is the source of the electrons, and also because for very strong retarding potentials positive ions penetrate into the region between N and G. The first of these effects causes the drop after the potential exceeds an integral multiple of the ionization potential to occur not suddenly but to take place over a 1.3-volt stretch. The second effect causes the maxima to grow more slowly for larger retarding potentials than they ordinarily would. The results of our measurements given in [Fig. 46–3 and Fig. 46–4] show that our expectations were completely fulfilled. The maxima are extraordinarily sharp and therefore allow

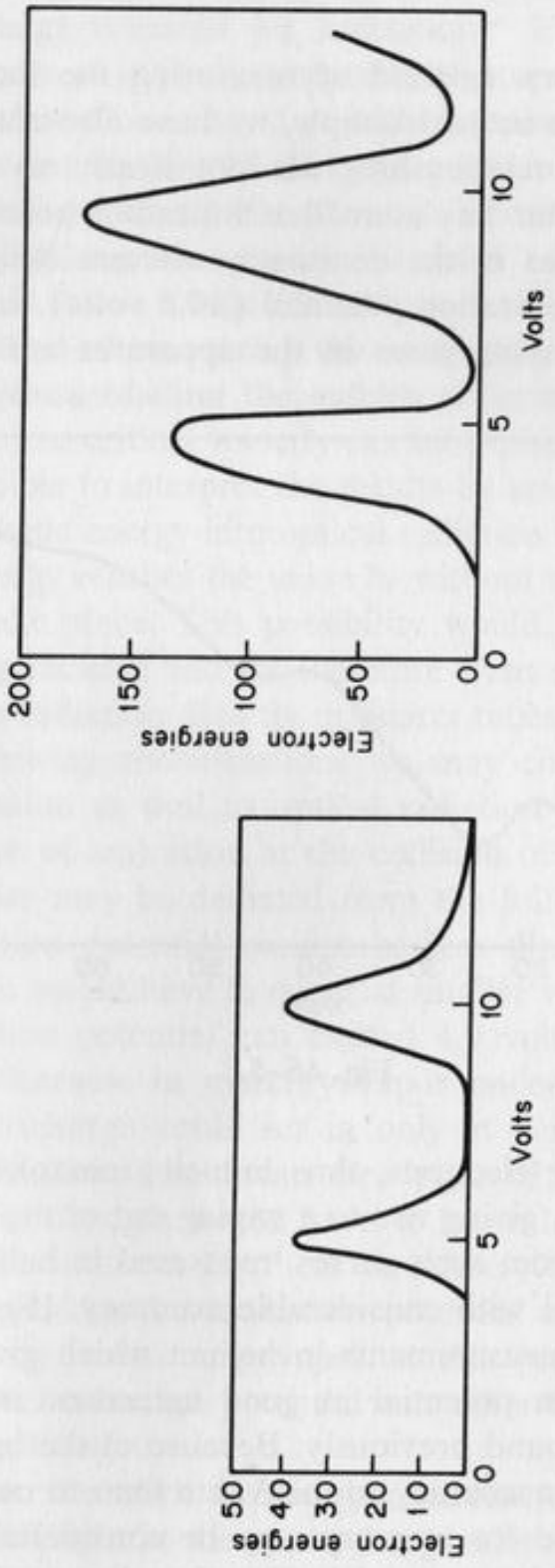
Electron energies
200
150
100
50
0
0
5
10
Volts
Electron energies
50
40
30
20
10
0
0
5
10
Volts

Fig. 46–4.

one to measure the ionization potential very accurately. The values for the spacings between any two successive maxima all lie between 4.8 and 5.0 volts, so that we may take 4.9 volts as the ionization potential of mercury vapor.

To compare this new method of measuring the ionization potential with the old one for an actual example, we have also made measurements on helium. Here the relationships are not nearly so favorable as for mercury, since the latter has a smaller ionization potential than any of the contaminating gases in the container, whereas helium, on the contrary, has the largest ionization potential (20.5 volts). In this case, therefore, all the accompanying gases in the apparatus are ionized at lower

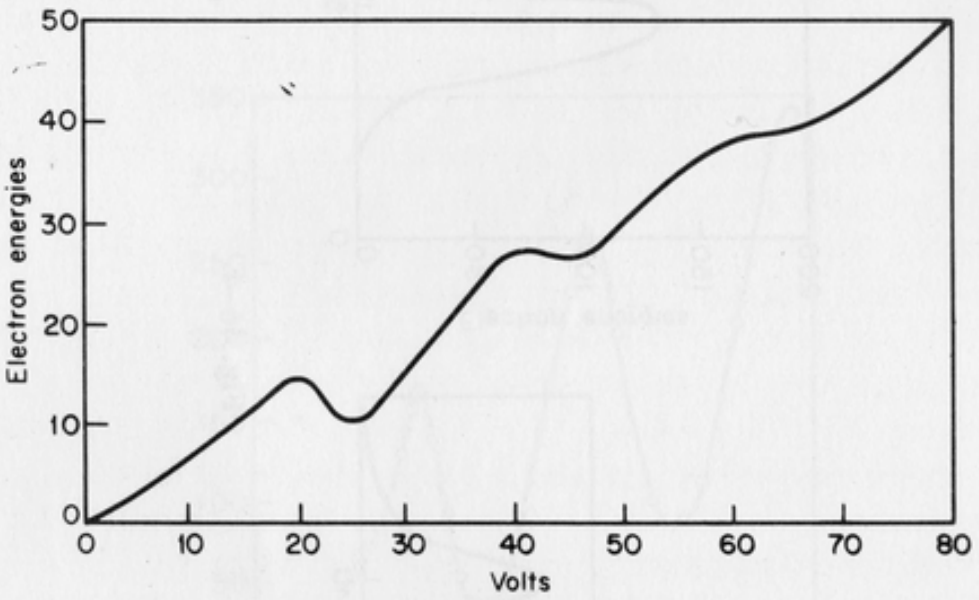

Fig. 46–5.

speeds of the colliding electrons, thus inducing completely inelastic collisions and, as a result, giving rise to a wiping out of the maxima. In spite of this, it is possible from such curves, measured in helium, to determine the ionization potential with considerable accuracy. [Fig. 46–5] shows a curve obtained from measurements in helium which gives a value of 21 volts for the ionization potential in good agreement with the value of 20.5 volts which we found previously. Because of the broad maxima, we must assign a greater inaccuracy to this value than to our previous result, so that the value found for mercury may be considered as the most accurately known ionization potential. This fact has enabled us to prove qualitatively a relationship (first stated in various ways by J. Stark), derived from quantum theory, between the ionization potential and the proper frequency of the electron to be torn out, at least for the case of mercury vapor. Until now all hypotheses which are found in the literature about this agree qualitatively more or less, as required by the order of

magnitude relationship among λ, ν, e, m and r expressed by Sommerfeld. Most of the hypotheses state essentially that the frequency of a definite proper vibrational mode of an electron multiplied by the constant h is equal to the energy required for ionization.* For mercury vapor one most readily thinks of the very pronounced proper frequency of the so-called resonance line of mercury $\lambda = 253.6\ \mu\mu$ discovered by Wood. If we calculate the product $h\nu$ for this frequency, we obtain the energy which an electron would have after falling through a potential drop of 4.84 volts. This is in such good agreement with the value we obtained that we can hardly believe that this is a coincidence.

Since our method of measuring the ionization potential is an indirect one, we must discuss whether the sudden onset of inelastic collisions of the electrons at some critical velocity can be explained in some other way. Indeed, it is possible to interpret the results by assuming that the electron transforms its kinetic energy into optical radiation of wavelength 253.6 $\mu\mu$ as soon as its energy reaches the value $h\nu$ without at the same time ionization having to take place. This possibility would, naturally, be of quantum theoretic significance and we therefore want to try to detect the appearance of such radiation directly in quartz tubes.

From the following considerations we may conclude with great certainty that ionization as well as optical radiation occurs.

The occurrence of ionization at the collision of 4.9-volt electrons with mercury molecules may be deduced from the following facts:

1. The ionization potential cannot be less than 4.9 volts since then inelastic collisions would have to occur at smaller voltages.

2. The ionization potential can exceed 4.9 volts only by infinitesimal amounts since otherwise in mercury vapor under a pressure of several atmospheres a discharge could set in only at very high field strengths. Since at these pressures the mean free path of the electrons is about 10^{-6} cm, the field strength would have to be so large, that the electrons could in a distance of about 10^{-6} cm pass freely through a potential difference that is equal to the ionization potential minus 4.9 volts. Since, however, ionization in mercury vapor at this pressure occurs for very small voltages, the ionization potential can differ from 4.9 volts only by an extremely small quantity.

3. According to the work of Steubing, mercury vapor is ionized when it is irradiated with light in the spectral region around the line 253.6 $\mu\mu$. Also Wood concludes from the complete absence of polarization of the

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* We take this opportunity to point out that the order of the ionization potentials of gases previously investigated, as well as their magnitudes, are obtained if we use the dispersion frequency of the gas as the frequency. For a rigorous proof, however, it is not sufficient to know with certainty the proper frequency from the dispersion.

resonance radiation excited by polarized light that, corresponding to Stark's hypothesis, this resonance radiation—contrary to the sodium resonance radiation—occurs during ionization processes.

SUMMARY

1. We have demonstrated that the electrons in mercury vapor suffer elastic collisions with the molecules up to a certain critical speed.

2. We have described a procedure for measuring this critical speed accurately up to a tenth of a volt. It is equal to the speed acquired by an electron that falls through a potential difference of 4.9 volts.

3. We have shown that the energy of a 4.9-volt electron beam is exactly equal to the quantum of energy associated with the mercury resonance line 253.6 $\mu\mu$.

4. We have discussed why, in the transfer of the energy from the 4.9 volt beam to the mercury molecule, some of the collisions lead to ionization, so that it appears that the ionization potential of mercury is 4.9 volts. Another part of the collisions appears to stimulate the emission of radiation and we surmise that this corresponds to the line 253.6.