6 On the Excitation of the 2536 Å Mercury Resonance Line by Electron Collisions†

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It was shown in our experiments on collisions between electrons and molecules of an inert gas or of a metal vapour that the electrons are reflected in such collisions without loss of energy, as long as their kinetic energy does not exceed a certain critical magnitude, but that as soon as their energy becomes equal to the critical value, they lose all of it on collision. The critical velocity is a quantity, characteristic for each gas and is in the cases studied so far equal to the ionisation energy.[1] This result is completely in agreement with quantum theory since according to that theory the vibrations of the electrons in an atom can receive energy only in certain quanta and not in arbitrary amounts. The question whether, indeed, as follows also from quantum theory, the smallest amount of energy which can be transmitted is equal to the product of Planck's constant h and the frequency ν of the electron receiving the energy‡ could only be decided with a certain amount of certainty for the case of mercury vapour. In the case of this vapour one has not only measured with relatively high accuracy the critical kinetic energy, but one also knows very probably the frequency of the vibrating electron as Wood's experiments[2] on the mercury resonance radiation have proved that there is in every mercury atom an electron which can vibrate with a frequency

† *Verh. Dtsch. Phys. Ges. Berlin* **16**, 512 (1914).

‡ The hypothesis that the ionisation energy is equal to the product $h\nu$ has first been made by J. Stark.

corresponding to a wavelength of 2536 Å. It turned out that the value measured by us corresponding to the smallest energy quantum which can be transferred agreed within the limits of accuracy with the product $h\nu$.

To conclude with certainty from our results that the phenomena studied take place in agreement with quantum theory, we can, however, not restrict ourselves to proving that the energy is transferred only in certain quanta. Rather, it is still necessary to prove that the total energy quantum transferred, $h\nu$, is given to a single electron which can vibrate with frequency ν. The aim of the present paper is to give this proof.

As we emphasised in our earlier paper[1] the majority of collisions which transfer to the vibrating electron an energy $h\nu$ do not lead to ionisation. In the atoms which have undergone such collisions, there is thus an electron of energy $h\nu$, vibrating with frequency ν. One should, therefore, expect that such collisions which do not lead to ionisation but just to an energy loss $h\nu$ should be accompanied by an emission of light of frequency ν, that is, that one should be able to observe the emission of resonance radiation. This means that if one introduces electrons in mercury vapour and enables them to attain a velocity corresponding to a voltage difference of 4·9 Volt, one should be able to observe light emission corresponding exclusively to the emission of the mercury 2536 Å resonance line. Experiments have fully confirmed this expectation.

In Fig. 6.1 we give the apparatus used. The vessel was made of quartz; the bottom part and the two tubes at the bottom were filled with mercury. A circular gas flame heated the apparatus to about 150°. The platinum wire D, which was heated by an electric current served as electron source. The platinum mesh N at the other side was connected to earth via a galvanometer, and we put a voltage to accelerate the electrons between the wire and the mesh. The soldering places which could not be avoided were, as far as possible, away from the heated parts of the apparatus and were cooled with water. We used a Fuess ultraviolet spectrograph kindly put at our disposal by Professor Goldstein to study the emitted radiation.

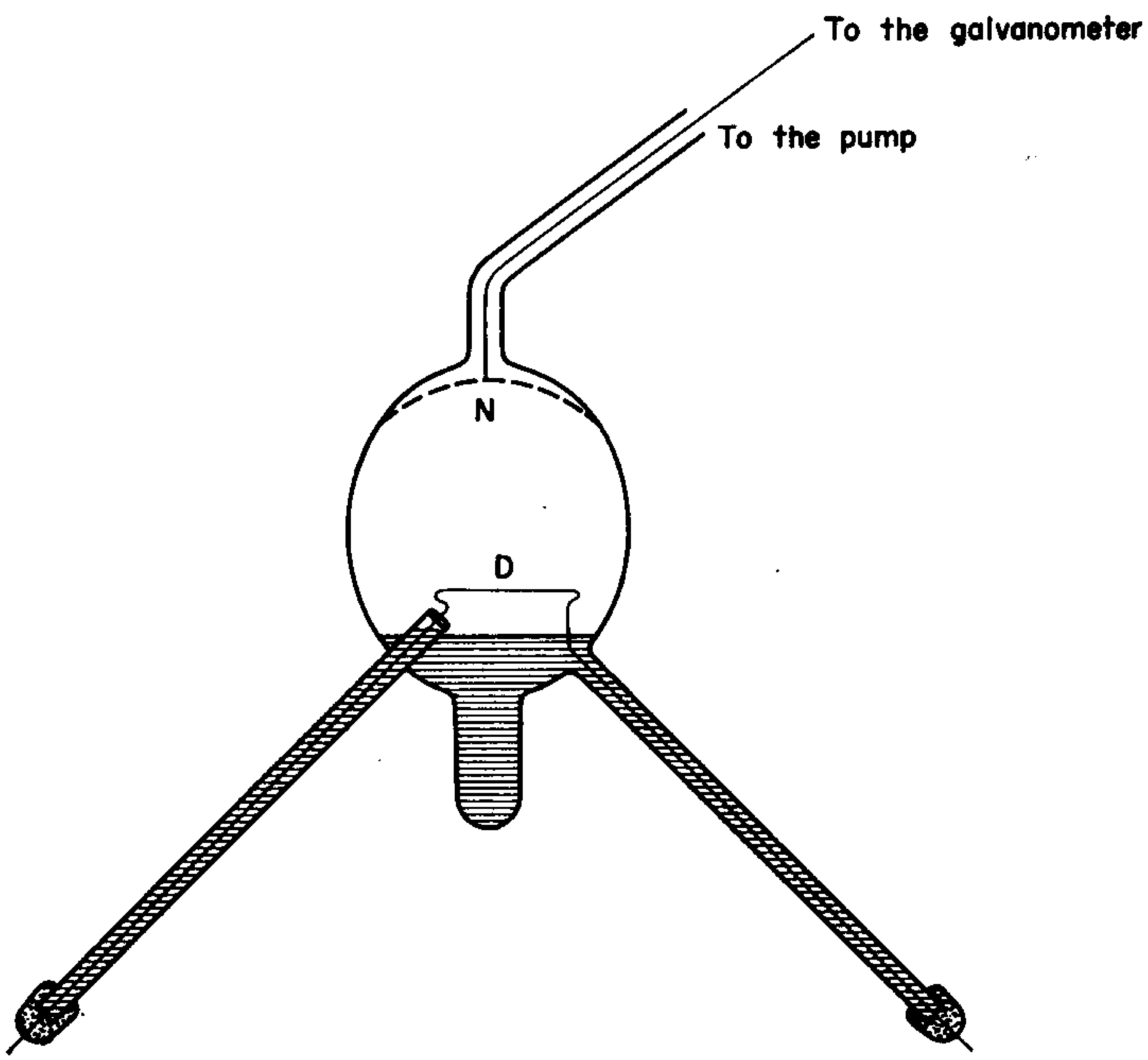

FIG. 6.1

We know from our earlier investigations that as soon as the applied voltage exceeds 4·9 Volt† for carefully chosen values of pressure and voltage electrons occur with a velocity corresponding to a voltage of 4·9 Volt, but not with higher velocities. We can, however, not state with any certainty that no electrons of that velocity are present when the applied voltage is lower than 4·9 Volt as the electrons leave the platinum wire with a certain

† A pressure of about 1 mm and a field gradient of 2 V/cm completely satisfy these conditions as is shown by the measurements on the velocity distribution of the electrons discussed in our earlier paper.[1] As soon as the electrons have attained a velocity corresponding to 4·9 Volt, one of the subsequent collisions will certainly lead to a complete loss of energy; along the few mean free paths which the electron can still traverse with the critical velocity, the increase of velocity is small compared to the critical velocity.

initial velocity which for the wires used goes up to about 1 Volt. The photographs obtained after exposing for one or two hours showed a continuous spectrum, stretching into the violet, caused by the light emitted by the incandescent wire, and then, a long distance away from it, clearly the 2536 Å line; however, in no case was there even a suspicion of the other mercury lines which in the mercury arc spectrum have partially far greater intensities than the resonance line. The identification of the line was made by comparison with a wavelength scale built for the apparatus and also by imposing upon the spectrum the arc spectrum of mercury as a comparison spectrum.

Figure 6.2 is such a photograph,† taken when the potential applied to the electrons was 8 Volt. It shows clearly (we hope also in the reproduction) the appearance of the 2536 Å resonance line. The intensity of the emitted light depends essentially on the value of the vapour pressure, as can be understood from Wood's results on the scattering and absorption of resonance radiation in mercury vapour. The best results were obtained for a temperature of about 150° so that the vapour pressure of the mercury vapour is more than 1 mm. We have followed the appearance of the line, varying the experimental conditions for different applied voltages and we never saw a suspicion of the line for a potential less than the critical one; for instance, under the same conditions for 4 Volt there is no indication of the line, while it is clearly visible already for 6 Volt.

As we have now shown that the energy quantum transferred is indeed exactly equal to $h\nu$, we can use an accurate measurement of this energy quantum for a determination of the value of the constant h which should not be less accurate than the determinations of this constant based upon measurements of radiation. As apart from the measured potential difference, traversed by the electrons, only the elementary quantum and the wavelength of the resonance radiation enter into the calculations, one can in this way determine the quantity h with the same accuracy with which we can measure the critical velocity of the electrons. From our

† Figure 6.2 is reproduced as a drawing, sketched from the original [D. t. H.].

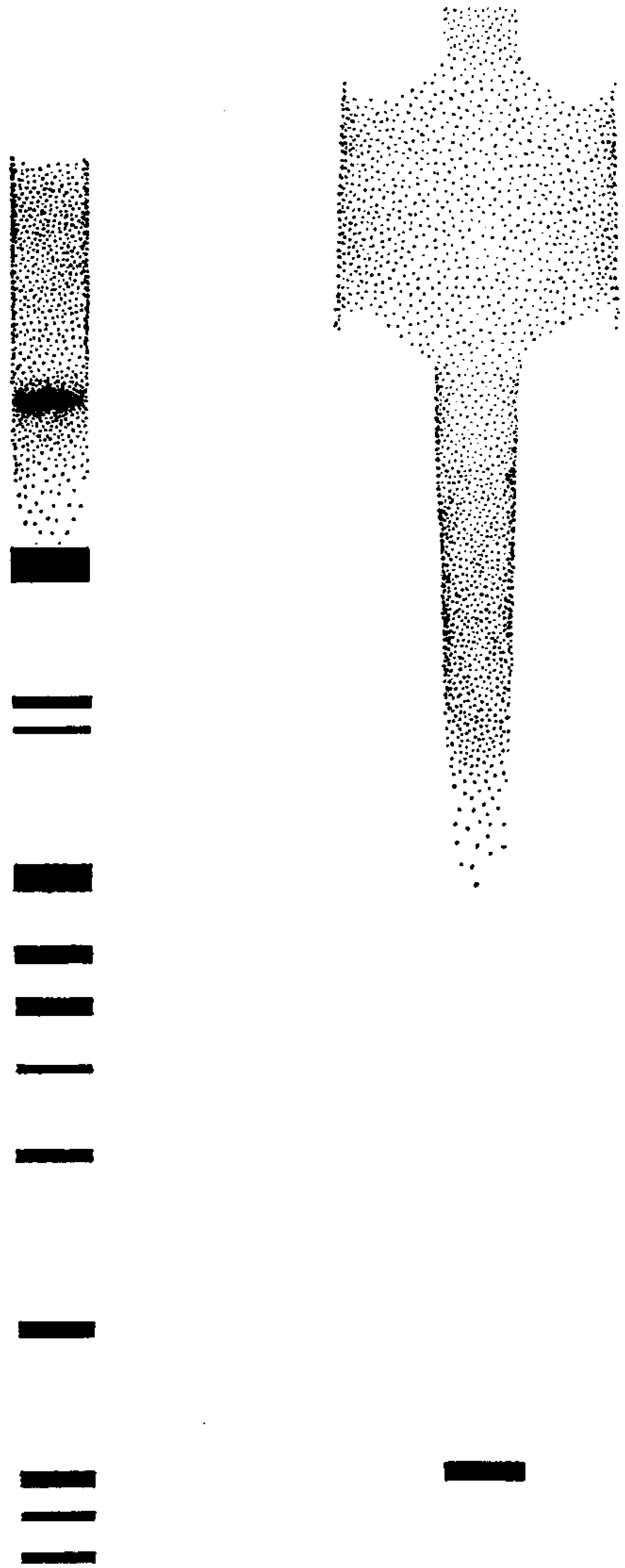

FIG. 6.2

measurements we find $h = 6{\cdot}59 \times 10^{-27}$ erg sec with a possible error of 2 percent, whereas the values of the radiation constant found by several observers differ by far more than 2 percent. If we use the Warburg[3] value of the constant c_2 of the radiation law, $c_2 = 1{\cdot}437$ cm degree and the Westphal[4] value of the constant σ in Stefan's law, $\sigma = 5{\cdot}57 \times 10^{-12}$ Watt cm^{-2} degree^{-4}, we find $h = 6{\cdot}47 \times 10^{-27}$ erg sec. Using for σ the average value of the latest measurements, $\sigma = 5{\cdot}70 \times 10^{-12}$, we find $h = 6{\cdot}62 \times 10^{-27}$. Both values agree with ours within the limits given.

These results lead to new questions, the answers to which will have to be given by later experiments, which we are to some extent preparing. The interesting experiments of Gehrcke and Seeliger[5] and of Holm[6] show that the situation is far less simple for higher electron velocities. According to Gehrcke and Seeliger, even electrons of about 10 Volt excite visible light in mercury vapour. It would be of great interest to extend these investigations to the ultraviolet region. One should also investigate whether for other metal vapours and for the inert gases a similar radiation occurs the wavelength of which can be evaluated from the energy of the electrons which transfer the energy in inelastic collisions. The easiest would probably be to study alkali metal vapours.

Summary

The results of our two papers on the collisions between electrons and mercury atoms can be summarised as follows:

1. The electrons are reflected by the mercury atoms without energy loss, as long as their kinetic energy is less than the amount $h\nu$, where ν is the frequency corresponding to the resonance line.

2. As soon as the kinetic energy of an electron has reached the value $h\nu$, this energy quantum is transferred in one of the subsequent collisions to the spectrum of frequency ν, present in the atom.

3. The energy transferred is partly used for ionisation and partly emitted as radiation of light with a frequency ν.

4. The quantity h turns out to be according to these experiments equal to $6{\cdot}59 \times 10^{-27}$ erg sec with a possible error of 2 percent.

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