

electron must travel from the cathode before it ionizes is a factor of fundamental importance in fixing the magnitude of the positive ion current.

¹ Jones and Langmuir, *G. E. Rev.*, **30**, 310 (1917).

² Langmuir and Mott-Smith, *G. E. Rev.*, **27**, 449, 538, 616, 762, 810 (1924).

ON THE RAMAN EFFECT IN DIATOMIC GASES

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The only observation on Raman effect in gases, as far as I know, is due to Ramdas.¹ The substance investigated was ethyl ether vapor, and the Raman spectrum was found to be identical with that of the liquid.

The aim of the present paper is to give some information about the Raman spectra of molecules of simple and well-known structure. It would have been perhaps more interesting to observe the effect in atoms, but it seems hard to get appropriate metallic vapors of sufficient density, and the rare gases, on the other hand, have no energy levels above the normal state low enough to give a Raman effect in the optical region. But, in the last years, our knowledge of molecular spectra has progressed far enough to enable us to verify if the Raman spectrum of a given molecule is connected with its band spectrum as is to be expected from the theory.

The theory of the Raman effect was given, long before the experimental discovery of the phenomenon, in Kramers and Heisenberg's treatment of dispersion² from the point of view of the correspondence principle. In this theory some of the fundamental assumptions of the later-developed matrix mechanics were already implied, so that the formula given by Kramers and Heisenberg for the electric moment of a system perturbed by the field of a light wave is exactly the same as it is when derived with the methods of wave mechanics.

It has been shown³ that if we take an atom in the quantum state distinguished by the index k (and which we will assume to be the normal state), the perturbation due to a light wave of frequency ν gives rise to harmonic components in the electric moment of the system having frequencies given by

$$\nu_{lk}^* = \nu - \nu_{lk} = \nu - \left[\frac{E_l - E_k}{h} \right],$$

where l represents any other state of the system satisfying only the condition that the expression above must be positive.

Considering the simplest case, in which the electric moment associated with the transitions involved in the process has the same direction, x say, of the electric vector of the light wave, then the amplitude in the direction x of the harmonic component ν_{lk}^* in the electric moment is proportional to

$$\sum_s x_{ls} x_{ks} \left[\frac{1}{\nu_{sl} + \nu} + \frac{1}{\nu_{sk} - \nu} \right],$$

where the quantities

$$x_{ls} = \int x \psi_l \psi_s d\tau$$

give the transition probabilities between the states l and s (in particular, if $x_{ls} = 0$, the corresponding transition is "forbidden").

From this it appears clearly that the condition for observing a transition (kl) as a Raman shift is not that this transition should occur in emission or absorption (which means $x_{kl} \neq 0$), but that *both* the k and l states should combine with a third state s (or with more than one), in order to give at least one of the products $x_{ks}x_{ls}$ different from zero.

This means that in an atom with a simple spectrum, such as that of any element in the first three columns of the periodic system, practically only forbidden transitions can take place in Raman effect; for instance, if the normal state is multiple (such as Al, Ga, In, Tl) the transitions between the terms of the multiplet.

All this applies also to the case of a diatomic molecule. Only, if the molecule is not polar, such as O_2 or N_2 , transitions between the different vibrational states, without change in the electronic levels, do not give rise to radiation because of the absence of an electric moment, and therefore do not occur; though they are not properly "forbidden" transitions, as the integral $x_{kl} = \int x \psi_k \psi_l d\tau$ does not vanish, the eigenfunctions being the same (Hermite's orthogonal functions in the case of the harmonic oscillator) for both the polar and the non-polar molecule. Such transitions are expected to take place in the Raman effect, exactly as the "forbidden" transitions in atoms, because of the fact that different vibrational states belonging to the same electronic level combine with other states with a change in the electronic configuration.

I have undertaken experiments on diatomic gases to test this consequence of the theory.

The gases were used at atmospheric pressure, and contained in a glass tube, about 4 cm. in diameter. A quartz mercury arc 12 cm. long was placed close to the tube, and a cylindrical aluminum reflector was used to concentrate as much light as possible. The light scattered by the gas was collected by a lens at the end of the tube and projected on the slit of a spectrograph.

Considerable care had to be taken to prevent any stray light from falling on the slit. Therefore the glass tube was cemented at one end of a wide iron tube, about one meter in length, accurately blackened on the inside, and provided with many diaphragms with circular holes, in such a way as to ensure a perfectly black background; several diaphragms had to be placed also between the lens and the illuminated part of the tube.

The spectrograph employed was very luminous, having a Tessar Zeiss 1:2.7 aperture lens for the camera. The length of the spectrum on the plate was 16 mm. from λ 3650 to λ 5460. An exposure from 48 to 60 hours proved necessary to obtain Raman lines from gases at atmospheric pressure.

The gases investigated were N_2 , O_2 and CO; all of them gave Raman lines, excited by λ 4047 or λ 4358 of mercury.

The wave-lengths were measured by comparison with a copper arc spectrum, a linear interpolation on a frequency scale between neighboring copper lines being accurate enough.

The error in the measurements, evaluated from the constancy of the shift for a given transition excited by the two intense mercury lines, was always of a few $cm.^{-1}$, so that the data given here may be considered as accurate within ten $cm.^{-1}$.

The results are reported in the following table:

	ν_R	λ_{Hg}	$\Delta\nu$	$\nu_{osc.}$
O_2	21384	4358	1553	1552
N_2	22374	4047	2330	2332
	20598	4358	2339	
CO	20781	4358	2156	2133
	22550	4047	2154	

The first column gives the frequencies of the observed Raman lines, the second, the mercury exciting lines, the third, the shift in $cm.^{-1}$, the last, the energy of the first excited vibrational state of the molecule (in the lowest electronic state), as given by R. T. Birge.⁴

The agreement is very good in the case of N_2 and O_2 , something less for CO; but the difference is not much larger than the error in the measurements, and can be easily accounted for by the structure of the bands due to rotational motion. With the dispersion available, the Raman line is not resolved, and its position depends on the relative intensities of the rotational components.

In the case of CO, the Raman line corresponds to the known infra-red band at 4.66μ .

The Raman line excited in O_2 by λ 4047 could not be observed, as it happened to fall very near the over-exposed line λ 4358 of mercury.

The harmonics of the fundamental frequency were not observed; probably their intensity is much smaller, and the exposure was just long

enough to bring out the Raman lines given above. Theoretically, they should be expected to occur.

All the observed facts can be accounted for by the quantum theory of dispersion, the fact that oscillation frequencies of molecules without an electric moment appear in the Raman effect being closely connected with the existence of electronic transitions. This appears very clearly if we consider how, when the frequency of the exciting light coincides with an absorption frequency, the Raman effect becomes the fluorescence observed, for instance, by R. W. Wood on iodine vapor.

Between the two phenomena exists the identical relationship as between the Rayleigh non-selective scattering of light by gases, and the resonance of mercury or sodium vapor.

¹ Ramdas, *Indian J. Phys.*, **3**, 1928.

² Kramers, H. A., and Heisenberg, W., *Z. S. Phys.*, **31**, 681, 1925.

³ Klein, O., *Z. S. Phys.*, **41**, 407, 1927; Dirac, P. A. M., *Proc. Roy. Soc.*, **114**, 710, 1927.

⁴ Birge, R. T., *Bull. Natl. Res. Council*, **11**, 132, 232, 1926.

ADIABATIC EXPANSION IN CASE OF VANISHING INCREMENTS. II.

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1. *Introductory Apparatus.*—The apparatus is the same as that used (figure 3a) in the preceding experiments and consists of an interferometer U-gauge, mm' , with one cell (v , capacity 80 cm.³) closed and in communication with a relatively capacious (555 cm.³) Dewar flask D . The other cell, v' , is open to the atmosphere and hence windy days are to be avoided. The half-inch clear way stopcock was used at C . It was opened and closed *suddenly*, by reversing the handle, and the number of such successive releases of the tension in the Dewar flask is given in the abscissas of the following diagrams (figures 1–3). Nearly ten of these, curiously enough, were admissible without fresh initial exhaustion or compression of the air content of the Dewar flask.

The degree of exhaustion is measured in terms of the parts s of an arbitrary scale of the ocular micrometer in the telescope of the U-gauge interferometer. One division of s corresponded to 48.1×10^{-6} cm. of difference of level of the mercury pools of the U-gauge and thus to about 6.3×10^{-7} of an atmosphere. The initial increment of pressure or ex-