

A Study of the Raman Effect in Certain Substances with a New Apparatus.

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(Plates XXVII and XXVIII)

ABSTRACT.

An apparatus for the study of the Raman effect in which the exciting arc is produced in the annular space between two coaxial tubes, the inside one being of fused silica and the outside one of pyrex glass, is described. The substance under examination is placed in the inner quartz tube and is surrounded on all sides by the exciting arc. In this arrangement strong ultra-violet lines such as the resonance line of mercury (2536\AA) may be used as the exciting radiation. The temperature of the substance can be varied by sending a current of air through the inner tube; the effect of change of temperature on Raman lines has been thus examined. Calcite and aragonite have been studied with this new apparatus. Halite and fluorite give negative results. Acetylene gas gives Raman lines corresponding to the infra-red absorption bands at $2.45\ \mu$ and $7.5\ \mu$; the latter comes up as a double line corresponding to the points of maximum absorption recorded by Levin and Meyer. The strong absorption band at $13.7\ \mu$ gives no corresponding Raman line. The temperature effect on the continuous wings accompanying unmodified lines in the scattered spectrum has been studied and their origin suggested.

The original method of Raman¹ which consists in concentrating the exciting radiation on the scattering material by means of a lens and that of Wood² in which a long mercury

¹ Ind. J. Phys., Vol. 2, p. 387 (1928).

² Nature, Vol. 123, p. 166, Feb. 2 (1929).

arc is placed parallel to the tube containing the substance, a liquid usually, are now well known. Wood has used another method¹: he surrounds the tube having the substance under examination by a spiral discharge tube containing helium. Recently in the case of solids Menzies² and others use the substance in the form of powder.

The arrangement of apparatus described below is the result of an attempt to secure the following ends in the study of the Raman effect.

(i) The method must be applicable to solids (including powders), vapours and gases.

(ii) The temperature of the scattering material must be capable of being varied and under control.

(iii) It must be possible to use as the exciting radiation such strong lines in the ultraviolet as 2536\AA of mercury.

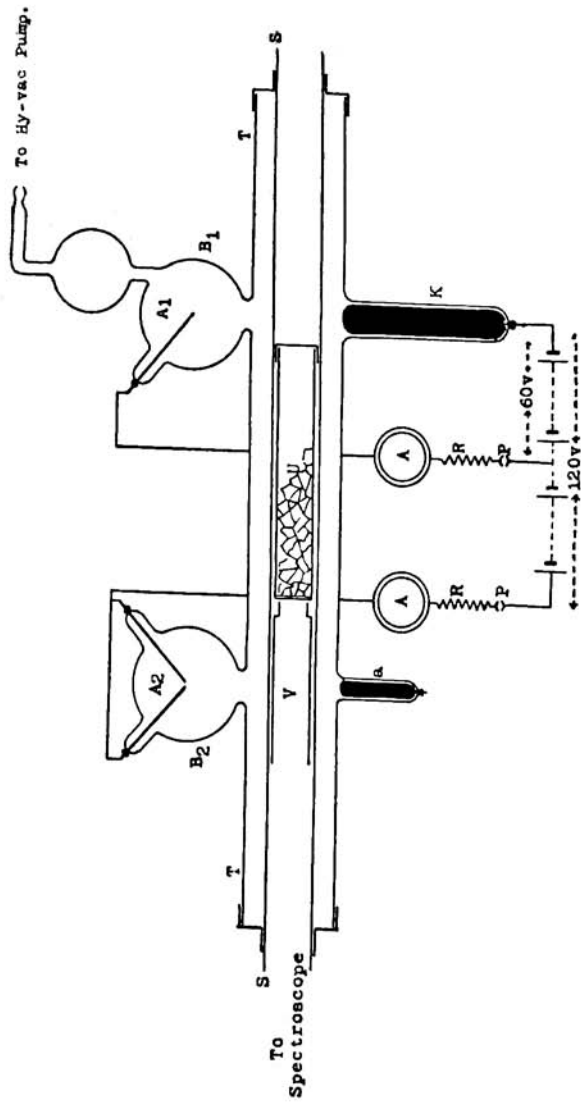
The present apparatus has been designed with the idea of surrounding a quartz tube containing the scattering material by a long column arc discharge in mercury. The inside tube, S, (Plate XXVII) is of clear fused silica passing centrally through an outer pyrex tube, T. The tubes are joined together by two iron caps with shellac or DeKhotinsky's cement. The main arc runs between the double tungsten anode A_2 and the mercury cathode K. In order to facilitate the starting of this long column arc, provision is made for a subsidiary arc between A_1 and K. Bulbs B_1 and B_2 are intended to prevent the glass from melting by coming too near the hot anodes. The region of discharge between the inner and outer tubes is kept constantly pumped out by a Hy-vac pump. The following is the procedure adopted in starting the arc:—When the vacuum is sufficiently low the mercury in K is heated till it

¹ Phys. Rev., Vol. 33, p. 294 (1929).

² Menzies, Nature, Oct. 5 1929).

B&R, Nature, Nov. 2 (1929).

Krishnamurti, Nature, Mar. 22 (1930.)



An apparatus for the study of the Raman Effect.

A—ammeter. A₁ A₂—anodes. a—subsidiary anodes. B₁ B₂—Pyrex glass bulbs. SS—Inner Quartz tube.

K—cathode. TT—outer Pyrex tube. RR—rheostats.

U.—Quartz tube containing the scattering material. PP—switches. V—iron tube.

boils and an induction coil discharge is passed between it and an additional anode, a, provided for the purpose; the arc between K and A₁ now lights up and carries a current of about 5 amperes. Next the portion between B₁ and B₂ is well heated and on again passing the induction coil discharge the main arc between K and A₁ is established. After this arc has run for about five minutes the subsidiary arc may be put out. On the completion of an experiment, when it is desired to switch off the main arc, the current must be gradually reduced and the outer pyrex tube slightly warmed and annealed after putting out the arc. This will invariably ensure a longer life on the average for the pyrex tube, which otherwise by sudden cooling is liable to crack.

The diameter and thickness of the annular space determine whether the arc completely surrounds the inner quartz tube or not. In our experiments when the arc completely surrounded the inner tube the diameters of the tubes were 2 and 3 cms. In other cases, especially when the diameter of the inner tube was increased, the arc nearly but not completely surrounded the quartz tube. Various distances between B₁ and B₂ ranging from 15 cms. to 50 cms. have been tried: but when this distance is very much diminished the arc takes a spiral form.

The main arc runs steadily for hours without much attention and usually the shellac at the iron caps, when sufficiently far from the region of discharge, does not soften. But when it is desired to cool the scattering material by a stream of air from an electric blower, the iron cap at the end where the air warmed by passing over the hot arc escapes, is cooled by a blast of air, say, from an electric fan or a hair-dryer. By the proper control of the supply of air for cooling the scattering material the temperature can be altered by more than 200°C and the material can be maintained at any desired temperature within five degrees. The range of available temperature is from about 120°C to 400°C. The

current in the main arc is usually ten amperes with a potential drop of 50-60 volts between the terminals; the current density in the arc is about two amperes per square centimetre.

Raman effect in solids.—The substance is placed in the form of powder (crystalline or amorphous) in a fused silica tube, U, with a silica plate fused on to one end, the other end being closed by a loosely fitting iron cap. An iron tube, V, is placed on the spectrometer side against the silica plate to allow only the scattered light from the substance in the central portion of the tube to fall on the spectrometer. A quartz lens is used to concentrate the light on the slit.

Raman effect in vapours and gases.—A fused silica tube (Fig. 1) with a graded seal ending in pyrex glass is used.



FIG. 1.

The amount of scattering material whether it be a gas or a vapour should be so regulated before sealing off the tube as to develop a pressure not exceeding ten atmospheres at the temperature of the arc. In the case of vapours, after the introduction of the required quantity of the liquid, the tube is evacuated to remove air and sealed off.

With the view of testing the effectiveness of the method calcite was tried at two different temperatures. It was placed in the tube, U, in the form of small crystals. The following table embodies the results obtained:

TABLE I

Exciting Line.		Raman Lines.			$\Delta\nu$ Obs. cm ⁻¹ .	Δ Raman in μ .	λ in μ values of other ob- servers.	
λ in Å.	ν vac.	λ in Å.	Int.	ν vac.				
2586-52	89412	2545-8	2	89269	143	70-4	68	Vide Plate xxviii
		2527-5	1	89552	140			
		2549-0	1	89219	198	51-5	...	
		2524-0	0-5	89607	195			
		2554.1	2	89141	271	35-6	35-8	
		2519-0	1	89686	274			
		2583-2	1	33700	712	14-05	14-08	
		2508-4	4	33326	1086	9-25	9-23	
		2468-7	1	40495	1083			
		2632-1	1	37981	1431	6-98	6-96	
3125-66	31983	3235-5	2	30898	1085	9-25	9-23	
3131-56	31923	3242-2	2	30834	1089			

While these results are in substantial agreement with those obtained by other investigators^(1, 2, 3, 4), there are also the following new features. The highly intense resonance line of mercury 2536Å gives a sharp Stokes line of great intensity corresponding to the inactive frequency 1086 cm⁻¹ of the CO₂-radical. The anti-Stokes line for this frequency comes out clearly on the plate. The intensities of anti-Stokes lines in the case of the low frequencies 142 and 273 cm⁻¹ are comparable with those of the corresponding Stokes lines whereas in the case of the inactive frequency the anti-Stokes line is very feeble. It is interesting to note that the infra-red absorption band at 11.4 μ gives no corresponding Raman line.⁵ This band, according to Nielsen,⁶ arises on

¹ Krishnan, Ind. J. Phys., IV, p. 131, Aug. (1929).

² Wood, Phil. Mag., Vol. 6, 729 (1928).

³ Kimura and Uchida, Inst. Phys. Chem. Research, Tokyo Sc. Papers, 203, pp. 199-204 (1929). Jap. J. Phys., 5, p. 97 (1928).

⁴ Nisi, Proc. Imp. Acad., Tokyo, 5, p. 127 (1929).

⁵ Kimura and Uchida, Inst. Phys. Chem. Research, 203, (1929).

⁶ Phys. Rev., Vol. 32, pp. 773-778 (1928).

account of the vibration of the carbon atom along the axis of symmetry in the CO_2 radical.

Effect of temperature.—The Raman line corresponding to the inactive frequency is not perceptibly affected in sharpness when the temperature is increased from 150°C to 250°C . But all the other Raman lines become distinctly more diffuse with rise of temperature. The anti-Stokes lines are enhanced in relative intensity as the temperature increases. Raman has directed attention to this effect in the following words; "As the temperature is increased, since the proportion of molecules in a higher energy level also increases, we should expect the negative lines to brighten up relatively to the corresponding positive lines."¹

Our results with aragonite, though in general agreement with those of others,² show that the Raman line corresponding to the inactive frequency is relatively far fainter than in calcite (Plate XXVIII). It is not however clear whether the presence of this Raman line is due to traces of calcite invariably found mixed up with aragonite or to the slow polymorphous conversion of aragonite into calcite at our working temperatures.³ Chalk powder gave a negative result.

Landsberg and Mandelstam,⁴ Nisi and others working with fluorite (CaF_2) have invariably obtained a negative result. Under the favourable conditions of our experimental arrangement, we have tried fluorite and halite (NaCl). Even the strong line 2536\AA of mercury gave no trace of Raman lines after long exposures amounting to 40 hours. In the case of fluorite, however, the usual fluorescence spectrum came out on the plate with marked intensity extending from 5000\AA to 2900\AA with an intensity maximum at about 3400\AA .

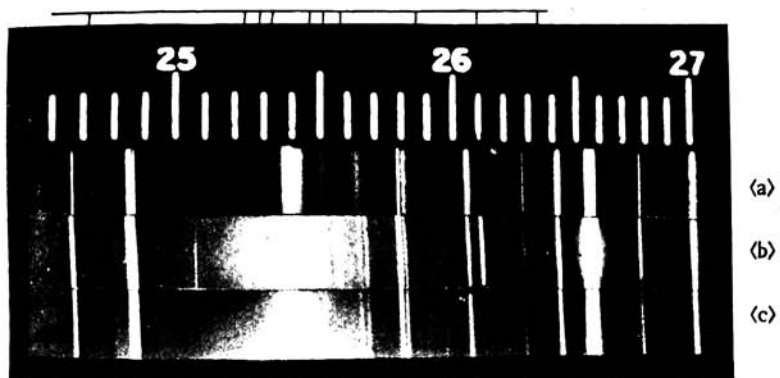
Raman Effect in Acetylene.—The infra-red absorption

¹ Proc. Roy. Soc., Vol. 122, p. 29 (1929).

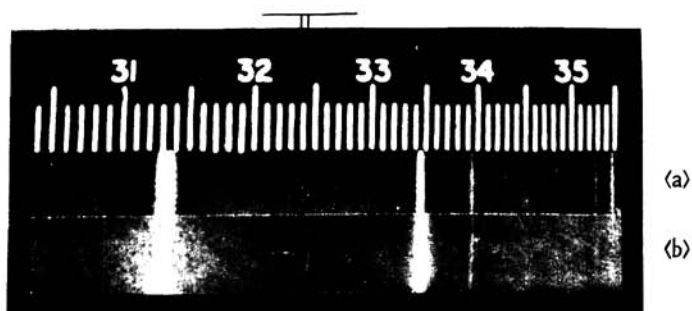
² Kimura and Uchida, Tokyo Sci. Papers, p. 203 (1929).

³ Bulletin 770; The Data of Geochemistry, pp. 557-558 (1924).

⁴ Zs. f. Phys., 50, p. 769 (1928).



(a) Incident spectrum
(b) Raman spectrum of Calcite
(c) Raman spectrum of Aragonite.



(a) Incident spectrum
(b) Raman spectrum of Calcite.

spectrum of acetylene has been studied by Coblenz¹ who finds absorption maxima at 13.7μ , 7.5μ and 2.5μ . We examined spectroscopically the radiation scattered by a column of about 40 cms. of acetylene contained in a long pyrex tube at a pressure of 2.5 atmospheres. This pyrex tube occupied the place of the central silica tube, S, thus limiting our observations to the visible region. The following table contains the results obtained:—

TABLE II

Exciting Line.		Raman Line.			Observed $d\nu$ cm^{-1}	λ Raman in μ	Infra-red values of λ in μ .
λ (Å).	ν vac.	λ (Å).	Int.	ν vac.			
4046.6	24705	4845.7	1	20631	4074	2.45	2.5
4077.8	24516	4889.3	1	20447	4069	2.45	2.5
4046.6	24705	4269.2	0.5	23418	1287	7.76	7.5
4046.6	24705	4294.8	1	23277	1428	7.00	
4077.8	24516	4300.7	0.5	23245	1271	7.86	7.5
4077.8	24516	4325.4	0.5 diff.	23113	1403	7.12	

We see that there is no Raman line corresponding to the strong infra-red absorption band at 13.7μ . There have been instances of strong infra-red absorption bands of which the corresponding Raman lines do not appear. Pringsheim and Rosen² have listed several such cases. This however, does not rule out the possibility of the faint appearance of the Raman line for 13.7μ on longer exposure than we have been able to give. The wave-number shifts of the Raman lines for 7.5μ seem to correspond to the points of maximum absorption of this band as recorded by Levin and Meyer.³

¹ Carnegie Inst. Pub., 35 (1905).

² *Zs. f. Phys.*, 50, XI, p. 741 (1928).

³ *J. O. S. A.*, Vol. 16, Mar. (1928).

One of the features that comes out markedly on the plates (Plate XXVIII) is the hazy wing extending on either side of strong exciting lines in the scattered spectrum. This phenomenon has been observed by several investigators¹ and its origin is even now a matter for speculation. On our plates these wings are seen not only in the case of substances like calcite which show the ordinary Raman effect but also in substances like halite and fluorite which do not exhibit the effect. We find that the temperature of the scattering substance influences the wings in that an increase of temperature relatively enhances the effect on the violet side (anti-Stokes side) of the incident line with the result that the wing develops a decided asymmetry about the unmodified line when as in the case of calcite the temperature of the substance is raised from 150°C to 250°C. The wings may be traced to about 25 Å on the violet side and to about 15 Å on the red side of the incident line 2536 Å in calcite at 250°C. This behaviour of the wings with change of temperature suggests that the phenomenon has to be traced to the interaction of the thermal energy of the molecules, considered for instance as Planck's oscillators, with the incident quantum.

We take this opportunity of thanking the Geology Department of this College for kindly lending us aragonite, fluorite and halite used in this investigation.

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¹ Daure, C. R., 186, p. 1533 (1926). Raman and Krishnan, Proc. Roy. Soc., 122, p. 28, (1929). Faraday Society Discussion on Molecular Spectra, Cabannes, p. 808 (1929).