

(The calculated ratio $D:C$ depends on the way in which the averaging is done; see, for example, Condon and van Amunge, *Phil. Mag.*, **3**, 604; 1927. However, the order of magnitude of this ratio always remains the same.)

Unfortunately, the failure of the experimental data on the heats of dissociation of twin molecules and Sutherland's constant makes it impossible to prove the correlation (2) in many examples. The values of D and C simultaneously are known only in the case of oxygen. Thus, in order to explain the fact that the oxygen does not obey Curie's law, Lewis (*Jour. Amer. Chem. Soc.*, **46**, 2027; 1924) assumed that in liquid oxygen as well as in oxygen gas, the molecules O_2 are associated to some extent into O_4 . Using data of Perrier and Kamerlingh Onnes for the magnetic susceptibility of oxygen at various temperatures, he estimated the molar heat of dissociation of O_4 into $2O_2$ to be about 128 cal. (for liquid oxygen). There are some grounds for regarding this value as approximately correct for the gas. The existence of molecules of O_4 has also been suggested by Wulf (*Jour. Amer. Chem. Soc.*, **50**, 2596; 1928; *Proc. Nat. Acad. Sci.*, **14**, 609; 1928), on the ground of optical data, concerning the absorption spectra of liquid and gaseous oxygen. The identity of absorption spectra due to molecules of O_4 in the liquid and the gaseous states shows that the action of oxygen molecules does not produce any appreciable change in the energy levels of the molecule O_4 . On account of this fact, we may suppose that the dissociation energy of O_4 cannot differ considerably in the liquid and gaseous states. For Sutherland's constant for oxygen, different authors give values varying from 127 to 138. These figures are very near to that obtained by Lewis for D . Further experiments will show whether it is a mere coincidence or not.

Experimental work on this problem is in progress in the laboratory of Prof. N. N. Semenov in this institute. In conclusion, we wish to extend our thanks to Prof. J. Frenkel for his kind advice.

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The 'Common Third Level' in the Raman Effect.

IN recent communications to NATURE, Langer and Dieke have pointed out that generally the shifts observed in the Raman spectra correspond not directly to the absorption frequencies of the scattering substance but to differences between its absorption frequencies, and that this is in accordance with the dispersion theory of Kramers, Heisenberg and Schrödinger. As a consequence of the quantum dispersion theory, the probability that we should observe a shift of Raman lines corresponding to the transition $E_i \rightarrow E_k$ is dependent on the probabilities of the transitions from $E_i \rightarrow E_n$ and from $E_k \rightarrow E_n$ where E_n is any third common level. The purpose of this note is to point out the significance of the common level from a physical point of view.

In the case of scattering of light by free electrons Pauli (further extended by Einstein and Ehrenfest) (*Zeits. für Phys.*, Band 18 and 19) showed that the probability of scattering of light of frequency ν' , when the incident light has the frequency ν , is $\alpha\rho\nu + \beta\rho\nu\rho'$. From the classical point of view, scattering is really made up of two processes taking place simultaneously, namely, (1) absorption, (2) re-emission. Hence, even in cases when the frequencies of the incident and scattered light are different—that is, the scattering is not classical—we should expect, from the general

ideas of correspondence between classical and quantum concepts, that the mechanism of the process should still be essentially the same as it will be in the limiting classical case. In all cases of scattering, two processes must always take place, (1) absorption and (2) emission. The probability of (1) from the point of view of Einstein is $B_{12}\rho\nu$, and of (2) $A_{21}' + B_{21}'\rho\nu'$, and hence the probability of scattering of ν' is $=\alpha\rho\nu + \beta\rho\nu\rho'$, where

$$\nu = E_2 - E_1, \nu' = E_2 - E_1'$$

These considerations can now be applied to the Raman effect.

Let us consider scattering from a molecule possessing only two levels E_i and E_k . When light of frequency ν is incident and is then scattered, the two processes which take place are:

- (1) Absorption—the molecule passes from $E_i \rightarrow E_k$,
- (2) Re-emission—the molecule passes from $E_k \rightarrow E_i$,

and thus, on the whole, the molecule neither takes nor gives anything to the incident quantum, and so the frequency of the scattered light remains ν . If a molecule has only two levels, it cannot give rise to combination (Raman) scattering.

If there be a third common level E_n , the molecule during the processes

- (1) may pass from $E_i \rightarrow E_n$,
- (2) may return from $E_n \rightarrow E_i$ or $E_n \rightarrow E_k$,

giving rise to the unmodified and the modified lines.

Combination scattering (Raman effect) is, therefore, entirely dependent upon the existence of a third level, and this view also enables us to calculate the intensity of the modified lines.

Kramers and Heisenberg in their original paper discussed the possibility of another allied effect which is theoretically as important as the Raman effect, but has not yet been observed. Generally ν_{ik} is much $\ll \nu$, but if $\nu_{ik} > \nu$, as we should expect only in electronic transitions, then when the molecules are illuminated by light of frequency ν , it should excite in the scattered radiation light of frequency ν and $\nu_{ik} - \nu$. A molecule in the excited state k , when subjected to the field of frequency ν , is forced to emit radiation ν . To do this the molecule should revert from the state ν_k to the normal state ν_i , and the balance of energy $\nu_{ki} - \nu$ will appear as another quantum. It can be easily seen that the experimental verification of this prediction will be much more difficult than that of the Raman effect, as we must have a sufficiently large number of molecules in the much largely energy-richer state ν_k .

We may be permitted to mention that the possibility of such an effect was discussed in the local Science Colloquium on Nov. 22, 1929, but we did not publish our views in the hope of gaining some experimental verification. The same view has been expressed by Göppert in a recent note in *Die Naturwissenschaft* (Nov. 29, 1929), but no experimental verification has yet been obtained.

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The Fallacious Determination of the Specific Heats of Gases by the Explosion Method.

THE recent gales suggest how fortunate a thing it is that the rate of motion of gas in an equilibration of pressure is not that of sound, which is of the order of 740 miles per hour. The phrase, common among students of gas-explosion phenomena, that 'pressure-equilibrium is attained at the speed of sound' has, indeed, on analysis, no meaning whatever; the rate at which gas moves over a point is a function of the pressure-gradient at that point.