THE SCATTERING OF X-RAYS FROM GASES

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The angular distribution of intensity of X-rays scattered from amorphous substances is affected by two types of diffraction phenomena: interference between rays scattered by groups of molecules, and interference between rays from groups of electrons within the atoms. It has been repeatedly suggested¹ that experiments with amorphous substances may lead to definite information about the distribution of electrons in atoms through this latter effect. Debye² has shown that in an ideal gas the effect due to neighboring molecules is negligible under ordinary conditions. For studying electron distribution, therefore, the ideal gases are considered most desirable as scattering substances, and that the problem may be simple the light gases have been recommended. Mark and Schocken³ have recently obtained the intensity distribution of Mo K_a rays scattered from carbon dioxide and argon. With the latter gas they find no interference effect between 30° and 160°; with carbon dioxide they observe none between 40° and 140°, but their 30° observation shows a small excess over the $(1 + \cos^2\theta)$ law of scattering of electrons at rest scattering independently. Experiments with hydrogen or helium have long been wanted. If the classical electrodynamics are applicable they should serve to locate the pair of electrons in the molecule, while if the Compton effect is very prominent they should show almost no interference effects.

The apparatus used in the present experiment is drawn to scale in figure 1. A water-cooled molybdenum target X-ray tube was operated at 55,000 peak volts, 60 milliamperes, while connected to mercury pumps. The radiation was passed through filters at F, through slit S_1 and entered chamber C through a window of thin celluloid. The pressure of a gas contained in C could be varied from 0.5 to 335 cms. Secondary radiation from a small volume of this gas passed through slits S_2 and S_3 into an ionization chamber. The ionization current at each angle θ was measured by the rate of deflection of a Compton electrometer, and was found to vary linearly with the pressure of the gas in C.

Commercial electrolytic hydrogen (containing 0.03% oxygen), oxygen (containing 0.1% impurity) and commercial carbon dioxide were admitted to the chamber C through drying tubes and a tube of glass wool. Electrometer readings with the gases at 0.5 cm. pressure were subtracted from the readings at 335 cms. at each angle. To determine the volume of the gas effective in causing ionization at the different angles, the path of the primary beam in C was filled with loose cotton, and the ionization thus

obtained was compared with that from a small string of the same cotton, which gave a constant volume at all angles. The intensity curves for the different gases are more accurate relative to each other than relative to the cotton, which is only approximately homogeneous, so the conclusions drawn from the curves are based more on the ratios of their ordinates than on the absolute values of them.

Monochromatic radiation was obtained by a filter method recently used by Prof. P. A. Ross. Filters of strontium oxide and zirconium oxide were adjusted to such thickness that each absorbed 50% of the Mo K_{β} line. They then were found well matched at all wave-lengths except those between their K absorption limits. Placing first one then the other in the primary beam and taking the difference of the intensity transmitted,



a spectrum shown by the black area in figure 2 was obtained. (The dotted curve is the spectrum with no filter in the beam.) Considering the cross-sectional area of this monochromatic beam compared with that obtained with a crystal reflected beam, the energy used in these experiments was at least several hundreds of times greater than obtained by the usual crystal method.

Figure 3 gives the weighted mean of measurements with hydrogen as the scatterer. Within a probable experimental error of 5% the intensities using 0.71 Å monochromatic radiation (circles) do not differ from the intensities obtained with one filter in position (dots), though the spectrum of the latter resembles the dotted curve of figure 2, and has a mean effective wave-length less than 0.71 Å. No interference effect, which would be a

function of the wave-length, is noticeable. If the two electrons of a hydrogen molecule are assumed to be a constant distance of 1.1 Å apart, as postulated in an old form of Bohr's theory, the classical theory gives the dotted curve of figure 3. The intensity on this theory at θ degrees from the direct beam is proportional to

$$(1 + \cos^2\theta) \left[1 + \frac{\sin\left(\frac{4\pi s}{\lambda}\sin\frac{\theta}{2}\right)}{\frac{4\pi s}{\lambda}\sin\frac{\theta}{2}} \right]$$

where s is the electron separation and λ the wave-length of the rays.

On the other hand, if the radiation scattered at these angles were mostly



modified, the intensity should be practically independent of the wavelength used, as is observed here. The intensity formulas of Compton, Breit, Dirac (Heisenberg-Born mechanics) and Gordon (Shroedinger theory) agree approximately in predicting the intensity proportional to

$$\frac{1+\cos^2\theta}{\left(1+\frac{h\nu}{mc^2}\operatorname{vers}\theta\right)^3}.$$

This formula, for the frequency used, is plotted as the solid curve in figure 3. The deviations from it that are observed may be due to errors in determining the volume of gas scattering, or possibly the unmodified radiation becomes appreciable at small angles and causes excess scattering. The points at small angles, however, cannot be taken as decisive evidence of the latter because at those angles the scattering from the walls of the chamber was larger than at greater angles and the accuracy of the gas readings consequently lower.

In figure 4 it is seen that the oxygen curve is a function of the wavelength. Reduced to the same scale as the hydrogen curve at 70° it shows that excess scattering for θ less than about 60° is very prominent. A few observations with carbon dioxide gave a curve hardly distinguishable from that for oxygen; excess scattering appeared at approximately the same angle. Work on other gases is in progress.

One may conclude on the basis of these experiments that interference is present in X-rays scattered from a single molecule of carbon dioxide or oxygen, and absent in rays scattered from a hydrogen molecule—at least in the range 30° to 90°. This may be interpreted as evidence of considerably unmodified radiation in the former case and of completely or nearly completely modified radiation in the latter, confirming Woo's measurements and in accord with Jauncey's theory of the intensities of the different kinds of radiation in the Compton effect.

It is a pleasure to acknowledge the many helpful suggestions of Prof. A. H. Compton, Prof. P. A. Ross and Dr. J. A. Bearden.

¹ Compton's X-Rays and Electrons, p. 74, gives complete references and a summary of the work in this field.

² Debye, P., Phys. Zeit., 28, 135, 1927.

⁸ Mark and Schocken, Naturwiss., 15, 139, 1927 (Feb. 11).

THE DISTRIBUTION OF ENERGY IN MOLECULES

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The author has recently attempted to account for the rates of unimolecular reactions by a theory¹ which assumes activation by collision and treats the reacting molecules as mechanical systems with many internal degrees of freedom. A somewhat similar theory had been advanced earlier by Rice and Ramsperger.²

For the complete development of the author's theory it is necessary to solve the problem: Given a number of oscillators, classical or quantum, harmonic or otherwise, and a value for the total energy of these oscillators, calculate the chance that a specified one of the oscillators shall have energy in excess of some given value. The solution of this problem for the case