

The Velocities of Electrons in Hydrocarbon Bonds

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Fast electrons when scattered inelastically by gas molecules furnish information as to the *distribution of component velocities* (and therefore as to the distribution of resultant velocities) among the electrons in the molecules. An experimental determination of the distribution of energies among the electrons scattered inelastically from a beam of 8000-volt electrons by acetylene, ethylene, ethane, and methane has been made. The results give information as to the velocities of the bonding electrons, but not the *K* electrons of the carbon atoms. It is found that the distribution curves are substantially the same for acetylene and ethylene. The same statement applies also to ethane and methane. The curves for the distribution of component velocities for the first two gases lie above the corresponding curves for the last two gases. A convenient parameter to summarize the results is the value of the component velocity at "half maximum," which is closely analogous to the half width of a spectrum line. The values of the component electron velocities at half maximum for C_2H_2 , C_2H_4 , C_2H_6 , and CH_4 are, respectively, 29.7, 29.7, 26.7 and 26.7, multiplied by 10^7 , cm/sec. A short discussion is given of the bearing of these results on the various types of bonds in the molecules investigated.

INTRODUCTION

WHEN conditions are properly chosen, it is possible to use the results of experiments on electron scattering by gases to determine the distribution of velocities of the electrons in the molecules of the scattering gas. Results have been obtained for helium,¹ hydrogen,² nitrogen and methane.³ In the case of helium and hydrogen the results agreed remarkably well with those obtained by DuMond and Kirkpatrick.⁴ As these authors obtained their results from a study of the profile of the modified band in the Compton effect, which is a totally different approach from that involving electron scattering, one may have considerable confidence in the experimental results, for it is difficult to believe that the same type of error could occur in the two methods. No Compton effect results are available for nitrogen and methane, but since the electron scattering experiments were carried out in precisely the same manner with these two gases as with hydrogen and helium, it may be assumed that the results obtained are equally accurate. For helium, the experimental results for the atomic electron

velocity distribution agreed very well with the theoretical calculations of Hicks, but the agreement was less satisfactory in the case of hydrogen.⁵ No theoretical calculations have been made for the other gases.

In this paper we give an account of an investigation of the distribution of electron velocities in the molecules of methane, ethane, ethylene, and acetylene. The electrons involved are those in the carbon-hydrogen and the carbon-carbon bonds. The conditions were such that the electron energies were not high enough to tell us anything about the *K* electrons in carbon. The distance between the atoms in a molecule has been investigated very extensively during the last decade. The equally fundamental parameter, the distribution of the velocities or momenta of the electrons in the various bonds, has received very little attention in comparison. Except for the experimental investigations on hydrogen, nitrogen, and methane already referred to^{2,3} and the theoretical discussions of Hicks on hydrogen and hydrocarbons^{5,6} and those of Coulson⁷ and Duncanson⁸ on hydrocarbons, the field is untouched. It seemed therefore desirable to make an experimental study of the distribution of ve-

¹ A. L. Hughes and M. M. Mann, Jr., Phys. Rev. **53**, 50 (1938).

² A. L. Hughes and M. A. Starr, Phys. Rev. **54**, 189 (1938).

³ A. L. Hughes and M. A. Starr, Phys. Rev. **55**, 343 (1939).

⁴ J. W. M. DuMond and H. A. Kirkpatrick, Phys. Rev. **52**, 419 (1937); **54**, 802 (1938).

⁵ B. L. Hicks, Phys. Rev. **52**, 436 (1937).

⁶ B. L. Hicks, Phys. Rev. **57**, 665 (1940).

⁷ C. A. Coulson, Proc. Camb. Phil. Soc. **57**, 55 (1941); **57**, 74 (1941).

⁸ C. A. Coulson and W. E. Duncanson, Proc. Camb. Phil. Soc. **57**, 67 (1941).

locities among the bonding electrons in methane, ethane, ethylene, and acetylene in the hope that some light would be thrown on the momentum characteristics of the various bonds in these hydrocarbons.

METHOD

As a full discussion of the principles used in deriving the distribution of velocities among atomic electrons was given in an earlier paper,¹ only a summary will be given here. When an electron of energy 200 volts or less is scattered by an atom, the atom as a whole is involved. But if the energy be increased to a sufficiently high value, 2000 volts or more for hydrogen and helium and for the outer electrons of heavier atoms, the scattering observed at considerable angles is essentially due to the interaction of the incoming electrons with just one scattering center which may be either the nucleus or any one of the atomic electrons in the molecule. The scattering observed is to be thought of as Rutherford scattering by a center which attracts, or repels, the incoming electron with a force varying inversely as the square of the distance between the electron and the center. The "collision parameter," i.e., the distance between the scattering center and the prolongation of the path along which the incoming electron travels, determines the angle of scattering. For electrons of sufficiently high energy the collision parameter is so much smaller than the dimensions of the atom that we may safely ascribe any observed scattering to one and only one scattering center. The chances of the incoming electron passing sufficiently near to *two* scattering centers within an atom so that both contribute finite deflections are small enough to be neglected. Cases can arise in which the energy of the incoming electron is high enough to permit us to regard interaction between the incoming electron and the outer atomic or molecular electrons as "single center" scattering, but in which the energy is not high enough to treat the effects of the *K* electrons and the nucleus as separable. This in fact is the case in the experiments to be described in this paper.

When the electrons interact with nuclei they are deflected with no loss of energy; they are scattered elastically. When they interact with electrons in the atom or molecule they lose

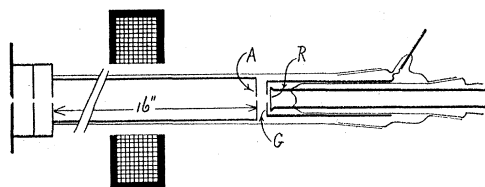


FIG. 1. The electron gun with magnetic focusing.

energy; they are scattered inelastically. The energy which an electron of initial energy V_0 retains after deflection by an atomic electron through an angle θ is $V = V_0 \cos^2\theta$. Thus there will be two distinct groups of electrons among those scattered through a certain angle, those scattered elastically and those scattered inelastically. The relation $V = V_0 \cos^2\theta$ is true only if the atomic electron is at rest before the collision. Actually it is in motion, and the energy with which an electron comes away from a collision in a direction θ differs from V by an amount V'' which is a function of the velocity and direction of motion of the atomic electron before the collision occurred. What we measure experimentally is the distribution of energies, $f(V'')$, among the electrons scattered through a selected angle θ . By means of a very important relationship first pointed out by Jauncey,⁹ it turns out that $f(u)$, the distribution of *component velocities* among the electrons in the atom or molecule, has precisely the same shape as $F(V'')$, the distribution of *energies* among the electrons scattered at a selected angle. V'' is the difference between the actual value of the energy of the scattered electron and the value, $V = V_0 \cos^2\theta$, which it would have had, had the atomic electron been at rest. Thus an experimental investigation giving $F(V'')$, the distribution of energies among the scattered electrons, gives us at once the shape of $f(u)$ for the component velocities of the electrons in the atom or molecule. (If one needs the distribution of total velocities among the electrons in the atom or molecule, one can get it by plotting $V''dF(V'')/dV''$ against V'' and properly re-labeling the abscissas in terms of the resultant velocity.)

The scattering gas can be thought of as providing a mixture of nuclei and electrons all scattering independently of each other, the

⁹ G. E. M. Jauncey, Phys. Rev. **50**, 326 (1936).

electrons, however, retaining the distribution of velocities characteristic of the atom or molecule to which they belong. Single scattering is secured by limiting the total number of molecules exposed to the electron beam, which in our apparatus is done by keeping the pressure below about 0.001 mm.

EXPERIMENTAL DETAILS

The apparatus was identical with that described in a former paper,¹ except for the electron gun and a minor change in the electrostatic analyzer. In these experiments the accuracy of the experimental results is limited by the fact that only a minute fraction of the primary beam is scattered through a finite angle. In our previous experiments, the maximum electron current scattered in the inelastic group did not amount to more than about 2×10^{-15} amp. It is desirable to measure this current, and also the smaller currents found on both sides of the maximum of the inelastic band, with as high a degree of accuracy as possible. We increased the opening of the slit just in front of the Faraday cylinder located at the exit end of the electrostatic analyzer by a factor of about four to increase the number of electrons collected. Increasing this slit opening impairs the resolution somewhat. This is of little importance in the present experiment since we are concerned not so much with absolute electron velocity distributions as with the change in these as we go from one hydrocarbon molecule to another. To secure better "single center" scattering conditions the energy of the incident electron beam was increased from 4000 volts, the maximum used in previous experiments, to 8000 volts. This increase, however, automatically diminishes the number of scattered electrons by a factor of four. The sensitivity of the electrometer tube circuit was such that a one-mm deflection on the scale meant a current of 2.5×10^{-17} amp. The maximum inelastic scattered current was of the order 5×10^{-15} amp. As the readings were somewhat unsteady at the high sensitivity used, one could not determine any individual reading to better than four or five percent. This situation was met by taking the average of a great many observations.

The new electron gun is shown in Fig. 1. The source of electrons is a tungsten ribbon, *R*, 0.002" thick, 0.04" wide, and 0.19" long. At a distance of 0.06" in front of it is a "grid," *G*, which is a tantalum sheet with a central hole 0.12" in diameter. The anode, *A*, is a tube of brass 16" long, closed at one end with a copper disk in the center of which is a hole of 0.08" diameter. The distance between the grid and the end of the anode is 0.31". A magnetic lens is located about 5" from the end of the anode nearest the electron source. A potential difference of 8000 volts is applied between the filament and the anode. The current in the coil forming the magnetic lens and the voltage on the grid is varied until the maximum electron current into the collision chamber is obtained. Currents through the set of 1.5-mm diameter holes into the collision chamber as high as 2.0 ma have been obtained, but it was found more convenient to carry out the experiments described in this paper with a current of 0.6 ma. (This is a current about four times as strong as that used in previous measurements on electron scattering.)

The gases, methane, ethane, and ethylene, were obtained under pressure in steel cylinders

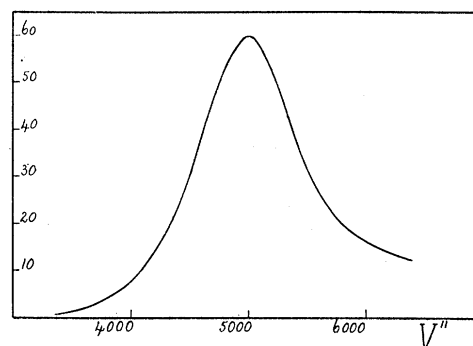


FIG. 2. The distribution of energies among the electrons scattered inelastically by acetylene through 34.2° .

from the Ohio Chemical Company. The methane was said to be 86 percent pure. A certain amount of it was liquefied. The first third was allowed to boil away, the second third was led into a reservoir supplying gas through a capillary leak into the collision chamber, and the last third was rejected. The same procedure was applied to the ethane and the ethylene, which were stated to be 95 and 99.5 percent pure, respectively. The acetylene was prepared by dropping water on

commercial calcium carbide. A bulletin issued by the Linde Air Products Company stated that the acetylene evolved was 99.5 percent pure, except for water vapor which was removed by a drying agent.

The tungsten filament had to be replaced frequently during the experiments on ethylene and very frequently during those on acetylene.

EXPERIMENTAL RESULTS

The distribution of energies among the electrons scattered inelastically by acetylene is shown in Fig. 2. (The height of the elastic peak, which is omitted as it is of no importance in this investigation, is 1240, while the height of the maximum of the inelastic band is 60.) Similar curves were obtained for the other gases.

To determine $f(u)$, the distribution of component velocities among the electrons in the molecule, we proceed as described in the first paper in the series.¹ The curve in Fig. 2 is, by definition, $F(V'')$ where V'' is measured from the center of the band in either direction. We shall use only the left side of the inelastic band as the lower part of the right side is distorted somewhat by the "foot" of the elastic peak. As was shown in previous papers,¹⁻³ $f(u)$ is obtained by taking the $F(V'')$ curve and changing the abscissas in V'' into abscissas in u or β , which are related through $u/c = \beta$, by the equation

$$\beta (= u/c) \times 10^3 = V'' \div (0.5782) V_0^{1/2}, \quad (1)$$

where V_0 is the velocity of the electrons before collision. The same curve also gives the distribution of intensity across the Compton modified band for a primary wave-length of 695 x.u. and a scattering angle of $\theta = 90^\circ$, if we use the relation

$$\lambda'' = \beta \times 10^3 \quad (2)$$

to give wave-length abscissas in x.u.'s. Thus the experimental curve $F(V'')$ gives simultaneously the distribution of energies among the electrons scattered inelastically when we use V'' as abscissas, the distribution of component velocities among the electrons in the molecule when we replace V'' by u by means of Eq. (1), and the profile of the Compton modified band (for 90° scattering of a primary wave-length $\lambda = 695$ x.u.) when we replace u by λ'' by means of Eq. (2).

The final values of $f(u)$ were obtained as follows. Each individual point of $f(u)$ calculated from the corresponding experimental reading for $F(V'')$ was plotted on a large sheet of accurately ruled graph paper. A smooth curve was drawn through the points to give as equal weight as possible to all the points. Values for selected abscissas were read off this curve, which was then obliterated and the process repeated several times. A final curve was obtained by taking the mean values of the ordinates from these curves for the selected abscissas. Final curves for ethane, ethylene, and acetylene are shown in Fig. 3. The values from which these curves were plotted are given in Table I. Just as the breadth of a spectrum line is often arbitrarily indicated by its breadth at half maximum, so we find it convenient to give in Table II the values of the abscissas at half maximum and also at quarter maximum.

There are several ways of roughly summarizing our information about the motion of electrons in molecules. Because it is natural to express our results in the form of a curve giving the distribution of component velocities, we can associate with this as a convenient parameter the component velocity value at half maximum. Other equally good parameters would be the average component velocity, the average resultant momentum (or velocity), as used by Coulson and Duncanson, and the most frequent resultant momentum (or velocity). These parameters are approximately proportional to each other for the sort of distributions we meet in these experiments, and so the sequence in magnitude of any one parameter in a set of distributions

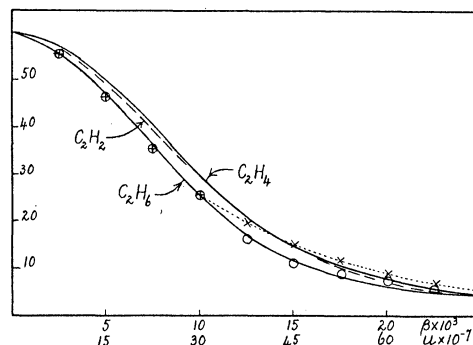


FIG. 3. The distribution of component velocities among the electrons in the molecules of acetylene, ethylene, ethane, and methane. The curve for acetylene is shown as a broken line except where it is indistinguishable from that for ethylene. The curve for methane is indicated by crosses which are joined by a dotted line where the methane curve breaks away from the ethane curve. The circles indicate the curve for methane when corrected in the manner suggested in the text.

is the same as that for any other parameter. Any generalization relating to the "component velocity at half maximum" will also apply to the "average component velocity," since they are approximately proportional to each other. We shall usually use the latter parameter in the discussion to follow merely because its implication is more readily grasped.

The degree of accuracy of the final curves may be indicated by the fact that the successive "best" curves drawn through the points representing values of $f(u)$ all passed through the "half maximum" ordinate at abscissa values within about ± 0.9 of the values given in Table II.

TABLE I. The distribution of component velocities for the bonding electrons in acetylene, ethylene, ethane, and methane. $f(u)$ is identical in shape with $f(\lambda')$, the profile of the associated Compton modified band. Values in parentheses for methane are alternative values obtained as described in the text.

$\beta \times 10^8$ AND λ'' (X.U.)	$u \times 10^{-7}$ CM/SEC.	$f(u)$ (OR $f(\lambda'')$)			
		C ₂ H ₂	C ₂ H ₄	C ₂ H ₆	CH ₄
0.0	0.0	60.0	60.0	60.0	60.0
2.5	7.5	56.8	57.1	55.6	57.7
5.0	15.0	49.1	49.9	47.0	46.6
7.5	22.5	39.4	40.0	36.4	35.4
10.0	30.0	29.5	29.5	25.4	25.7
12.5	37.5	21.0	21.1	16.9	19.4 (16.1)
15.0	45.0	14.7	14.9	11.8	15.2 (12.3)
17.5	52.5	10.0	10.7	8.6	12.0 (9.4)
20.0	60.0	7.1	7.8	6.6	9.4 (7.8)
22.5	67.5	5.2	5.7	5.3	7.0 (5.8)
25.0	75.0	3.9	4.5	4.2	5.0 (4.2)
27.5	82.5	2.9	3.1	3.5	3.3 (3.7)
30.0	90.0	2.2	2.5	2.9	2.0 (1.7)
35.0	105.0	1.3	1.7	2.0	
40.0	120.0	0.8	1.4	1.5	

Two conclusions may be drawn from these experimental results. (1) The average velocities of the bonding electrons in ethylene and acetylene are substantially identical and greater than the average velocity of the bonding electron in ethane. (2) The abscissas at about one quarter maximum indicate the ethane has considerably fewer fast electrons than acetylene and ethylene.

The results for methane call for comment. This was the first gas investigated in the present research and as it had been investigated before,³ not so much time was spent on it as on the other gases. This turned out to be unfortunate. The $f(u)$ curve for methane in this investigation is wider than the one in the earlier investigation. The width at half maximum in the earlier investigation was 22.5 as against 26.4 here. It is probably to be explained by the fact that to secure higher currents we opened the slit in front of the Faraday cylinder and thus impaired the resolution, which made the curve wider. This introduces an error in the

absolute values of $f(u)$, but this is of little importance because in this research we are concerned more particularly with a comparison of curves obtained for different gases under identical experimental conditions.

We find that the $f(u)$ curves for methane and ethane are indistinguishable from $u=0$ to $u=30 \times 10^7$. At $u=30 \times 10^7$ the methane curve breaks away rather abruptly from the ethane curve. Unfortunately few observations were available for these points, and it was not possible to make further measurements when the collected results on all the gases pointed to the need for a new set of measurements on methane especially in the high velocity region. If we take the trend of the methane curve as established in a former paper³ and use it to extrapolate the present methane curve beyond $u=30 \times 10^7$, we get a curve which differs but little from the ethane curve in the high velocity part as well as in the low velocity part. If this doubtful procedure is accepted, then we can say that the $f(u)$ curves for methane and ethane are substantially equal. It would have been much more satisfactory to re-investigate methane than to attempt to fit together two investigations as we have done, but circumstances prevented our doing so. For the present we can say that the methane and ethane curves are identical up to $u=30 \times 10^7$ and possibly beyond.

DISCUSSION

There are no quantitative theories available with which we can compare our experimental results. The next best thing to do is to make use of qualitative considerations. Let us suppose, as a tentative hypothesis, that the velocity distributions of the electrons in the C-H bonds in all the four gases investigated are identical, but that the velocity distributions of the electrons in the CC bonds change in such a way that the average velocities increase as we go from C-C in C₂H₆ to C=C in C₂H₄ and finally to C≡C in C₂H₂. (A reasonable assumption would be that the average velocities are approximately inversely proportional to the square root of the separation of the carbon atoms. This results in the average velocities of the electrons in the CC bonds in C₂H₆, C₂H₄, and C₂H₂ being in proportion to 1.00, 1.08, and 1.13.) For each molecule the contribution of the different bonds to the experimental velocity distribution curve is in proportion to the number of electrons involved in each bond. In C₂H₆, the contribution of the C-H bonds to that of the C-C bonds should be weighted in the ratio of 6 to 1, which means that, unless the electron velocity distribution for the C-C bond differs considerably from that of the C-H bond, the distribution for the molecule as a whole will be

nearly identical with that for the C-H bond alone. This is in line with our experimental result that the electron velocity distribution curves for CH₄ and C₂H₆ are substantially identical. (This is true for the lower velocities, but, as was mentioned earlier, there is some doubt as to the accuracy of that part of the distribution curve representing the scattering of the faster electrons in methane.) In C₂H₄, the ratio of the contribution of the C-H bond to that of the C=C bond is 2 : 1, while in C₂H₂ the corresponding ratio is 2 : 3. The assumption we have made leads to the conclusion that the average velocities of the electrons should increase as we follow the sequence ethane, ethylene, acetylene. This prediction is supported by our experimental results for ethane and ethylene, but we do not find any substantial change as we go from ethylene to acetylene. So long as we treat the C-H bond as identical in all three molecules, there seems to be no way of accounting for the change in average velocities from ethane to ethylene and the absence of a change from ethylene to acetylene.

It is possible that one is not justified in assuming that the electron velocity distributions are identical in the C-H bonds, when the adjacent CC bonds differ as they do in the three molecules considered. In a very recent paper, Coulson and Duncanson¹⁰ published a theory from which it may be inferred that the mean

¹⁰ C. A. Coulson and W. E. Duncanson, Proc. Camb. Phil. Soc. **37**, 67 (1941).

TABLE II. Abscissa values for $f(u)$ at half maximum and quarter maximum. (Values when multiplied by 10^4 are in cm/sec.) The value in parentheses for methane is an alternative quarter maximum value obtained as described in the text.

	C ₂ H ₂	C ₂ H ₄	C ₂ H ₆	CH ₄
half max.	29.7	29.7	26.7	26.7
quarter max.	44.7	44.7	39.6	45.3 (39.6)

momenta of the electrons in the C-H bonds in ethane, ethylene, and acetylene are in proportion to 1.00, 0.98, and 0.93: It will be observed that this sequence for the C-H bond is just the reverse of that assumed for the CC bonds in the same molecules. The result is that as we go from ethane to ethylene and then to acetylene the diminution in the average velocities in the C-H bonds will more or less offset the increase in the average velocities in the CC bonds. In view of these considerations one perhaps would not expect to find differences in the average velocities of the electrons in ethane and in ethylene as large as those implied in Table II. It is also difficult to see why there is no substantial difference between the curves for ethylene and acetylene when there is a difference between ethylene and ethane.

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