

## Elastic and Inelastic Electron Scattering in Hydrogen

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A study of both the *energy distribution and the angular distribution of electrons scattered by hydrogen molecules* was made. *Elastic scattering* was investigated in the range between  $40^\circ$  and  $165^\circ$ , for collision energies between 35 and 200 volts. The number of electrons scattered at any angle was smaller the greater the energy of impact. In all the curves a minimum was found between  $90^\circ$  and  $110^\circ$ , while for the 35 and 50 volt collisions the curves rose to a definite maximum at  $155^\circ$  to  $160^\circ$ . *Inelastic scattering* was found to occur with energy losses ranging from a minimum of about 12.0 volts, through a sharply defined *most probable* loss at 12.6 volts, to a complete loss of all the energy. It was found that as the energy of collision was increased the probability of the larger energy losses increased with respect to the probability of the smaller energy losses. Angular distribution curves were steeper, the smaller the amount of energy lost at collision for a given collision energy. Also, for any particular energy loss, the steepness increased with the speed of the colliding electrons. The electrons which are torn off from atoms in ionizing collisions are termed *ejected electrons* and are presumably those which appear in our experiment with but little or no energy. The angular distribution of the ejected electrons, having various amounts of energy (1 to 8 volts), were studied for different collision energies (35 to 340 volts). In every case there was a noteworthy absence of considerable scattering at small angles, so characteristic of the scattering of faster electrons. In many cases, pronounced peaks were found in the angular distribution curves at large angles ( $90^\circ$  to  $160^\circ$ ). These peaks change in position and size in a regular manner with the energy of collision and the energy of the ejected electron.

THIS paper is an account of a continuation of our experimental investigations on electron scattering in gases. The results of our investigations on argon have already been published in this journal.<sup>1</sup> As argon is monatomic, it seemed desirable to select a diatomic gas for the second investigation; hence hydrogen was chosen for study. The method of experimentation with hydrogen was identical with that used in the work on argon.

Scattering of electrons by hydrogen has been studied by Harnwell,<sup>2</sup> McMillen,<sup>3</sup> Arnot,<sup>4</sup> Bullard and Massey,<sup>5</sup> and by Ramsauer and Kollath.<sup>6</sup> Harnwell and McMillen found that the number of electrons scattered elastically fell off steeply as the angle was increased (angle range  $7^\circ$  to  $60^\circ$ ; energy range 40 to 180 volts). Arnot, working with electrons between 30 and

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<sup>1</sup> A. L. Hughes and J. H. McMillen, Phys. Rev. **39**, 585 (1932). It is convenient to mention here that several paragraphs were accidentally omitted from the end of the paper referred to. The omission was rectified in a letter to the Editor of the Physical Review **40**, 469 (1932). An error in Eq. (2) of the same paper was also corrected.

<sup>2</sup> G. P. Harnwell, Phys. Rev. **33**, 559 (1929); **34**, 661 (1929); **35**, 285 (1930).

<sup>3</sup> J. H. McMillen, Phys. Rev. **36**, 1034 (1930).

<sup>4</sup> F. L. Arnot, Proc. Roy. Soc. **133**, 615 (1931).

<sup>5</sup> E. C. Bullard and H. S. W. Massey, Proc. Roy. Soc. **133**, 637 (1931).

<sup>6</sup> C. Ramsauer and R. Kollath, Ann. d. Physik **12**, 529 (1932).

800 volts energy, confirmed these results, but found that, at about  $90^\circ$ , the curve representing the number of elastically scattered electrons began to increase. (His angular range extended to  $120^\circ$ .) Similar results were obtained by Bullard and Massey who studied the elastic scattering of electrons having energies between 4 and 30 volts. Ramsauer and Kollath also found, for very slow electron (1.5 to 11.0 volts), a definite but rather slow increase in the elastic scattering as the angle was increased above  $90^\circ$  to as far as  $165^\circ$ . So far as we know there have been no investigations of the distributions of electrons scattered inelastically by hydrogen.

#### EXPERIMENTAL METHOD

The same apparatus was used in the study of electron scattering in hydrogen as in the previous work on argon.<sup>7</sup> The reader is therefore referred to the previous article for a description of the apparatus and method of experimentation. Hydrogen was prepared by the action of pure dilute sulphuric acid on pure zinc. The gas was dried by passing through a tube immersed in liquid air. It was then stored in a reservoir over mercury and admitted to the apparatus through a capillary tube and a liquid air trap to freeze out the mercury. A suitable constant pressure could be maintained in the apparatus by regulating the driving pressure of the hydrogen on the high pressure side of the capillary tube, the gas being pumped out of the apparatus by a condensation pump. This constant flow method provides us with pure hydrogen in the scattering experiments. In experiments on scattering in hydrogen it is particularly important to avoid impurities, as the scattering by a hydrogen molecule is small compared with the scattering by heavier molecules.

Our results on hydrogen are expressed in the same units as those used in the previous article; that is, we measure the number of electrons diverted from the main beam at an angle  $\theta$  and then multiply by  $\sin \theta$  to compensate for the change with angle of the effective scattering path length. The final values are therefore proportional to the scattering coefficient as defined on page 589 of our previous paper.<sup>8</sup>

#### ELASTIC SCATTERING

In view of the recent comprehensive work of Bullard and Massey and of Arnot on elastic scattering of electrons in hydrogen, we did not make an extensive study of the elastic scattering. It seemed worth while, however, to attempt to extend the studies to large angles, inasmuch as the investigators referred to did not go beyond about  $120^\circ$ . Our results are shown in Fig. 1. It will be seen that we confirm the discovery of Bullard and Massey and of Arnot that there is a minimum at about  $90^\circ$ . In addition, we find a definite maximum at large angles which is contrary to the expectations of Arnot who thought that "the curves probably continue to rise steadily as the angle is increased to  $180^\circ$ ."

We have indicated the positions of Arnot's 29 volt curve and Bullard

<sup>7</sup> A. L. Hughes and J. H. McMillen, *Phys. Rev.* **39**, 585 (1932).

<sup>8</sup> A. L. Hughes and J. H. McMillen, *Phys. Rev.* **39**, 585 (1932).

and Massey's 30 volts curve in the neighborhood of our 35 volt curve. It is evident that although all three curves agree in giving a minimum at about  $90^\circ$ , no two curves are in satisfactory accord. We can only say, therefore, that there is qualitative agreement insofar as the curves rise and fall together.

#### INELASTIC SCATTERING

The distributions of energy lost by 50 volt primary electrons, when scattered at various angles, are shown in Fig. 2. The various curves have been arbitrarily adjusted to the same height for a loss of energy amounting to 20 volts. It will be seen that the "most probable" energy loss is approximately 12.6 volts. It is evident that the larger energy losses are relatively more

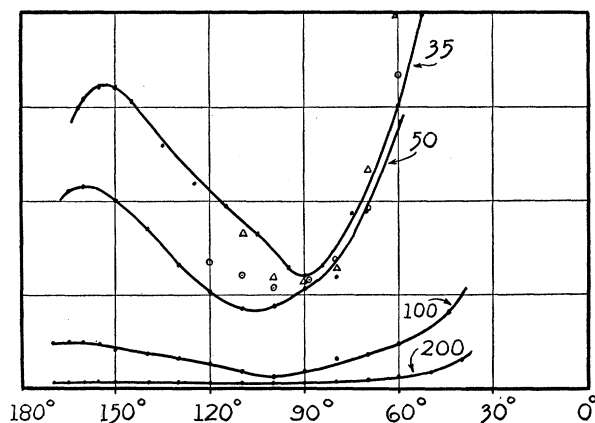


Fig. 1. Elastic scattering of electrons by hydrogen molecules. The numbers attached to the curves represent the electron energies in volts. Circles with dots, Arnot's curve for 29 volt electrons. Triangles, Bullard and Massey's curve for 30 volt electrons.

probable for the larger scattering angles. A small subsidiary maximum appears at about 16 volts in the  $30^\circ$  and  $45^\circ$  curves. In Fig. 3 we have the energy distributions of electrons, all scattered at  $10^\circ$ , for various primary energies between 35 and 200 volts. (The curve for 412 volt electrons, scattered at  $5^\circ$ , is included). As before, the curves are arbitrarily fitted together at the 20 volt loss. It is seen that, for a given scattering angle, here  $10^\circ$ , the 12.6 volt loss becomes relatively *more* probable the *lower* the primary electron energy. It will be noticed that there is a distinct slowing up in the rate of the fall of the curve between 15 and 20 volts, and in one curve (the 412 volt,  $5^\circ$  curve) there is a small subsidiary maximum at 17.5 volts.

Various energy losses, *viz.*, 12.6, 16.4, and 25.0 volts, were selected for a study of their angular distributions. The 12.6 volt loss, the most probable loss, is an excitation loss. The 16.4 loss is just above the ionization potential which is 15.9 volts. (The 15.9 volt loss was not studied, as the resolution of the apparatus was imperfect and consequently the electrons selected at a 15.9 volt setting would really include a number of electrons causing excitation). Finally the 25 volt loss was chosen because it was well above the minimum ionization loss and, at the same time, the yield was not too small to

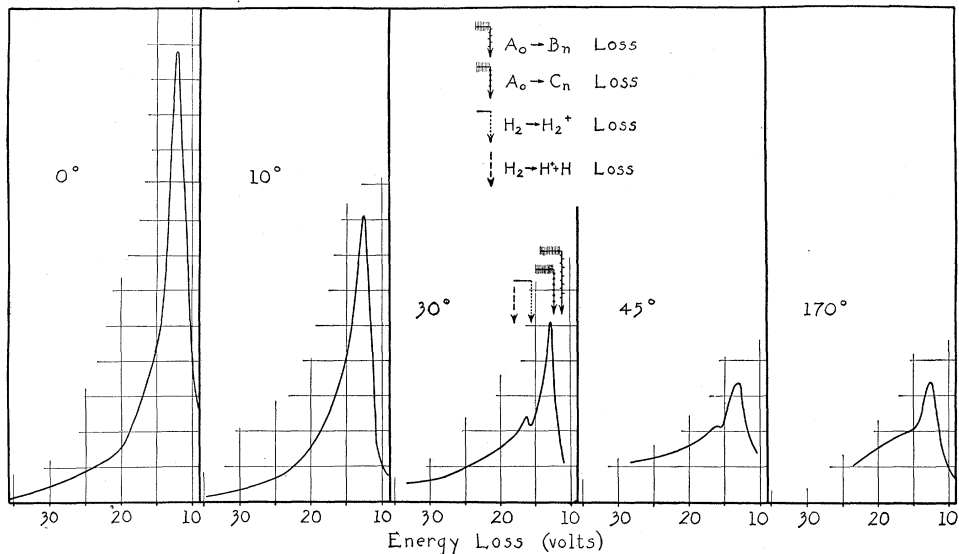


Fig. 2. Energy distribution of electrons scattered inelastically by hydrogen molecules, showing variation with *angle*. Primary energy in all cases = 50 volts. All curves are adjusted arbitrarily to the same height at the 20 volt loss. On the  $30^\circ$  curve, the positions of the theoretically possible types of effects are indicated by suitable vertical lines. The associated horizontal lines indicate the possible vibrational levels.

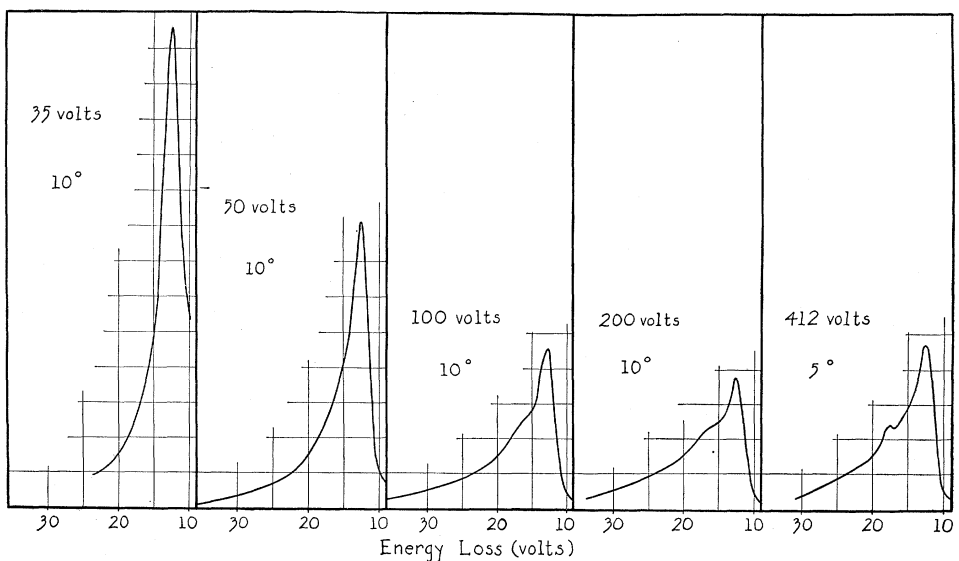


Fig. 3. Energy distributions of electrons scattered inelastically by hydrogen molecules, showing variation with *primary energy*. All curves are adjusted arbitrarily to the same height at the 20 volt loss.

make measurements unreliable. According to Fig. 4, the less the energy loss, the the steeper the angular distribution curve, a result already implied in the previous paragraph. The curves are all adjusted to the same value at  $10^\circ$ .

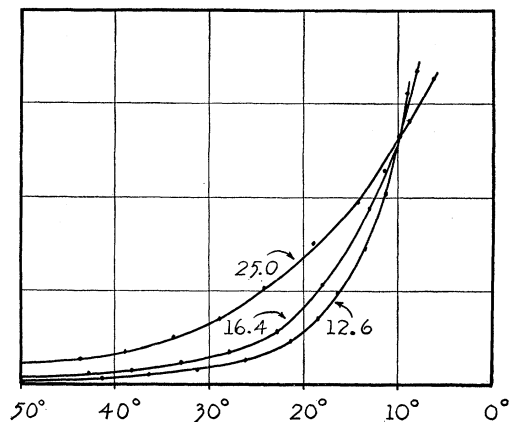


Fig. 4. Angular distribution of electrons scattered inelastically. Primary electron energy in all cases = 50 volts. Energy losses in volts are indicated on the curves. All curves are adjusted arbitrarily to the same height at  $10^\circ$ .

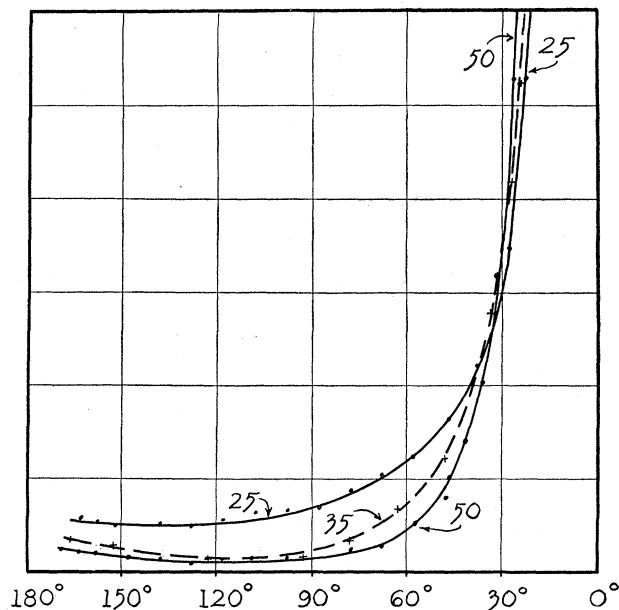


Fig. 5. Angular distribution of electrons scattered with 12.6 volts loss of energy, showing dependence on primary electron energy. The primary energy, expressed in volts, is indicated for each curve.

Finally, in Fig. 5, we show how the angular distribution curves for a constant loss, *viz.*, 12.6 volt (corresponding to excitation of the molecule), depend on the energy of the electrons before collision. Up to about  $90^\circ$  or so, the curves are steeper the higher the primary energy. (Too much reliance

should not be placed on the exact shape of the curves above  $90^\circ$ , as the readings were extremely small).

### EJECTED ELECTRONS

Following the terminology used in our previous paper on argon,<sup>9</sup> we call those electrons which appear with very low energies the ejected electrons. When ionization takes place, an electron is detached from the atom. Consequently, after an ionizing collision we have two electrons; the faster we assume to be the colliding electron and the slower the ejected electron. (We

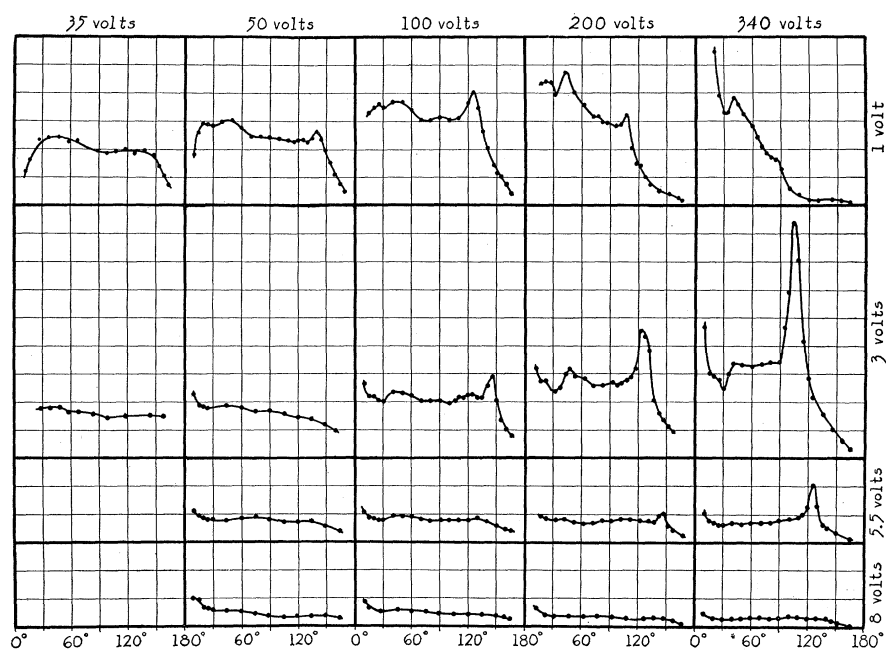


Fig. 6. Angular distributions of ejected electrons. Each row represents a single ejected electron energy which takes the values 1, 3, 5.5, and 8 volts as we go from one row to the next. Each column corresponds to a different energy of collision. All curves are to the same scale.

cannot, of course, demonstrate that the slower of the two electrons is the one ejected from the atom; it seems probable, however, and suggests a convenient terminology.) For a study of the angular distribution of ejected electrons we selected the 1, 3, 5.5, and 8 volt ejected electrons resulting from a collision between hydrogen molecules and primary electrons having energies ranging from 35 to 340 volts. The results are shown in Fig. 6. Perhaps the most striking feature common to all the curves is the absence of the excessively large scattering at small angles which is so characteristic of electrons scattered inelastically with considerable amounts of energy (see Fig. 4). The next feature worthy of mention is the presence, in many cases, of certain highly preferred directions for the emission of ejected electrons. A certain regularity in the way in which these peaks shift can be traced. Thus for any

<sup>9</sup> A. L. Hughes and J. H. McMillen, *Phys. Rev.* **39**, 585 (1932).

one ejected electron energy, an *increase* in the energy of the primary electrons is accompanied by a progressive shift of the position of the peak to *smaller* angles. On the other hand, if we keep the primary energy fixed and study the various groups of ejected electrons, we find that the *higher* the energy of the ejected electrons the *larger* the angle at which the peak is to be found. For 8 volt ejected electrons the angular distribution curves have become practically featureless. It is to be noticed, too, that the peaks in the angular distribution curves for all the ejected electrons practically disappear when the primary energy is low (35 and 50 volts).

#### DISCUSSION

Several theoretical physicists have amplified and extended the pioneer work of Born, who first applied wave mechanics to the scattering of electrons by atoms, with the result that certain features of electron scattering are now accounted for theoretically. Very little, however, has been done on the corresponding problem for molecules. Massey and Mohr<sup>10</sup> have carried through a calculation of the scattering of electrons by diatomic molecules. It is assumed that the diatomic molecule may be represented by a suitable potential field having axial symmetry over which passes an electron wave. The amplitude of the wave scattered in any desired direction is calculated. An average is then taken for all possible orientations of the molecular axis with respect to the direction of the primary wave. Finally it is found that the scattering by such a diatomic molecule is obtained on multiplying what is substantially the scattering by the constituent atoms by a diffraction factor  $(1 + \sin x/x)$ , in which  $x = 4\pi d \sin (\theta/2)/\lambda$ , where  $d$  is the distance between the atoms in the molecule and  $\lambda$  the electron wave-length. This diffraction factor changes sign periodically as  $x$  increases. Because of the extremely steep character of the curve for atomic scattering, however, it is not easy to detect the superposed oscillation of the diffraction pattern.<sup>11</sup> Thus Massey and Mohr were unable to show that Arnot's experimental curves (for 80 volts and above) for the scattering of electrons by hydrogen were in better accord with their formula for scattering by molecular hydrogen than with the formula for scattering by atomic hydrogen. Massey and Mohr state that the scattering curves obtained by McMillen<sup>12</sup> fall off much more rapidly with angle of scattering than the calculated values. This is incorrect, for McMillen's curves are almost superposable on Arnot's, and if anything, they are less steep. Arnot's range of angles was nearly twice as great as McMillen's, and so afforded a better test.

The rise in the scattering curves with angle as the angle is increased beyond about 90° as shown in Fig. 1 of this paper and in Arnot's work is not accounted for by Massey and Mohr's theory. This theory is probably too simplified to do more than describe the part of the scattering curves below

<sup>10</sup> H. S. W. Massey, Proc. Roy. Soc. **129**, 616 (1930); H. S. W. Massey and C. B. O. Mohr, Proc. Roy. Soc. **135**, 258 (1932).

<sup>11</sup> The oscillations of intensity superposed on rapidly falling atomic scattering curves, contributed by factors such as  $(1 + \sin x/x)$  have been considered by Mark and Wierl, principally in connection with their scattering of high speed electrons. (See H. Mark and R. Wierl "Die experimentellen und theoretischen Grundlagen der Elektronenbeugung." Gebrüder Borntraeger, Berlin, 1931).

<sup>12</sup> J. H. McMillen, Phys. Rev. **36**, 1034 (1931).

about  $90^\circ$ . To account qualitatively for the presence of maxima and minima in the scattering of electrons by *atoms*, Bullard and Massey<sup>13</sup> called attention to the necessity for considering the effects of distortion of the electron wave, electron exchange and polarization. These effects have not been included in Massey and Mohr's treatment of scattering by diatomic molecules.

We are accustomed to think of a clear cut distinction between an inelastic and an elastic collision between electrons and atoms. In the latter case the electron leaves the atom unchanged, while in the former case the electron excites (or ionizes) the atom. The lowest excitation state differs in energy so

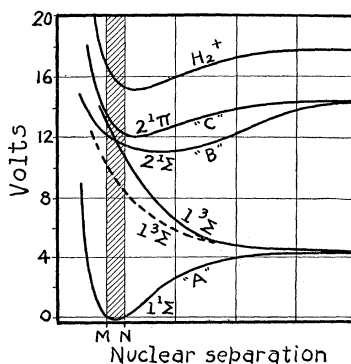


Fig. 7. Franck-Condon diagram for hydrogen. The diagrams given by Smyth and by Mulliken agree substantially in the case of all curves except the  $1^3\Sigma$  curve. Mulliken's  $1^3\Sigma$  curve is shown as a broken line.

considerably from the normal state that there is no difficulty in identifying an electron which has rebounded from an atom elastically and one which has rebounded inelastically. With a molecule, however, it is conceivable that an electron collision could change the vibrational state and the rotational state of the molecule without altering the electronic state. We should therefore be prepared, perhaps, to find evidences of energy losses of the order of a few tenths of a volt. Experimentally these might cause an asymmetrical broadening of the so-called elastic peak towards the low energy side. We have made as yet no special search for such an effect but it seems possible that it could be detected in view of the experimental work of Ramien<sup>14</sup> on the average energy lost by electrons in colliding with many hydrogen molecules, and in view of the theoretical discussion of Massey.<sup>15</sup>

The possible molecular changes resulting in a hydrogen molecule after an electron impact may be visualized by the help of a Franck-Condon diagram. In Fig. 7 we reproduce a somewhat simplified copy of the diagram given by Smyth<sup>16</sup> for hydrogen. The curve *A* is for the normal molecule, and the stable state is the one corresponding to a nuclear separation varying between *M* and *N* (corresponding to the lowest vibrational state). Excitation by electron impact is represented by a vertical displacement, within the shaded area, to one of the other curves. If the transition is to the  $1^3\Sigma$  state, the atoms immediately fly apart and dissociation results. If, on the other hand, the transi-

<sup>13</sup> E. C. Bullard and H. S. W. Massey, Proc. Roy. Soc. **A133**, 637 (1931).

<sup>14</sup> H. Ramien, Zeits. f. Physik **70**, 353 (1931).

<sup>15</sup> H. S. W. Massey, Proc. Camb. Phil. Soc. **28**, 99 (1932).

<sup>16</sup> H. D. Smyth, Rev. Mod. Physics **3**, 347 (1931).



tion is to the  $B$  state (i.e., to the  $2^1\Sigma$  state), we get an excited molecule which does not dissociate so long as it is in this state. The energy necessary to produce either state is not sharply defined because of the finite width of the shaded column resting on  $MN$ . Thus a transition to the  $1^3\Sigma$  state requires anything between 10.9 volts and 13.5 volts, while a transition to the  $2^1\Sigma$  state requires an amount of energy between 11.5 and 12.2 volts and a transition to the  $2^1\Pi$  state calls for something between 12.2 and 13.6 volts. This overlapping makes it impossible to decide whether our most probable loss—12.6 volts—corresponds to a transition to the  $1^3\Sigma$  state to the  $2^1\Sigma$  state or to the  $2^1\Pi$  state. It should be stated that the Franck-Condon diagram as given by Mulliken<sup>17</sup> differs slightly in scale from that given by Smyth, yet in such a way as to suggest a different interpretation of our results. Briefly, if the Mulliken representation is correct, we cannot regard our 12.6 volt loss as indicating transitions to either the  $1^3\Sigma$  or to a low vibrational level of the  $2^1\Sigma$  state; we must attribute it to a transition to the  $2^1\Pi$  state, or to a high vibrational level of the  $2^1\Sigma$  state. Dr. E. U. Condon informs us that, on account of the approximations made in the calculations of these curves, they cannot be regarded as exact; thus the position of the  $1^3\Sigma$  curve above  $MN$  (Fig. 7) may be in error by 2 or 3 volts. In view of this situation it is evident that the identification of our 12.6 volt loss with one or other of the possible transitions cannot be made with certainty. It may well be that our 12.6 volt peak corresponds to transitions to all three states. In view of the sharpness of the energy losses to be expected in *atomic* excitation, as compared with this blurring to be expected in molecular excitation, it is possible that the most probable energy loss peak in hydrogen (e.g., in Fig. 2) would be appreciably less steep (especially on the side next to the elastic peak) than the 11.6 volt peak in argon taken under identical conditions. Tests, however, showed that if the 12.6 volt peak in hydrogen and the 11.6 volt peak in argon were superposed, then the hydrogen peak had no more *spread* toward the elastic peak than had the argon peak.

Massey and Mohr have calculated by wave mechanics the angular distribution of electrons which collide inelastically with hydrogen molecules to give rise to the  $2^1\Sigma$  state. These distributions have maxima at certain angles, e.g., for 30 volt primary electrons, a sharp maximum appears at  $20^\circ$ . Fig. 5 gives the angular distribution of the 12.6 volt loss. Unfortunately the curve does not extend to angles smaller than  $25^\circ$ , but it seems obvious that there is no indication of the presence of a maximum at  $20^\circ$ . Massey and Mohr do not give curves for the angular distributions of electrons which have collided with hydrogen molecules and put them into the  $1^3\Sigma$  state. Consequently we are unable to compare them with our experimental curves. There is one point of significance, however. By integrating over all angles Massey and Mohr have determined the probabilities of excitation of the  $2^1\Sigma$  state and the  $1^3\Sigma$  state of hydrogen as a function of the energy of electron impact. The scale of their curves implies that the probability of excitation of the  $1^3\Sigma$  transition is about 10,000 times as large as the probability of excitation of the  $2^1\Sigma$  state. If this is correct, then our 12.6 volt peak must be associated almost wholly with transitions to the  $1^3\Sigma$  state and the number of transitions to the

<sup>17</sup> R. S. Mulliken, *Rev. Mod. Phys.* **4**, 1 (1932); see also W. Finkenburg and W. Weizel, *Zeits. f. Physik* **68**, 577 (1931).

$2^1\Sigma$  state must be negligibly small. (This ignores, of course, the possibility of transitions to the  $2^1\Pi$  state).

In the case of scattering of electrons by argon atoms, we saw that if the energy lost by the colliding electrons was greater than 15.7 volts, the ionization potential of argon, then a second electron, which we termed the ejected electron, must appear. Thus the parts of the scattering curves corresponding to energy losses greater than 15.7 volts give us the distributions of the colliding, or ionizing electrons, as well as the distributions of the ejected electron. It was found convenient to assume that the ejected electron was always the slower of the two electrons moving away from the atom after an ionizing collision. The situation is still more complicated when we have a diatomic molecule like hydrogen instead of an atom like argon. When the collision is of the type which leaves a molecular ion, we have, as in the case of argon, two electrons and an ion. However, as Tate, Lozier and Bleakney<sup>18</sup> have shown, some types of ionization result in dissociation with the constituent atoms flying apart with considerable kinetic energy. We thus have, after collision, two ions and two electrons moving away from the place of collision, each with its own angle distribution characteristic of its energy and of the energy of the electron before collision. So far as we know, no attempt has been made to solve such a problem theoretically. It is evident, from the curves shown in Fig. 6, that, when electrons are ejected with a certain amount of energy from certain types of collisions, strongly preferred directions of emission are to be found. We can also trace certain regularities in the displacement of the peak representing preferred directions of emission as the energies concerned are progressively altered. Thus, for a given energy of ejection, the position of the peak moves to smaller angles as the energy of collision is increased. On the other hand, if we keep the energy of collision unchanged we find that, as the energy of the ejected electron is increased the position of the peak moves to larger angles. There is also a regularity in the way in which the magnitude of the peak changes as we go across a row or down a column. A comparison of these results with those for argon will show that the distributions of electrons ejected from argon atoms are similar in certain respects to the distributions for hydrogen.

The results for hydrogen were obtained with the same apparatus as that in our work on argon. In our previous article we pointed out that the method of speeding up the electrons by a suitable field into the analyser introduced a certain amount of *blurring* of the sharpness of the curves which was greater the smaller the energy of the electrons under investigation. The same comment applies also to this work on hydrogen.

So far as we know, there has been no attempt to work out a theory for the distributions of the ejected electrons. The frequent occurrence of strongly preferred directions of emission for these electrons suggests a peculiar kind of diffraction effect.

We take great pleasure in thanking Dr. E. U. Condon for his helpful comments on the situation relating to the interpretation of the Franck-Condon diagram for hydrogen.

<sup>18</sup> W. Bleakney, Phys. Rev. **35**, 1180 (1930); W. W. Lozier, Phys. Rev. **36**, 1285 (1930); J. T. Tate and W. W. Lozier, Phys. Rev. **39**, 254 (1932).