

INTERFEROMETRIC STUDIES OF LIGHT SCATTERING IN GASES

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Received April 25, 1942

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

Introduction

RAYLEIGH'S theory of light-scattering in gases is based on the assumption that the molecules of the irradiated gas behave as Hertzian dipoles and emit secondary radiation in all directions. It is assumed further that these secondary radiations are incoherent with each other. The justification for the latter assumption is to be found in the fact that the molecular positions in a gas are distributed at random, and the phases of the scattered radiations as received at any point in space are therefore uncorrelated. The matter may also be considered from another standpoint. The molecules of the gas are in motion, and hence the scattered radiations suffer Doppler shifts of frequency varying from molecule to molecule and in consequence are incapable of interfering with each other. Hence, if the incident radiations consist of a sharp spectral line, the scattered radiations should exhibit a spectral broadening, the magnitude of this depending on the mass of the molecule, on the temperature of the gas, as well as on the direction of observation. It is evident that such Doppler broadening would be unobservable in the direction of the incident beam and would be a maximum in the backward direction. Such a state of affairs would subsist even in the case of highly compressed gases, so long as they continue sensibly to obey Boyle's law (C. V. Raman, 1922). It is therefore very different from what is experimentally observed in the case of dense media such as liquids where discrete Doppler-shifted components are observed in the spectrum of the scattered light, the magnitude of the shift depending on the velocity of sound in the medium and the direction of observation. The present investigation describes an interferometric study of the scattering of light in some compressed gases intended to test the theoretical considerations indicated above.

Experimental

It is obvious that the most favourable direction for the observation of the scattered light is backwards to the incident beam, as the Doppler

effect is then a maximum. Further, when the observation is made in this way, the depth of the illuminated gas can be made large with a corresponding gain in intensity while retaining the desirable definiteness in the angle between the incident and scattered rays. The intensity is also greater with backward than for transverse scattering, as both components of polarisation in the incident light are effective in the former case. For the successful observation of the spectral character of light scattering, it is very important to avoid parasitic light from the walls of the tube and to maintain the interferometer at a constant temperature. Indeed, Cabannes (1929) who studied the problem using butyl alcohol vapour and transverse scattering obtained a shift of the fringes towards longer wavelength, which has since been shown by Rao (1934) to be a spurious effect due to temperature variations in the apparatus. A satisfactory experimental arrangement used by the author is illustrated in Fig. 1. The cylinder T containing the gas is made of a mild steel tube $1\frac{1}{2}$ "

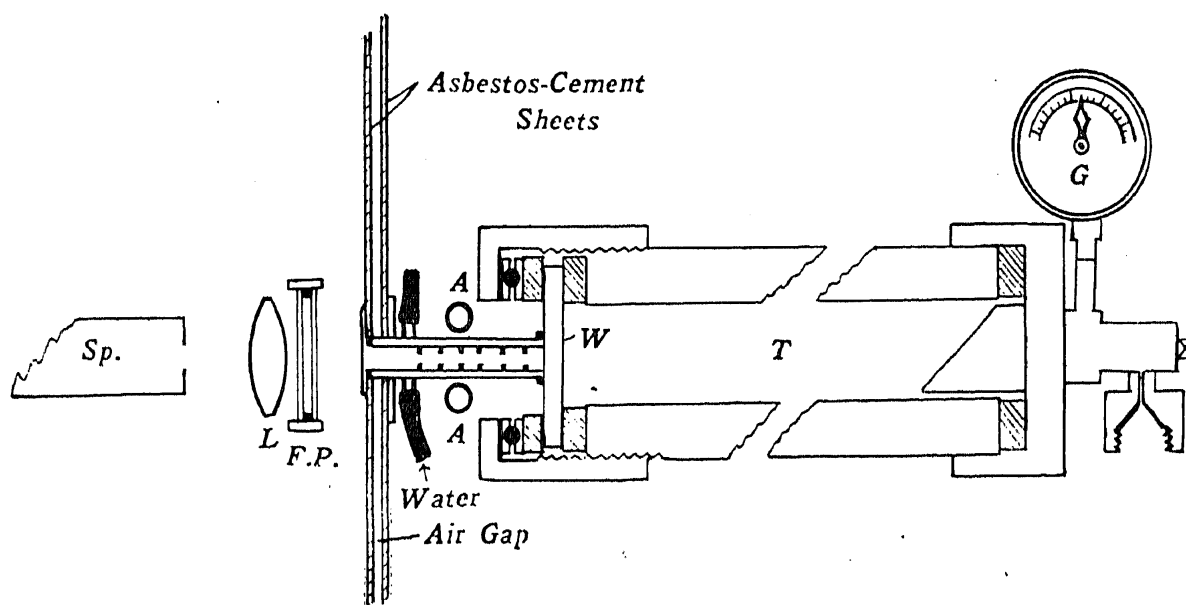


FIG. 1. The Diagram of Gas Container

in internal diameter, $\frac{3}{8}$ " wall-thickness, and $1\frac{1}{2}$ ' long, blackened inside by spray painting. The observation end is closed with a round glass plate W of $\frac{5}{8}$ " thickness and pressed air-tight by means of lead washers and a screw cap. The back end of the cylinder is similarly closed by another screw-cap to which is fitted a gas adapter. A satisfactory dark background is provided by a black glass plate fixed in a brass tube at 45° to the axis of the cylinder. A blackened brass tube which is water cooled and into which is fitted a series of circular apertures of $\frac{1}{4}$ " diameter, is fixed flush with the glass window. The source of light used is a semi-circular mercury arc A with water-cooled cathode and kept at high vacuum by continuous pumping. The light passes through the annular space,

about $\frac{1}{4}$ " broad, between the central brass tube and the outer screw-cap. The light scattered backwards is taken through the central tube and let fall on a quartz Fabry-Perot interferometer F. P. with invar separation pieces. The interference fringes are focussed on the slit of a Fuess glass spectrograph. The interferometer and the spectrograph are placed inside an air-tight enclosure made of asbestos-cement sheets. The whole outfit is situated in a large room with massive walls in which the temperature fluctuation is very small, and the provision of the additional enclosure for the optical system ensures constancy of temperature throughout the exposure extending over several days.

The plate-distance used for the etalon is 7.5 mm. For this separation of plates, the distance between consecutive orders is 0.66 cm^{-1} , and the hyperfine structure pattern of 4046 A.U. is given in Fig. 2. It will be seen that the satellites fall either on the principal maxima or at the centre, leaving a clear gap in between.

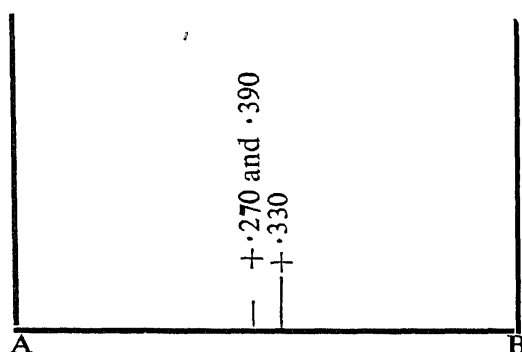


FIG. 2. Satellites of 4046 A.U. radiations

$$\delta\nu_{AB} = .66 \text{ cm}^{-1}$$

The gases used are hydrogen at 100 atmospheres, oxygen at 80 atmospheres, nitrogen at 80 atmospheres, and carbon dioxide at 50 atmospheres pressure. The gases are let into the experimental tube from commercial holders through a plug of cotton wool which filters out all dust particles. The scattering being extremely weak, nearly fifteen days exposure was required in each case.

Results and Discussion

Figures 4 a-e in the accompanying Plate show the interference patterns of 4047 A.U. radiations given by the arc and after it is scattered by hydrogen and nitrogen. The patterns given by oxygen and carbon dioxide are similar to those of nitrogen. In no case were shifted components analogous to those given by liquids observed. It may be recalled that the discrete line structure of the rotational Raman scattering in oxygen, nitrogen and carbon dioxide has been observed by Bhagavantam (1931), Trumphy (1933) and Weiler

(1935), to disappear at such high pressures. The absence of any Doppler-shifted component in the spectrum shows that though the mean free path of the molecules at these pressures lies between 11–16 A.U. and is thus fairly small, it is sufficiently great in comparison with the molecular dimensions to ensure the absence of any coherence between the scattering units. The interference patterns due to the heavier gases N_2 , O_2 and CO_2 are very nearly identical with that of the direct arc, except for a weak continuum between the rings, which is absent in the latter. In the case of hydrogen, the rings in the pattern show considerable broadening with the intensity falling off gradually on either side. Similar broadening is also exhibited by the 4358 A.U. radiations. It is observed that in accordance with the Rayleigh's fourth power law, the green radiation of the arc is recorded only weakly in the spectrum of the scattered light, while it appears with good intensity in the spectrum of the arc. This indicates that the scattered light is fairly free from parasitic illumination. The Raman spectrum of the gas obtained after removing the interferometer also shows that stray light does not interfere with the observations.

Assuming the validity of Maxwell's law of distribution of velocities of the molecules in the systems studied, we can ascertain the spectral intensity distribution in the scattered radiation. If a molecule possesses a velocity u along the bisector of the angle θ between the incident and the scattered beams, the frequency of the incident radiation would change by Doppler effect from n_0 to $n_0 \left(1 \pm \frac{2u}{c} \sin \frac{\theta}{2}\right)$, where c is the velocity of light, the positive sign corresponding to the case in which the molecule is moving towards the light and the negative sign for the molecule receding away from it.

As the velocity components of molecules in any particular direction vary from zero to a large value, the scattered light will have a range of frequencies about the central value n_0 . The intensity of light scattered with a particular frequency, $n_0 \left(1 \pm \frac{2u}{c} \sin \frac{\theta}{2}\right)$ corresponding to the velocity u , will depend on the number of molecules possessing that velocity, which is given by the Maxwellian distribution of velocities. The intensity I correspond-

ing to a velocity u may accordingly be written as $I = I_0 e^{-\frac{1}{2} \frac{mu^2}{kT}}$, where I_0 is the intensity corresponding to $u = 0$, while m , k and T are respectively the mass of the molecule, the Boltzmann constant and the absolute temperature. Now the velocity corresponding to the half-breadth of the line is given by the value of u at which $\frac{I_0}{I} = 2$, namely $u = \sqrt{2 \log_e 2 \cdot \frac{kT}{m}}$ and the change of

frequency corresponding to this velocity is $\delta n = \frac{2n_0}{c} \sin \frac{\theta}{2} \cdot \sqrt{2 \log_e 2 \cdot \frac{kT}{m}}$.

Expressed in wavenumbers this may be written as

$$\delta \nu = 2\nu_0 \cdot \sin \frac{\theta}{2} \sqrt{2 \log_e 2 \cdot \frac{kT}{mc^2}}.$$

At the room temperature and for the 4047 A.U., the calculated half-breadth for hydrogen comes to 0.22 cm.^{-1} and for the other three gases less than 0.06 cm.^{-1} . Though theoretically the half-breadth for the mercury vapour at the temperature of the arc should be only 0.03 cm.^{-1} , the actual half-breadth of the interference maxima measured microphotometrically gives a value of 0.08 cm.^{-1} . It will be seen that the expected half-breadths for nitrogen, oxygen and carbon dioxide are less than this value, which explains the observed results. Fig. 3 shows the microphotometer tracings of the 4047 A.U. line scattered by hydrogen and of the direct

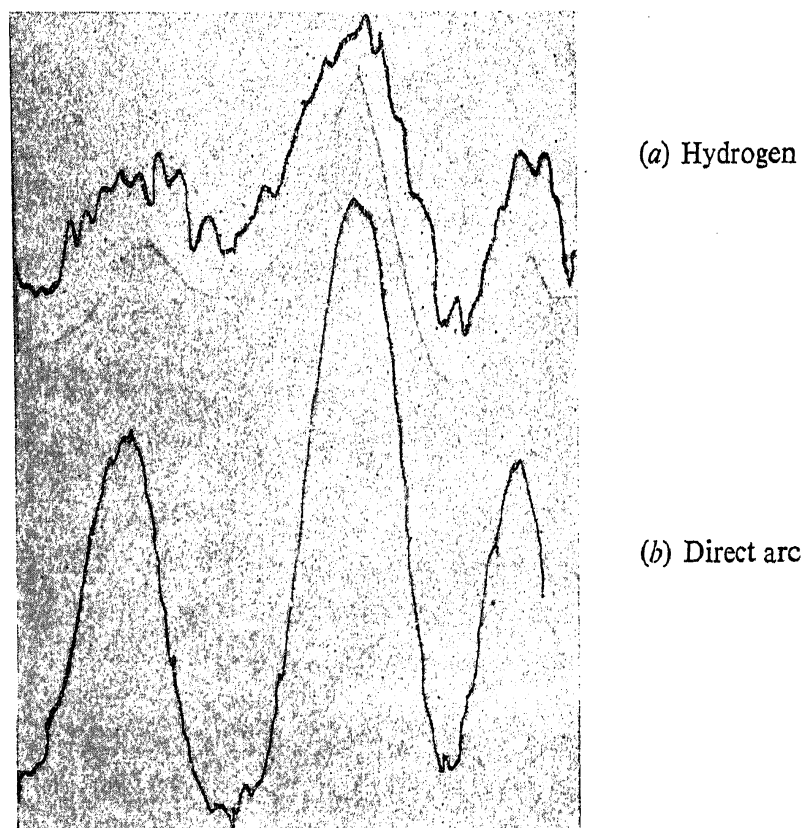


FIG. 3. Microphotometric tracings for hydrogen gas

arc. The half-breadth obtained from the above curve is 0.18 cm.^{-1} which is of the same order of magnitude as the theoretical value. The background that is observed in the patterns of the scattered light and which is particularly noticeable for hydrogen may be attributed to molecules having relatively high velocities.

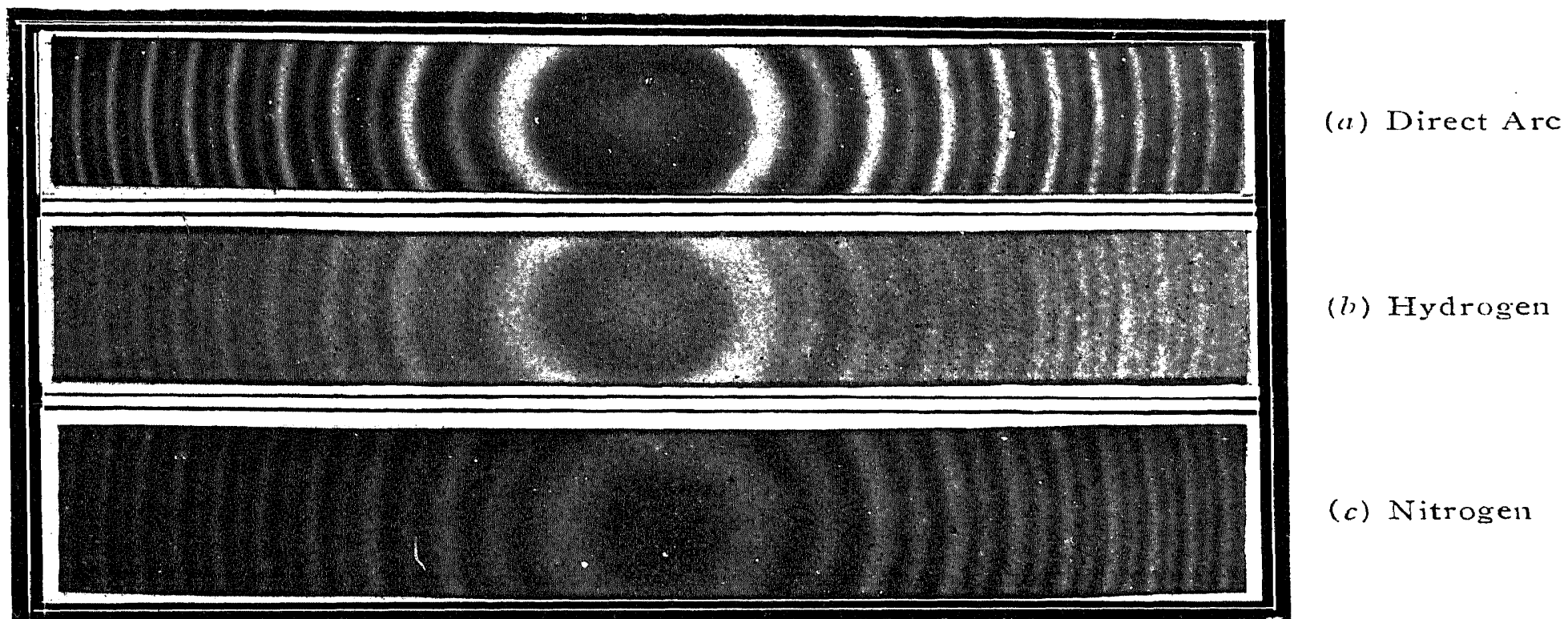
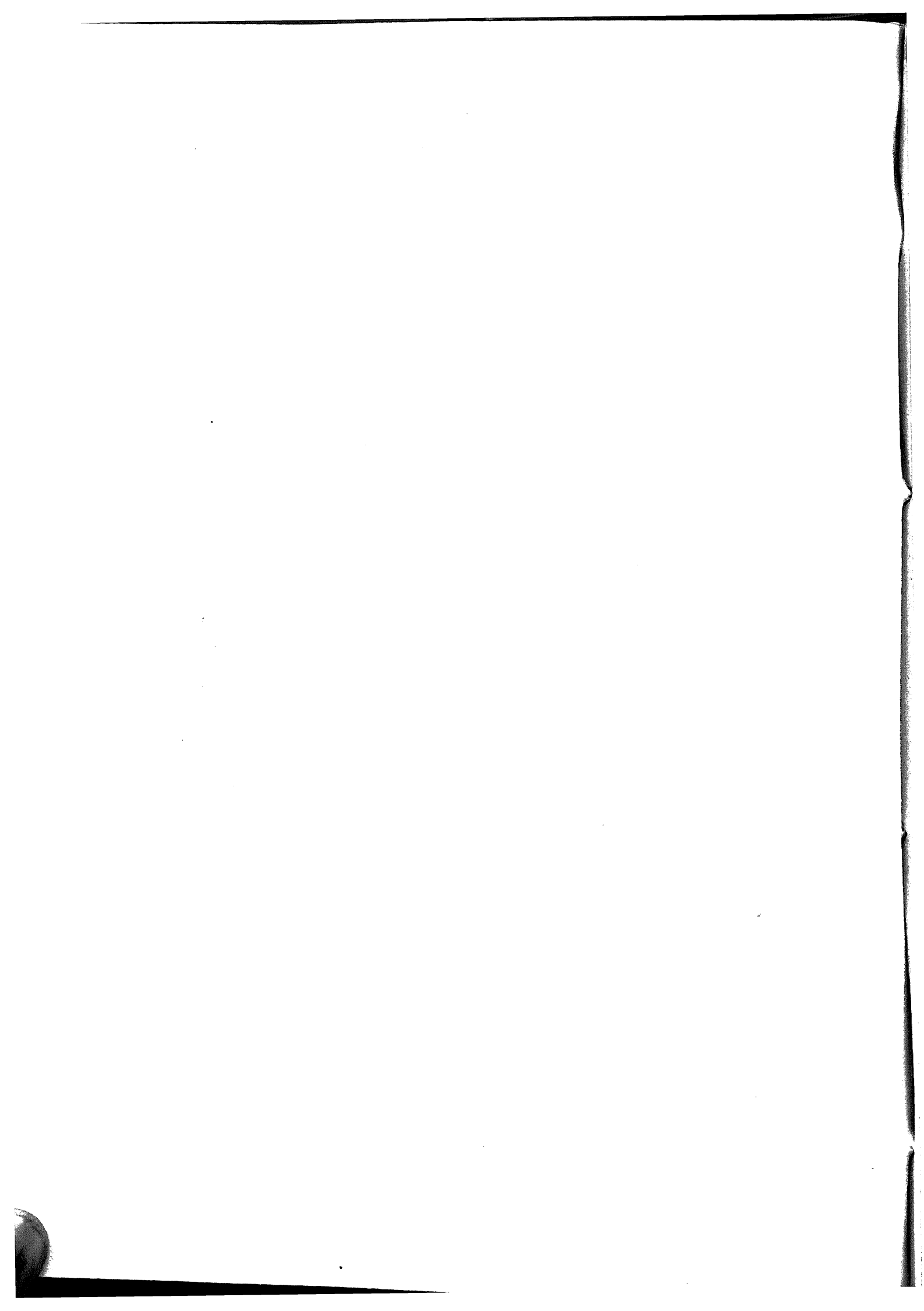


FIG. 4. Interferometer Patterns for Gases



In conclusion, the author wishes to express his thanks to Professor Sir C. V. Raman at whose suggestion the investigation was undertaken, for his kind interest in the work.

Summary

Light scattered backwards by four gases, namely, hydrogen, nitrogen, oxygen and carbon dioxide at high pressures has been analysed by a Fabry-Perot interferometer. None of the gases showed displaced components similar to those in liquids. For the heavier gases, N_2 , O_2 and CO_2 , the Doppler broadening was observed to be too small to be detectable with mercury radiations. The pattern obtained for hydrogen showed a broadening and the half-breadth of the line was found to be of the order to be expected from Maxwell's law of distribution of velocities. A weak background due to molecules having relatively high velocities was observed in the scattered patterns for all cases.

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