

Raman scattering liquid air.

FIG. 2.

Raman scattering liquid hydrogen.

FIG. 3.

[To face page 797.]

ON THE RAMAN EFFECT WITH LIQUID OXYGEN, NITROGEN AND HYDROGEN.

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Among the varied experiments carried out by numerous investigators on the Raman effect since its original discovery, those made by the writer in collaboration with his associate, Mr. H. J. McLeod, with liquid oxygen, nitrogen and hydrogen appear to merit special consideration. A preliminary account¹ of them has appeared elsewhere.

The apparatus used in these experiments is shown in Fig. 1. As the diagram indicates, the upper portion was provided with a Coil B, through which a gas to be liquefied such as argon could be led and the liquefaction of this gas was provided for by the use of a suitable liquid refrigerant held in the specially-constructed thermos flask A surrounding the coil. The lower portion of the apparatus which was made wholly of glass, was the one used in making exposures for the Raman effect. It consisted of a four-walled, double thermos flask, about 25 centimetres long. When liquid air, liquid oxygen, or liquid nitrogen was under investigation, each was held in the inner thermos flask, while the outer one was kept filled with liquid air. When liquid hydrogen was under observation, the outer flask was kept filled with liquid hydrogen. The use of the outer liquid enabled one to keep the inner one free from visible ebullition, and subject only to very slow evaporation. For illumination 4 or 5 mercury vapour arc lamps were used. These were made of glass, and were about 30 cm. long. They were placed standing vertically close to, and surrounding the thermos flask containing the liquified gas. Each lamp carried a current of between 3 and 4 amperes. E and F were mirrors of platinum made by cathodic spluttering on glass. The light from the lamps entered the liquid laterally, and after being scattered, modified and reflected by the two mirrors, was focussed on the slit C of a high light-power spectrograph. Exposures of about 8 hours sufficed to record the Raman lines. Enlarged reproductions of spectrograms taken are shown in Figs. 2 and 3.

In our experiments with liquid air, we found that the spectrum of the light scattered included four sharp and clearly defined lines not included in the irradiating light, which was that from the mercury arc.

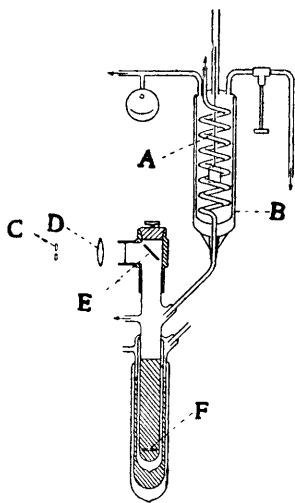


FIG. 1.

¹ *Nature*, Feb. 2, 1929; and *Trans. Roy. Soc. Canada*, Section III., 1929.

798 ON THE RAMAN EFFECT WITH LIQUID OXYGEN, ETC.

The wave-lengths of these lines were approximately 4317.7 Å., 4674.3 Å., 4468.9 Å., and 4849.3 Å. They, with their frequencies, are given below :—

Element.	Exciting Radiation.		Scattered (Raman) Radiation.			Observed.	Calculated from Band Spectra Data.
	(Å.)	(vac.)	(Å.)	Int.	(vac.)	cm. ⁻¹ .	cm. ⁻¹ .
Oxygen .	4046.6	24,705	4317.7	1	23,154	1552	1554
	4358.3	22,938	4674.3	2	21,387	1551	1554
Nitrogen .	4046.6	24,705	4468.9	1	22,371	2335	2331
	4358.3	22,938	4849.3	00	20,616	2322	2331

The experiment was repeated with pure liquid oxygen and again with pure liquid nitrogen, and it was found that the wave-lengths 4317.7 Å. and 4674.3 Å., only were obtained with liquid oxygen, and the wave-lengths 4468.9 Å. and 4849.3 Å., only with liquid nitrogen. The existence of two of the Raman lines with each liquid can be explained by supposing them to arise from irradiation by light of the two wave-lengths 4358 Å. and 4047 Å. The frequency difference for the mercury line 4047 Å. and the Raman oxygen line 4317.7 Å. is 1552 cm.⁻¹, and for the mercury line 4358 Å., and the Raman oxygen line 4674.3 Å. is 1551 cm.⁻¹. With the nitrogen lines, the one, 4468.9 Å., has a frequency difference with the mercury line 4047 Å. of 2335 cm.⁻¹, and the other, 4849.3 Å. with the mercury line 4358 Å.—a difference of 2322 cm.⁻¹.

It would seem that a mean vibration frequency of approximately 1551.5 cm.⁻¹ was involved in the Raman effect with liquid oxygen and a mean vibration frequency of approximately 2328.5 in the Raman effect with liquid nitrogen.

From the *Bulletin of the National Research Council*, Vol. II., Part III., No. 57, on "Molecular Spectra in Gases" (p. 232), 1554 cm.⁻¹ is indicated as the primary vibration frequency of the oxygen molecule in its normal state, and 2331 cm.⁻¹ as that of the nitrogen molecule in its normal state. Our results would suggest that the primary vibration frequencies were the ones involved in the production of the four Raman lines observed by us.

In experiments with liquid hydrogen irradiated with light from the mercury arc, we found that in addition to the usual mercury lines there were included in the spectrum of the scattered light lines corresponding to wave-lengths 4426.6 Å., 4473.1 Å., and 4863.5 Å. These, with their frequencies, are given below :—

Element.	Exciting Radiation.		Scattered (Raman) Radiation.			Observed.	Calculated from Band Spectra Data.
	(Å.)	(vac.)	(Å.)	Int.	(vac.)	cm. ⁻¹ .	cm. ⁻¹ .
Hydrogen .	4358.3	22,938	4426.6	2	22,584	354	347
	4358.3	22,938	4473.1	4	22,350	588	578
	4046.6	24,705	4863.5	1	20,556	4149	4159

By the use of suitable light screens, it was found that 4426.6 Å. and 4473.1 Å. were excited by the radiation 4358.3 Å., and 4863.5 Å. by radiation 4046.6 Å.

The frequency differences 354 cm.⁻¹ and 588 cm.⁻¹, it will be noted, are in the ratio 3 : 5.

In the original theory of the quantisation of the rotational energy of diatomic molecules, the energy of rotation is given by

$$E = \frac{m^2 h^2}{8\pi^2 I} = m^2 h B \text{ where } B = \frac{h}{8\pi^2 I},$$

m is the rotation quantum number, and I is the moment of inertia of the rotating molecule about the axis of rotation.

If we assume integral values for the quantum number $m = 0, 1, 2, 3, 4$, etc., the rotational energy states will be given by

$$E = 0, Bh, 4Bh, 9Bh, \text{ etc.}$$

These, it will be seen, provide no transitions with $h\nu = E_1 - E_2$ that will give two rotational spectral frequencies in the ratio 3 : 5.

On the other hand, if we assume the half integral values $\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \frac{7}{2}$, etc. for m as Czerny² was led to do in explaining the rotation spectrum of HCl, the energy states will be given by

$$E = \frac{Bh}{4}, \frac{9}{4} Bh, \frac{25}{4} Bh, \frac{49}{4} Bh, \text{ etc.}$$

If, now, we have a transition from the energy state $\frac{25}{4} Bh$ to the one $\frac{Bh}{4}$, and another from the energy state $\frac{49}{4} Bh$ to the one $\frac{9}{4} Bh$, we will have as a result two frequencies provided for having ratio 3 : 5.

This would, of course, afford an explanation of the frequency differences found in our Raman effects with liquid hydrogen, but it would involve the use of half-quantum numbers which is objectionable, and would besides require us to suppose that hydrogen molecules were continually in rotation when in their lowest energy state.

Wave mechanics, however, shows that the energy of rotation of a diatomic molecule is given by $E = Bm(m+1)$ with m having the integral values 0, 1, 2, 3, 4, etc.

This gives us energy levels

$$E = 0, 2Bh, 6Bh, 12Bh, 20Bh, \text{ etc.}$$

With these energy levels available, we see that a transition from $6Bh$ to 0, and another from $12Bh$ to $2Bh$ will provide us with frequencies in the ratio 3 : 5.

As we observed no trace of any Raman lines with liquid hydrogen with frequency differences in one or other of the ratios 2 : 3 ; 2 : 5 ; 3 : 4 ; 4 : 5 ; etc., it would appear that none such can exist.

We see, then, that in liquid hydrogen we have one set of molecules in which the transitions of rotation from $m = 2$ to $m = 0$ can occur, and a second set in which the rotational transitions $m = 3$ to $m = 1$ can occur.

² Czerny, *Z. Physik*, **34**, 227, 244, 1925.

Moreover, since 4159 cm.^{-1} is known to be the frequency of the $m = 0$ to $m = 1$ *vibrational* transition for hydrogen molecules in the non-vibrational state, we have direct evidence that in liquid hydrogen (1) some molecules are in the zero vibrational and zero rotational states; and (2) others are in the zero vibrational and first quantum rotational states. As the intensity of the Raman line $\lambda 4473.1\text{\AA.}$ was found by us to be between 2 and 3 times that of the Raman line $\lambda 4426.6$, it follows that in liquid hydrogen one must have between 2 and 3 times as many molecules in the second, as compared with the number in the first state described above.

The distinctness of the two states is emphasised by the fact that no Raman effects were obtained corresponding to $m = 0$ to $m = 1$, or $m = 1$ to $m = 2$ rotational transitions.

The results of our experiments appear to be the first to constitute direct experimental proof of the correctness of Dennison's³ view that hydrogen at low temperatures must be regarded as a mixture of two effectively distinct sets of molecules defined as symmetrical and anti-symmetrical by the theory of wave mechanics.

³ Dennison, *Proc. Roy. Soc.*, **151A**, 483, 1927.
