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THE QUANTUM THEORY IS TESTED

James Franck (1882-1964)

Gustav Hertz (b. 1887)

James Franck, one of the outstanding German experimental physicists of the decade prior to World War I, was born in Hamburg on August 26, 1882, and studied at both the universities of Heidelberg and Berlin. Soon after receiving his doctoral degree he went to the Kaiser Wilhelm Institute of Physical Chemistry at Berlin-Dahlem, where he was one of the departmental heads, and began his investigations into atomic structure.

At the Kaiser Wilhelm Institute he collaborated with Gustav Hertz and completed basic experiments on the collisions of electrons with atoms, which demonstrated that an atom can take on energy from collisions only in discrete amounts, in agreement with Bohr's theory. In 1920 Franck was called to the University of Göttingen as full professor of experimental physics. He served there from 1920 until 1935 when he left Germany because of the Hitler racial laws.

While at Göttingen, he established one of the outstanding atomic laboratories in the world, which attracted leading postdoctoral students from all countries. The United States, in particular, owes a great debt of gratitude to Franck for training and inspiring many of the best American experimental physicists.

Although Franck received the Nobel Prize for physics in 1925 for his electron-collision experiments, much of his best work was done in the

study of molecular structure, and later in photochemistry, particularly after he came to Johns Hopkins as professor of physics in 1935. In 1938 he was appointed professor of physical chemistry at the University of Chicago and played an important role in the development of atomic energy. He was the leader of a group of scientists on the Manhattan project who felt that the atomic bomb should not have been dropped before warning Japan that we had such a weapon. To this end, he prepared and circulated the famous "Franck Petition," urging President Truman to demonstrate the bomb before authorizing its use. After the war Franck devoted almost all of his research time to the study of photosynthesis. He died in 1964, when still active in his scientific work.

Gustav Hertz was born on July 22, 1887, in Hamburg and studied physics at the universities of Göttingen, Munich, and Berlin, where he served as an assistant in physics from 1913 until the beginning of World War I. After serving in the war and being severely wounded, he came back to Berlin as unpaid lecturer (*Privatdozent*) in 1917 and began the collaboration with Franck that led to the famous Franck-Hertz experiments and the Nobel Prize for physics.

Hertz served as professor of physics at the University of Halle from 1925 to 1928 and then in the same rank at the Technical Institute of Berlin-Charlottenberg. He resigned from this chair in 1934 for political reasons and became director of a research laboratory for the firm of Siemens.

In 1945, he went to the USSR where he is currently continuing his research.

After Niels Bohr had introduced his quantum model of the planetary atom and had used it to derive the correct formula for the Balmer lines of hydrogen, experimental physicists began to devise various ways of probing the atom to see if they could obtain some insight, other than that offered by the spectral lines, into the nature of the discrete orbits and stationary states. Now there are not many ways by which one can try to get a "look at the inside" of an atom; among the accessible methods, only two were available to physicists when Bohr announced his theory. Both involved bombarding the atom with particles: photons, on the one hand, and material particles, such as electrons or atoms, on the other. Since bombarding an atom with photons is essentially the same as studying its spectrum, only collisions between atoms and material particles, such as electrons, seemed to offer a possible new source of information. Consequently James Franck and Gustav Hertz, who were pioneers in this field, turned to electron collisions to study the interior of an atom.

To do this, Franck and Hertz devised a very simple instrument consisting of a long wire surrounded by a wire-mesh cylinder whose axis

coincided with that of the wire. Surrounding the wire-mesh cylinder, and very close to it, was an external solid foil cylinder. The apparatus was operated as follows: The atom, to be studied in the form of a gas or vapor under low pressure, were placed in the cylinder surrounding the wire. A current was then sent through the wire until, glowing, it became hot enough to emit electrons. A positive voltage was established between the wire and the mesh so that the electrons were attracted to the mesh. These electrons moved through the vapor to the mesh and passed through it. After passing through the mesh, the electrons reached the surrounding foil, where they were collected. The external foil cylinder G was connected to the ground through a galvanometer so that the number of electrons striking the foil could be measured. Finally, a constant retarding voltage (to decelerate the electrons passing through the mesh) was placed between the mesh cylinder and the outer foil cylinder. This retarding potential could be altered at will so that the number of electrons striking the foil could be controlled.

Suppose now that a certain voltage is placed between the mesh and the glowing, conducting wire. What do we find at the electron-collecting foil cylinder? That depends on a number of things: the accelerating potential between the wire and the mesh; the kind of gas in the cylinder; the retarding potential between the mesh and the external foil. If no gas is present in the cylinder and if the accelerating potential is smaller than the retarding potential, no electrons reach the outer foil and the current in the galvanometer is zero. This means merely that the electrons coming from the wire and passing through the mesh are not moving fast enough to overcome the retarding potential and thus reach the foil. If the accelerating potential is slowly increased until it is exactly equal to the retarding potential, or slightly larger, a current will suddenly be observed in the galvanometer.

We now consider a gas, let us say mercury vapor, present in the cylinder. A gradual increase in the accelerating potential is applied. What effect do the gas atoms have on the electrons? As long as the accelerating potential lies below a certain critical value, which is different for different gases, the situation is exactly the same as though no gas were present. We must keep in mind that the atoms exist only in certain discrete energy states and they can pass from a lower state to a higher (that is, from the ground state to an excited state) only by absorbing a discrete amount of energy, which must be furnished by the colliding electron. Furthermore, only a discrete amount of energy can tear an electron out of any one of the atoms and thus ionize the atom. If now an electron coming from the hot wire collides with a mercury atom, it can give up energy to this atom either by making the atom move faster or by exciting the atom internally. But if the potential that accelerates the electrons as they come from the wire is less than the smallest excitation

energy of the mercury atom, the electron, according to the quantum theory, with its discrete energy levels, cannot excite the atom; at most, it can only increase its velocity during a collision. Since a mercury atom is very massive compared to an electron, the colliding electron has little effect on the motion of the atom; the electron bounces off with no loss of energy like a ball bearing bouncing off a massive wall. Such collisions are called "elastic" collisions and have no effect on the stream of electrons coming from the hot wire. In other words, as long as the accelerating potential is below a certain critical value necessary for excitation, the electrons collide with the mercury atoms without loss of energy and the current in the galvanometer of the apparatus is just as though no mercury vapor were present.

Now suppose that the accelerating potential is increased slowly until the electrons acquire just enough energy to excite or to ionize the mercury atoms. Then, according to the quantum theory, these electrons should lose all their energy; their collisions with atoms are "inelastic," *i.e.* they do not "bounce off" the atoms. Franck and Hertz found that this is precisely the case and so demonstrated the existence of discrete energy levels. They discovered that for an electron to excite the mercury atom, it must have no less than 4.9 volts of energy. As soon as the electrons were accelerated to 4.9 volts of energy, the current in the detecting galvanometer fell to zero because the electrons lost all their kinetic energy by inelastic collisions and therefore could not reach the external foil cylinder against the retarding potential. Of course, electrons that were torn out of the mercury atoms could not reach the external cylinder either, because they could not acquire enough kinetic energy from the accelerating potential.

Consider now what happens when the accelerating potential is greater than 4.9 volts. Each electron still suffers an inelastic collision, but it does not lose all of its kinetic energy, only that part represented by falling through 4.9 volts potential difference. In other words, it still has some energy left and can reach the detecting cylinder. Thus, as the accelerating potential is increased steadily beyond 4.9 volts, the current in the galvanometer begins to increase again (after having fallen to zero at 4.9 volts). Now it reaches a greater intensity because added to the initial stream of the electrons from the wire are the electrons torn from the mercury atoms during the collisions. If the accelerating potential is steadily increased from 4.9 volts to twice this value, the current in the galvanometer again suddenly drops to zero because now each electron has just enough energy to excite two atoms in two separate collisions (it loses just 4.9 volts of energy in each collision); when it does so, it loses all its energy. At this higher accelerating potential the electrons acquire enough energy to ionize the atoms closer to the wire than previously. After these initial ionizing collisions near the wire, the electrons

(now with practically no energy) are speeded up again before reaching the mesh, and suffer ionizing collisions a second time. There is thus a second maximum in the galvanometer current when the accelerating potential is increased beyond twice the ionization potential.

Franck and Hertz then went on to show that as the accelerating potential is increased, a new maximum appears in the galvanometer current for each integral multiple of the ionization potential. They applied this technique not only to mercury but to other atoms as well. Moreover, they demonstrated that electrons moving with the ionization energy could also excite the mercury resonance line $\lambda = 2536$ angstroms, and showed that if one multiplies the frequency of this line by Planck's constant h, one obtains exactly the ionization potential of 4.9 volts.

The work of Franck and Hertz was important at this stage of the development of atomic theory because it was not clear from Bohr's theory of atomic spectra alone whether the quantum theory could be applied to ordinary mechanical energy of motion, or whether it was limited to the emission and absorption of radiant energy. These experiments demonstrated that a particle like an electron would transfer its energy in a collision only in multiples of a fundamental quantum. From this point on it was clear that the quantum theory would have to be taken into account in all processes. This is precisely what Bohr had predicted in the last few paragraphs of his fundamental paper, which we discuss in Chapter 45, and is also in line with what Einstein had insisted on at the first Solvay Congress in 1911.

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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.

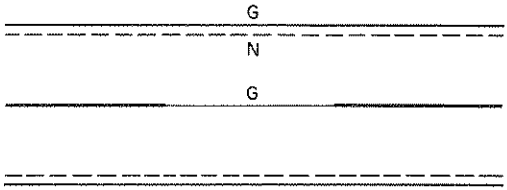

Fig. 46–1.

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

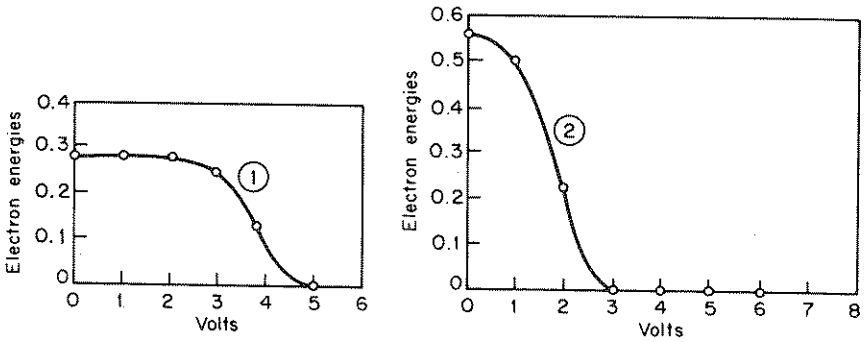

Fig. 46–2.

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

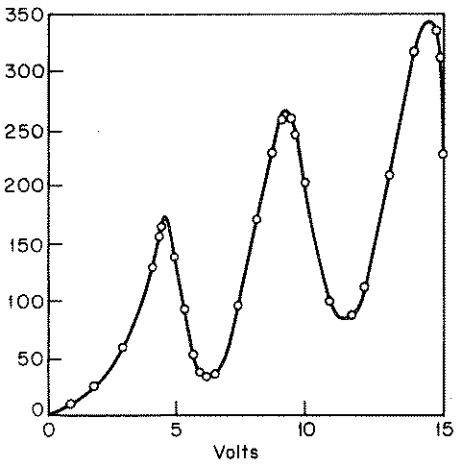

Fig. 46–3.

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

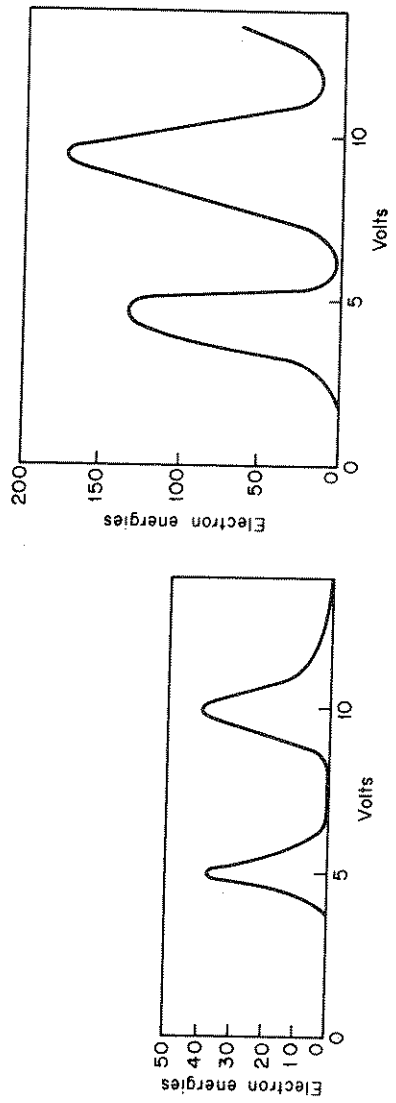
Electron energies
200
150
100
50
0
0
5
10
Volts
Electron energies
50
40
30
20
10
0
0
5
10
Volts

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

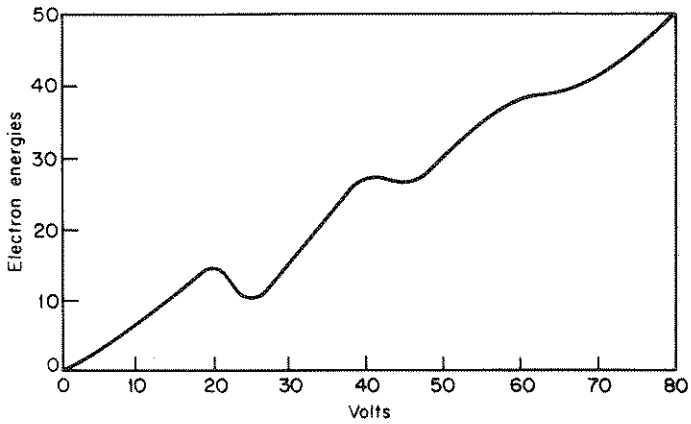

Fig. 46–5.

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
Stark's hypothesis, this resonance radiation—c
resonance radiation—occurs during ionization p

SUMMARY

1. We have demonstrated that the electrons
elastic collisions with the molecules up to a certa

2. We have described a procedure for meas
accurately up to a tenth of a volt. It is equal to t
electron that falls through a potential difference c

3. We have shown that the energy of a 4.9-volt
equal to the quantum of energy associated with
line 253.6 $\mu\mu$.

4. We have discussed why, in the transfer of
volt beam to the mercury molecule, some of the
tion, so that it appears that the ionization potentia
Another part of the collisions appears to stimulat
tion and we surmise that this corresponds to the

that, corresponding to
contrary to the sodium
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f 4.9 volts.
electron beam is exactly
the mercury resonance

the energy from the 4.9
collisions lead to ioniza-
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