Effect of Temperature on the Raman Spectrum of CCl_4.

I HAVE investigated the Raman spectrum of liquid CCl_4 over a wide range of temperatures extending from the room temperature up to 200° C. Rise of temperature brings about several progressive and striking changes in the Raman spectrum of this substance, as can be seen from the photograph reproduced below.

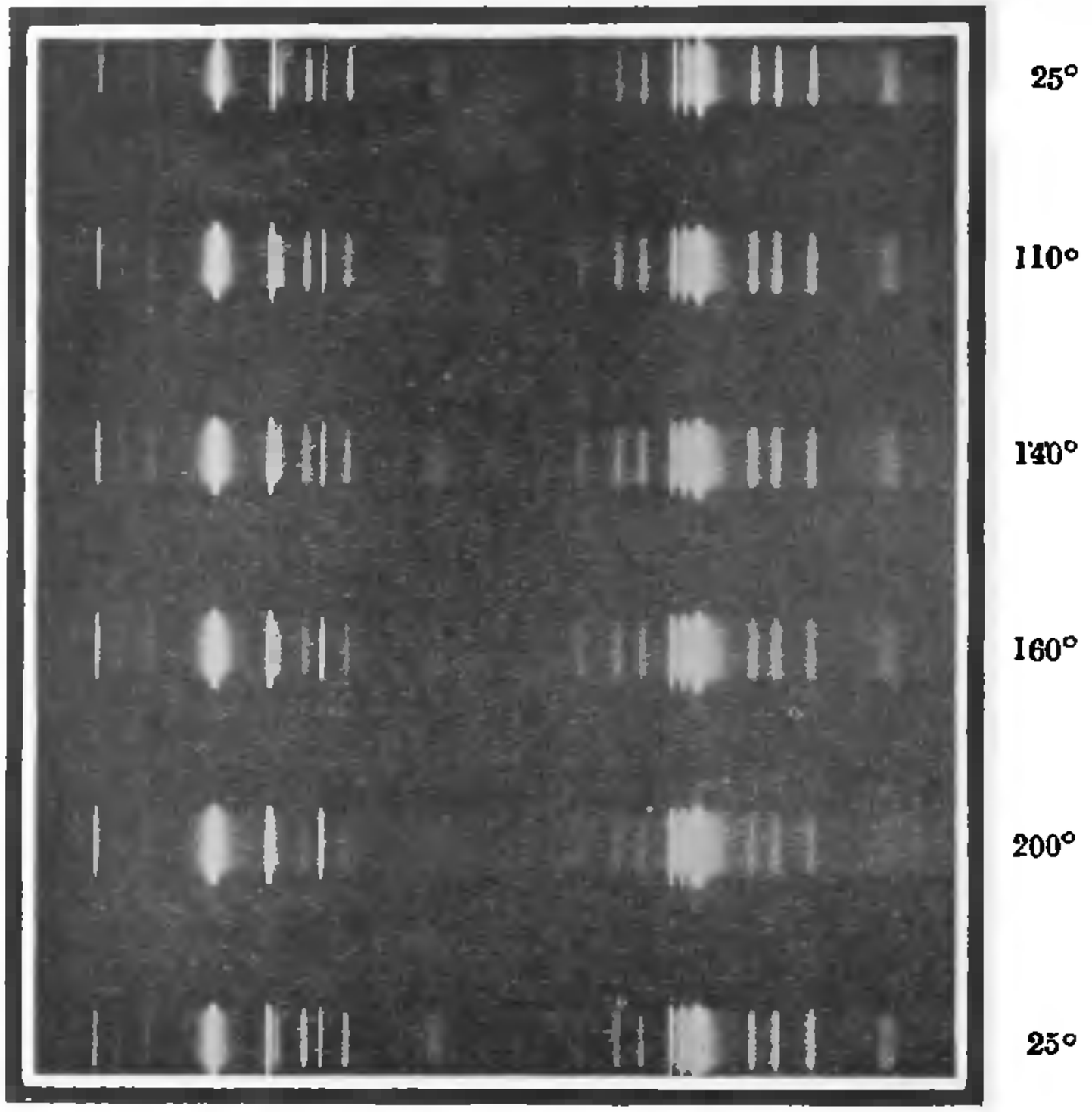

Fig. 1.

(1) The doubly degenerate Raman line at 218 cm.$^{-1}$ and the triply degenerate frequency at 314 cm.$^{-1}$ become considerably broad and diffuse as the temperature is elevated.

(2) The pair of Raman lines at 762 cm.$^{-1}$ and 790 cm.$^{-1}$ forming the triply degenerate frequency, which are very well resolved at the ordinary temperature become rapidly diffuse as the liquid is heated.[1] In the spectrum photographed at 200° C. these lines have merged into one another into a single broad and diffuse band.

(3) The totally symmetric vibrational Raman line at 459 cm.$^{-1}$ does not seem to be appreciably influenced by temperature.

(4) In the Raman spectrum of the liquid at 200° C. the Stokes lines are markedly weaker than those at room temperature. This observation is in contradiction to Placzek's theory which predicts an increase of intensity for the Stokes as well as the anti-Stokes components with rise of temperature. It also appears that the increase in intensity of the anti-Stokes components, if any, is much less than that demanded by the theory.

The increased width and diffuseness of the degenerate vibrations is presumably connected with the greater rotational freedom of the molecules at higher temperatures. The reason for the fall of intensity of the Stokes components with rise of temperature is in all probability due to diminution of $\left(\frac{\partial \alpha}{\partial q}\right)_0$ for the higher vibrational states whose population is more dense at higher temperatures. The full significance of the results will be discussed in detail in a paper which will shortly appear in the *Proceedings of the Indian Academy of Sciences*.

R. ANANTHAKRISHNAN.
Department of Physics,
Indian Institute of Science,
Bangalore,
June 5, 1936.

[1] See Fujioka, *Sci. Pap. Inst. Phys. Chem. Res., Tokyo*, 1929, **11**, 222.