Letters to the Editor.

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Doppler Effect in Light-Scattering.

IT is a problem of great interest to consider the changes in spectral character of monochromatic radiation resulting from the thermal agitation of a medium in which it is scattered. If we regard the subject classically, the result to be expected is obvious : there should be a Doppler broadening of the incident spectral line, varying with the angle of observation, and determined by the Maxwellian distribution of velocities of the molecules which scatter the light. It can readily be shown that, except in respect of the total intensity of scattered light, it would make no difference to the argument by which this result is deduced whether the molecules are loosely distributed as in a gas or are closely packed together as in a dense vapour or liquid.

It is very remarkable, however, that a wholly different result was deduced by L. Brillouin,[1] following the idea that the medium which scatters the radiation can be treated as a continuum filled with moving sound-waves of various wave-lengths which reflect the light-waves much in the same way that a moving crystal would give Bragg's reflection of X-rays. Brillouin's theory indicates that in the spectrum of the scattered rays the single line which represents the incident light should be replaced by a close doublet, the frequency shifts of which are given by the formula $\Delta\nu/\nu = \pm 2a/c \sin \frac{1}{2}\theta$, where a and c are the velocities of sound and light respectively, and θ is the angle of observation ; the incident line itself would be missing in the scattered light. Brillouin's deduction of this formula has outwardly the appearance of being based on classical ideas. Actually, however, the argument ignores the existence of discrete molecules in the medium, and the results to which it leads cannot be reconciled with the classical point of view, according to which the incident line should persist in the scattered light in the same position with no change except a Doppler broadening.

The paradox presented above is resolved if we adopt the following view of the matter based on quantum principles. In a medium scattering light we are dealing with an assemblage of photons having energy $h\nu$ and momentum $h\nu/c$, material particles having translatory energy $\frac{1}{2}Mv^2$ and linear momentum Mv and also associated with the latter, quanta of sound, having energy $h\nu_s$ and linear momentum $h\nu_{s/a}$. The result of an individual encounter must satisfy the equations of the Compton type :

$$\tfrac{1}{2}Mv^2 + h\nu_s + h\nu_i = \tfrac{1}{2}Mv'^2 + h\nu'_s + h\nu'_i$$
$$\overrightarrow{Mv} + \overrightarrow{h\nu_{s/a}} + \overrightarrow{h\nu_{i/c}} = \overrightarrow{Mv'} + \overrightarrow{h\nu'_{s/a}} + \overrightarrow{h\nu'_{i/c}}$$

The first is a scalar and the second is a vector equation. We obtain Brillouin's result immediately, if the energy and momenta of the material particles are ignored, and the equations are solved. If, on the other hand, the energy and momenta of the sound quanta are ignored, and the equations are solved, the classical Doppler broadening results. These are, however, two extreme cases, and in general both types of phenomena may be expected to be present and to influence each other.

It must here suffice to remark very briefly that the considerations set out above enable us readily to offer a satisfactory interpretation of the experimental results recently reported by Gross [2] on the modification of the fine structure of spectral lines produced by scattering in liquids and solids.

C. V. RAMAN.

210 Bowbazar Street,
  Calcutta, Sept. 5.

[1] *Annales de Physique*, vol. 17, p. 88 ; 1922.
[2] NATURE, vol. 126, pp. 201, 400, 603 ; 1930 ; and *Zeit. für Physik*, vol. 63, p. 685 ; 1930.

Activated Adsorption of Hydrogen by Zinc and Chromium Oxides.

THE adsorption of hydrogen by zinc oxide has been the subject of investigation [1] by one of my students, Mr. D. V. Sickman, on a so much more comprehensive scale than that recently recorded by Garner and Kingman [2] that it seems desirable to state the results in outline prior to their publication some months hence.

A slow adsorption of hydrogen on zinc oxide (from the oxalate by ignition at 400° C.) occurs from 0° C. upwards. On 20 grams of material at *circa* 400 mm. pressure adsorption reached 2·9 c.c. in 1345 minutes at 0° C. ; at 110° C. the velocity of adsorption increased so that 7·25 c.c. were adsorbed in 1200 minutes ; at 184° C. this same amount was adsorbed in 45 minutes and as much as 14 c.c. were adsorbed in the longer time interval. The adsorption is reversible, *all* the hydrogen being recoverable by evacuation at 450° C. The activation energy of the adsorption amounts to 14 kgm. cal. for the main surface covered, with smaller values on the more active areas. By a new mathematical analysis of the velocity measurements Sickman has deduced [1] a heat of adsorption of 21 kgm. cal. per mol, a more trustworthy figure than a value of 16 kgm. cal. deduced from isotherms at high temperatures on a partially deactivated surface. The higher value is in excellent agreement with the value recorded by Garner and Kingman for the heat of adsorption of hydrogen on their $ZnO - Cr_2O_3$ catalyst. This would indicate, as they conclude with respect to carbon monoxide, that the hydrogen is adsorbed on the zinc oxide of the mixed material.

Below 0° C. another type of adsorption occurs which attains equilibrium practically instantaneously with no activation energy. The heat of this adsorption is only 1100 calories per mol. As much as 21 c.c. at $-190°$ C. and 3 c.c. at $-78°$ C. are adsorbed on 20 grams of oxide at 400 mm. From the data cited it can readily be calculated that this type of adsorption is negligible at 0° C.

We are inclined to ascribe the minute adsorption of hydrogen found by Garner and Kingman on the single oxides of zinc and of chromium to the slowness with which activated adsorption occurs at ordinary temperatures on the single oxides in comparison with the rate of adsorption on the mixture.[3] That hydrogen is markedly adsorbed in an activated form by chromium oxide is evident from work by Sherman and the writer in which precipitated chromium oxide (ex nitrate) has been shown to be effective in producing the change from para to ortho-hydrogen at ordinary temperatures. This, as we have already shown,[4] is intimately associated with activated adsorption of hydrogen at such surfaces.

HUGH S. TAYLOR.

The University, Manchester,
  Sept. 14.

[1] Thesis, Princeton, (1931).
[2] Garner and Kingman, *Trans. Farad. Soc.*, **37**, 322 ; 1931.
[3] Cf. Taylor and Williamson, *J. Am. Chem. Soc.*, **53**, 813, 2168 ; 1931.
[4] Taylor and Sherman, *J. Am. Chem. Soc.*, **53**, 1614 ; 1931.