ON THE SCATTERING OF LIGHT BY SUPERSONIC WAVES

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1. *Introduction.*—In a paper published in 1922 Leon Brillouin[1] treated the problem of light scattering. In accordance with the fact that for low temperatures Einstein's theory of specific heat has to be abandoned for Debye's theory, Brillouin attributes the thermal density fluctuations in the body, which, in his theory, as in a previous theory of Einstein's,[2] are responsible for the scattering to a superposition of sound waves. He tries to apply his theoretical results to the explanation of x-ray scattering. We know now that this application is far from correct, as for such short waves the electronic density changes due to the atomic or molecular structure are much more important than the thermal fluctuations. For light waves, however, with a wave-length much longer than molecular distances, Brillouin's analysis leads to some remarkable results. They can be stated in the following manner. Suppose the primary light travels in figure 1 in a direction characterized by a vector $\vec{S_0}$ of length unity in this direction. Let it be assumed that of the scattered light a part is observed traveling in another direction characterized by a unit vector $\vec{S}$. Then firstly, of the sound waves of all possible directions, only those are important for the scattering which are traveling in or opposite to the direction of the vector $\vec{s} = \vec{S} - \vec{S_0}$. This can also be expressed by saying that the planes of the sound waves have to be situated such that the scattered light can be considered as optically reflected by these planes. But there is a second limitation. Of all the sound waves of direction $\pm \vec{s}$, only those of a definite wave-length Λ are effective. This wave-length is $\Lambda = \lambda/s$, if λ is the wave-length of the light and s is the length of the vector $\vec{s}$, which is $2 \sin \Theta/2$, calling Θ the angle between the primary and the secondary ray. This last condition can be expressed by saying that the consecutive planes of maximum density in the sound wave must be

separated by a distance Λ such that the well-known relation of Bragg holds. In this case the light rays reflected by the consecutive planes will have path differences of one wave-length (of light) each and therefore the reflections will be strong. So we are left with only two sound waves, traveling with the velocity of sound q, one in the direction $+ \vec{s}$ and the other in the direction $- \vec{s}$. The frequency of the reflected light, according to Doppler's principle, will be changed, and instead of the primary frequency v, we should find in the scattered light the two frequencies:

$$v = v_0 \left[1 \pm 2n \, q/c \, \sin \theta/2\right]$$

where c is the velocity of light in vacuo and n is the index of refraction of the medium.

Gross[3] reports that with an echelon he has been able to photograph several new components of a spectral line created by the scattering process.
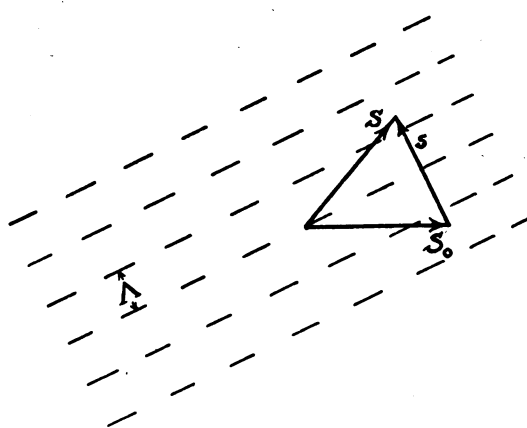

FIGURE 1

Recently, Meyer and Ramon[4] have published actual photographs of the effect. In contrast with Gross's results they were able to obtain two components only, one at either side of the primary line, which is in accordance with the theory. The shift is approximately 0.06 A. U. and checks satisfactorily with the value calculated from the known velocities of sound in the liquids used. Besides the two components, a central line of unchanged frequency v_0 appears which may partly be due to unavoidable traces of dust in the liquid, and partly to thermal fluctuations of the index of refraction as a result of molecular rotation, an effect which was not considered in the derivation of Brillouin's theory.

2. *Experiments.*—Brillouin[1] mentions the possibility of experimental verification of his calculations, making use of elastic waves set up in a liquid by a quartz crystal driven by a high-frequency oscillator, and it occurred to us that it would be interesting to try the scattering of light by these "artificial" sound waves. The experiment was set up in the following way. In a trough of rectangular cross-section, figure 2, filled with a liquid (benzene, carbon tetrachloride, etc.) a quartz crystal Q was immersed. The leads to the silvered faces of this crystal could be connected with a radio-frequency oscillator. Vibrations set up in the crystal

in this way excite supersonic waves traveling in the liquid in the direction $Q\ E$. Perpendicular to this direction a parallel beam of light from a slit S and a lens L_1 passes through the liquid. The parallel beams, scattered by the illuminated part of the liquid are focussed by a telescope lens L_2. As soon as the crystal is connected to the oscillator, spectra of different orders (like the spectra of an ordinary grating), appear at the left and right of the central image of the slit. The number of orders which can be observed depends on the intensity of the vibrations. Their spacing depends only on the frequency and increases if the frequency of the oscillator is increased.

. As in ordinary grating spectra, the blue is the least deviated, and the red the most. With a mercury arc source, the different mercury lines can be observed in every order. Under favorable conditions as to the intensity of the vibration more than 10 spectra to the right and to the left have been obtained. In order to see if the supersonic waves are markedly transmitted by a solid, a glass block of cross-section equal to the trough was immersed in the liquid. Light passed through the liquid in front of and behind the block showed the spectra, but through the block itself produced only the central slit image.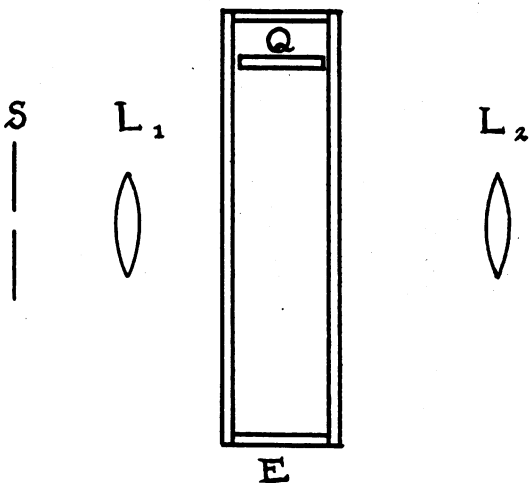 We may safely expect, however, that using a higher intensity the effect will also be seen in the solid. No marked decrease

FIGURE 2

in the number of orders visible could be observed in passing the light through portions of the liquid at different distances from the crystal with liquids like benzene or carbon tetrachloride. With glycerine, however, this effect is very pronounced, no doubt due to its high viscosity.

Fixing the attention on one of the spectra, preferably of higher order, one can observe that it attains its maximum intensity if the trough is turned through a small angle such that the primary rays are no longer parallel to the planes of the supersonic waves. Different settings are required to obtain highest intensities in different orders. If the trough is turned continuously in one direction, starting from a position which gave the highest intensity to one of the orders, the intensity decreases steadily, goes through zero, increases to a value much smaller than the first maxi-

mum, decreases to zero a second time and goes up and down again passing through a still smaller maximum. The same series of events occurs in turning the trough in the other direction. To make these observations it is necessary to watch the pattern carefully. One thing, however, which can be seen at first glance is the fact that the number of orders visible on the right and the left of the central image is different except for the case in which the primary rays are passing exactly parallel to the planes of the supersonic waves. Turning the trough continuously changes the number of orders to the right or the left in the same way as has been described for the intensity.

The whole effect is rather brilliant and can easily be projected on a screen so as to make it visible to an audience. Figure 3 shows a photograph of the effect obtained in passing monochromatic light of wavelength $\lambda = 5461$ A. U. through toluene, the frequency of the supersonic waves being 5.7×10^6.

3. *Interpretation.*—As a tentative explanation it was first thought that the primary rays passing through the liquid in sheets would, as a consequence of the periodic density variations due to the supersonic waves, acquire phase differences of periodical nature. The light emerging from the grating created in the liquid would show interference patterns of the same general kind as observed with an ordinary grating. The fact that the supersonic waves are not standing waves should make no difference.
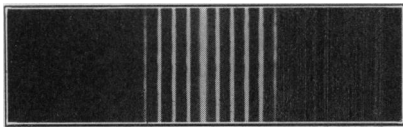

FIGURE 3

This explanation, however, fails to explain the observed intensity distribution in the various orders, as can be shown by a more detailed analysis, and a theory has been developed based on the assumption of a volume scattering, in which every volume of the liquid contributes to the total scattering in accordance with Maxwell's equations. In this way, it seems at first, following Brillouin's theory, that one would expect only one reflection for a definite angle of incidence of the primary light and one other reflection on the other side for the same angle taken with negative sign. Moreover, light passing parallel to the planes of the supersonic wave should show no effect at all. These results are evidently at variance with the observations. Taking into account, however, that the dimensions of the illuminated volume of the liquid are finite it can easily be shown that in our case Bragg's reflection angle is not sharply defined and that reflection should occur over a rather appreciable angular range. If l is the length of the path of light in the liquid, Λ the wave-length of the supersonic waves and λ the wave-length of the light, then two quantities are of importance; namely, the quotients l/Λ and Λ/λ. Only if

l/Λ is large compared to Λ/λ does a sharp definition of Bragg's angle exist. Working with a frequency of 10^7 cycles, Λ is about 0.1 mm., l is of the order 10 mm. and λ is about 0.5×10^{-3} mm. In this case, therefore, $l/\Lambda = 100$ and $\Lambda/\lambda = 200$, the quotient of these two quantities is 1/2 and cannot be considered as large. A detailed analysis shows that in such a case reflection will occur over a range of angles left and right of the critical angle which follows from Bragg's relation. Moreover the intensity variations predicted by the theory in varying the angle continuously are just the same as described in relating the rather peculiar experimental results on this point.

We are, however, still left with another difficulty. The theory predicts only the first order spectrum to the right and the first order to the left. But in the theory so far it has been assumed that the variations of the index of refraction are of purely sinusoidal character. If they are not, then we can consider the disturbance as a superposition of variations of frequencies v, $2v$, $3v$, etc., with the corresponding wave-lengths Λ, $\Lambda/2$, $\Lambda/3$, etc., provided a marked dispersion of the velocity of sound in the frequency region considered does not exist. A departure from sinusoidal character therefore accounts for the existence of the higher order spectra. This departure may be due to the non-sinusoidal cha acter of the crystal vibrations, although higher harmonics may be produced by the scattering itself, if the intensity of the supersonic waves is high enough. This is in agreement with the fact that the higher orders fade out if the intensity of the vibrations of the crystal is decreased.

Adopting the theory, the measurement of the angles θ of the different orders ρ with respect to the central image provides us with a measure of the wave-length of the supersonic wave in terms of the wave-length of the light which has been used. In fact, as in an ordinary grating

$$\sin \theta_\rho = \rho\lambda/\Lambda.$$

The frequency can easily be determined with an ordinary wavemeter and so we get a very simple method for the determination of the velocity of sound.

The following table shows some preliminary measurements performed with a very simple spectrometer, together with values calculated from the density and the adiabatic compressibility.

	VELOCITY CALCULATED M./SEC.	FREQUENCY	VELOCITY OBSERVED M./SEC.	FREQUENCY	VELOCITY OBSERVED M./SEC.
Toluene	1290	1.7×10^6	1330	16.5×10^6	1310
Carbon tetrachloride	920	1.7×10^6	940	16.5×10^6	930

Up to now no indication of a change in velocity with frequency has been observed. If it exists, a more careful measurement of the angles for

different orders should show it, as the measurement of say 10 orders simultaneously existing provides us with a frequency range of v to $10\ v$.

[1] L. Brillouin, *Ann. phys.*, **17**, 88 (1922).

[2] A. Einstein, *Ann. Phys.*, **33**, 1275 (1910).

[3] Gross, *Zeit. Phys.*, **63**, 685 (1930); *Naturwiss.*, **18**, 718 (1930); *Nature*, **126**, 201, 400, 603 (1930).

[4] Meyer and Ramon, *Phys. Zeitschr.*, **33**, 270 (1932).

THE ADDITIVITY OF THE ENERGIES OF NORMAL COVALENT BONDS*

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The chemical bond between two identical atoms, as in the molecules H_2, Cl_2, etc., may be considered as an example of a normal covalent bond, involving an electron pair shared by the two atoms. The wave function representing this bond cannot necessarily be closely approximated by a function of the Heitler-London type, with the electrons staying on different atoms, but may contain ionic terms, corresponding to the two electrons of the bond on the same atom, the term representing the configuration A^+A^- occurring, of course, with the same coefficient as that for A^-A^+. The contribution of these ionic terms to the wave function for the normal state of the hydrogen molecule has been discussed by Slater.[1]

In the wave function representing the bond between unlike atoms A and B, the ionic terms A^+B^- and A^-B^+ will occur with the same coefficient, of the order of magnitude of those for $A:A$ and $B:B$, if the two atoms have the same degree of electronegativity. We propose to call such a function a normal covalent bond wave function, and the bond a normal covalent bond; and to make the postulate that *the energies of normal covalent bonds are additive*, that is, $A:B = \frac{1}{2}(A:A + B:B)$, where the symbols $A:B$, etc., mean the energies of the normal covalent bonds. This postulate requires that the energy change for a reaction such as $\frac{1}{2}A_2 + \frac{1}{2}B_2 = AB$ involving only normal covalent substances with single bonds be zero. The energy of the normal covalent bond $A:B$ would be given by the integral $\int \psi^* H \psi d\tau$, with ψ the normalized normal covalent wave function. Inasmuch as the energy integral for any wave function for a system must be equal to or greater than the energy of the lowest state of the system, the energy of the actual bond between A and B will either be equal to that for a normal covalent bond $A:B$, or, in case the