

the caesium oxide on silver cell is to be used for measuring very small light intensities, the area of the cathode should not be any larger than is necessary to intercept the radiation; that is, the photoelectric emission should be made as large as possible relative

to the thermionic emission.

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A Case of Abnormal Molecular Rotation

In the fluorescence of mercury vapor with the addition of nitrogen and a trace of hydrogen, Gaviola and Wood¹ observed the band spectrum of the HgH molecule with an abnormal rotation corresponding to an apparent temperature of 3000°, although the gas was at room temperature. This observation has been interpreted² by the assumption of the following sequence of processes: formation of the HgH molecule, then excitation of this molecule with high oscillation and normal rotation according to the Franck-Condon rule, and finally change of oscillation into rotation during the life time of the excited state through collisions with N₂ molecules. In this interpretation, the high rotation observed in the band spectrum is therefore not directly excited but due to a secondary effect.

An interesting similar observation has recently been described by W. Lochte-Holtgreven.³ He found in the electric discharge in acetylene the C₂ bands with an abnormal rotational energy corresponding to 4700° and the CH bands with 2000°.

By varying the conditions, he found that these "rotational temperatures," being much larger than the real temperatures, are not due to secondary effects such as collisions during the life time of the excited state. Instead he concluded they must arise from the elementary process of excitation itself. Thus the interpretation must differ from that of the rotation of the HgH molecule just described. The present letter deals with this new observation, thus supplementing the interpretation of the HgH bands given in a previous paper.

It seems possible to understand the high rotation of the C₂ and CH bands in the acetylene discharge on the basis of the Franck-Condon rule dealing originally with oscillations. According to Hedfeld and Mecke, the HC≡CH molecule in its normal state forms a straight line.⁴ Let us assume that in its excited state it forms a crooked line. Professor Slater has pointed out to me that such a pro-

nounced change in the shape of the molecule is not all an arbitrary assumption, but should be expected, if in the excitation process the carbon atom goes over from the quadrivalent to the divalent state. The same change of valence by excitation has been found e.g. in the CN molecule.⁵ According to Slater's new theory,⁶ the straight line model of the normal state points to quadrivalent C atoms while the two valences of a divalent atom should always be at right angles, thereby forming a crooked molecule.

This pronounced change in the shape of the molecule lends itself to an application of Franck's idea. The change of electron configuration is fast compared with the motion of the nuclear masses. Immediately after the excitation process, the molecule in its new electronic state has still its old shape and therefore a large potential energy leading to intense vibration. Contrary to the vibration of the diatomic molecule, the motion is essentially transverse.⁷ This vibration might produce dissociation, if the potential energy exceeds the dissociation energy. Any dissociation process brought about by absorption of light can be recognized experimentally by the continuous absorption spectrum. In the case of the HCCH molecule, mainly continuous absorption has been observed as reported by

¹ E. Gaviola and R. W. Wood, *Phil. Mag.* **6**, 1191 (1928).

² H. Beutler and E. Rabinowitsch, *Zeits. f. physik. Chem. (B)* **8**, 403 (1930); O. Oldenberg, *Phys. Rev.* **37**, 194 (1931).

³ W. Lochte-Holtgreven, *Zeits. f. Physik* **67**, 590 (1931); G. B. Kistiakowsky, *Phys. Rev.* **37**, 276 (1931).

⁴ K. Hedfeld and R. Mecke, *Zeits. f. Physik* **64**, 151 (1930).

⁵ W. Heitler and G. Herzberg, *Zeits. f. Physik* **53**, 52 (1929).

⁶ J. C. Slater, *Phys. Rev.* **37**, 481 (1931).

⁷ Cf. R. Mecke, *Zeits. f. Physik* **64**, 173 (1930).

Lochte-Holtgreven and by Kistiakowsky. It might be assumed that this absorption corresponds partly to the described process.

This splitting up of the molecule by *transverse* vibration leads necessarily to strongly *rotating* molecules. (Fig. 1). The transverse vibration which splits up the centre bond of the $\text{HC}\equiv\text{CH}$ molecule leads to two CH molecules strongly rotating in opposite direction,

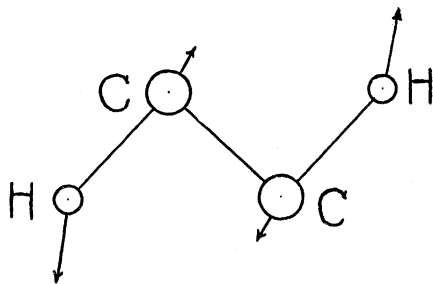


Fig. 1. Vibration of the excited HCCH molecule.

while the total moment of momentum of the system remains unchanged or changed only by unity. In the other dissociation process mentioned by Lochte-Holtgreven, the H atoms might fly away in the direction of the arrows (Fig. 1) leaving an excited C_2 molecule. This must have high rotation as indicated again by the arrows. Dissociation in steps might take place too.

In general any combination of increasing longitudinal and transverse vibration should lead to a dissociation resulting in a rotating and vibrating molecule, the energy of which is determined by the potential curves and not by the temperature of the gas. Thus we understand the observation reported by Lochte-Holtgreven, that the rotation of the excited molecules C_2 and CH is characteristic for this excitation process starting from $\text{HC}\equiv\text{CH}$ and that its energy shows some deviation from a Boltzmann distribution.⁸

Has this argument a bearing on the diatomic molecule? This might be the case, considering the diatomic molecule in collision with an atom. When by impact of the second kind the HgH molecule takes over excitation energy from the Hg' , it is generally assumed,

that the rotation of the HgH does not change considerably, but that the vibration might change on the basis of the Franck-Condon rule. It must be taken into account, however, that after the excitation process the H atom starts its fast vibration in the close neighbourhood of the colliding slow Hg atom. *In the same collision process*, therefore, this might turn over the motion of the H atom from *vibration* into *rotation*. No appreciable kinetic energy of *translation* is produced due to the heavy weights of the Hg atom and the HgH molecule. In other words, the H atom starts its motion in a modified field of force determined by the new electronic state of the HgH molecule and at the same time the presence of the colliding Hg atom. This motion might be rotation as well as vibration. (If in the case of good resonance the transfer of electronic energy by impact of the second kind takes place over an exceptionally large distance, this argument might fail, because in this case the HgH molecule would become excited without being disturbed in its vibration by the close neighbourhood of a colliding heavy body.)

The statement, therefore, that no appreciable rotation is produced by impact, holds for excitation by electron impact and for every thermal impact. However, it should not be supposed to hold for this type of impact of the second kind between heavy bodies.

This process in addition to the process discussed in the writer's recent paper² would be expected to play a part in Gaviola's and Wood fluorescence experiment.

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⁸ R. M. Badger and J. L. Binder (Phys. Rev. **37**, 800 (1931)). mention a certain difficulty in calculating dissociation energies of polyatomic molecules from band spectra, due to the fact the fragments might retain a considerable amount of energy in their *electronic* and *vibrational levels*. According to the present result, also the *rotation* is able to keep energy far exceeding the thermal value.

On the Effect of Resonance in the Exchange of Excitation Energy

I should like to add a few words to the letter recently sent to the Editor of the Physical Review, under the above title. The applica-

tion of the Franck-Condon principle to this problem brings out another point which supplements those already considered and which