

**A New Type of Absorption Spectrum: Double Rotational Quantification in Formaldehyde.**

THE quantification of the rotational motion of an asymmetrical molecule having three different moments of inertia,  $J_0, K_0, L_0$ , is a very difficult problem and has not yet been resolved mathematically. However, if two of the moments are equal,  $K_0 = L_0$ , the problem lends itself to solution, as has been shown by Sommerfeld, Born, Reiche, and others. The rotational energy of a molecule having an axial symmetry is equal to

$$W_{m,q} = \frac{h^2}{8\pi^2} \left[ \frac{q^2}{K_0} + m^2 \left( \frac{1}{J_0} - \frac{1}{K_0} \right) \right],$$

where  $m$  and  $q$  are quantum numbers.

The absorption lines corresponding to the different possibilities of rotational transitions of a molecule of this kind form a very complicated spectrum. This may be represented by the juxtaposition of two systems of parabolic branches:

$$\left. \begin{aligned} \text{I. } R(m) &= \nu_0 + (c_0 + c_1)m + c_2m^2, \\ &\quad \dots m - \frac{1}{2} \rightarrow m + \frac{1}{2} \\ P(m) &= \nu_0 - (c_0 + c_1)m + c_2m^2, \\ &\quad \dots m + \frac{1}{2} \rightarrow m - \frac{1}{2} \\ Q(m) &= \nu_0 + c_2m + c_2m^2, \\ &\quad \dots m + \frac{1}{2} \rightarrow m + \frac{1}{2} \end{aligned} \right\} q = \text{constant},$$

where

$$c_0 = \frac{h}{8\pi^2c} \left( \frac{1}{J_0} - \frac{1}{K_0} \right), \quad c_1 = \frac{h}{8\pi^2c} \left( \frac{1}{J_1} - \frac{1}{K_0} \right), \\ c_2 = c_1 - c_0, \quad c = 3 \times 10^{10} \text{ cm.}$$

$$\left. \begin{aligned} \text{II. } R(q) &= n_0 + (\sigma_0 + \sigma_1)q + \sigma_2q^2, \\ &\quad \dots q - \frac{1}{2} \rightarrow q + \frac{1}{2} \\ P(q) &= n_0 - (\sigma_0 + \sigma_1)q + \sigma_2q^2, \\ &\quad \dots q + \frac{1}{2} \rightarrow q - \frac{1}{2} \\ Q(q) &= n_0 + \sigma_2q + \sigma_2q^2, \\ &\quad \dots q + \frac{1}{2} \rightarrow q + \frac{1}{2} \end{aligned} \right\} m = \text{constant},$$

where

$$\sigma_0 = \frac{h}{8\pi^2c} \cdot \frac{1}{K_0}, \quad \sigma_1 = \frac{h}{8\pi^2c} \cdot \frac{1}{K_1}, \quad \sigma_2 = \sigma_1 - \sigma_0.$$

Hitherto, no one has reported an absorption spectrum of this kind, and it is not known if there may exist a double quantification of the rotation of molecules.

We have found that the ultra-violet absorption spectrum of formaldehyde vapour,



sponds exactly to this type of rotational spectrum, with two quantifications.

The absorption spectrum consists of 32 bands situated between 3550 and 2500 Å.U. Each of these bands is formed by hundreds of fine lines. These lines are of two types: type *a* consists of the more intense lines distributed through the whole band. The other type, *b*, consists of a great number of very fine, closely grouped lines forming regular series with accumulations near each line of type *a*.

The molecule of formaldehyde has, to a first approximation, an axial symmetry about the axis passing through the carbon and oxygen atoms. The moment of inertia,  $J_0$ , about this axis is expressed by  $J_0 = 2 \cdot \nu_0^2 \cdot m$ , where  $2\nu_0$  is the distance between the two hydrogen atoms, and  $m = 1.66 \times 10^{-24}$  gm. The other two moments,  $K_0$  and  $L_0$ , have very nearly the same value. This value depends upon the distance between the carbon and oxygen atoms, and upon

the angle,  $2a$ , between the bonds of the hydrogen atoms to the carbon atom, so that  $K_0 \gg J_0$ .

The physical interpretation of the spectrum is that the stronger lines (type *a*) are produced by rotation about the axis of symmetry, with the smaller moment  $J_0$ . The closely grouped fine lines (type *b*) correspond to the rotations about a perpendicular axis with the moment  $K_0$ .

The analysis of the distribution of the lines in the different bands has given a very satisfactory confirmation of this interpretation. We have found, for example, for the band *B* ( $\lambda = 3418$  to  $3378$ ) that the stronger lines form a doublet system of three parabolic branches each, the null-lines being  $\nu_0 = 29465.1$ ,  $\nu'_0 = 29422.0$ ,  $\lambda_0 = 3393.85$ ,  $\lambda'_0 = 3398.82$  Å.U. intern. vac., and the formulae of the parabolas

$$\begin{aligned} R(m) &= 29465.1 + 35m - 2m^2, \\ P(m) &= 29465.1 - 35m - 2m^2, \\ Q(m) &= 29465.1 - 2m - 2m^2, \\ R'(m) &= 29422.0 + 35.5m - 1.5m^2, \\ P'(m) &= 29422.0 - 35.5m - 1.5m^2, \\ Q'(m) &= 29422.0 - 1.5m - 1.5m^2, \end{aligned}$$

where  $m = 1, 2, \dots, 8$ . The correspondence between the calculated and the observed values is very good

( $\Delta \frac{1}{\lambda}$  calculated - observed  $< 1.0 \text{ cm.}^{-1}$ ). The distribution of the intensities is also quite regular and conforms to the theoretical one.

We deduce from these formulae the following values for the constants:

$$c_0 = 18.5, \quad c_1 = 16.5, \quad c'_1 = 17.0,$$

and therefore

$$\frac{1}{J_0} - \frac{1}{K_0} = 0.67 \times 10^{-40}, \quad \frac{1}{J_1} - \frac{1}{K_0} = 0.60 \times 10^{-40}, \\ \frac{1}{J_1} - \frac{1}{K_0} = 0.62 \times 10^{-40}.$$

A series of lines of type *b*, distributed in parabolic branches  $R(q)$  and  $P(q)$ , correspond to each line of these six parabolic branches. The value of  $\sigma_0 + \sigma_1$  is  $2.4 \text{ cm.}^{-1}$  with a precision of  $\pm 0.4 \text{ cm.}^{-1}$ .

We have, therefore,  $\frac{1}{K_0} = 0.04 \times 10^{-40}$ .

The two moments of inertia of the normal molecule of formaldehyde are  $J_0 = 1.41 \times 10^{-40}$  and  $K_0 = 25 \times 10^{-40}$ . Therefore, the distance between the hydrogen atoms is  $2\nu_0 = 1.30 \times 10^{-8} \text{ cm.}$ , and between the carbon and oxygen  $1.0 \pm 0.1$  Å.U. In the molecule of water the distance between the hydrogen atoms is  $1.64$  Å.U., and in the carbon dioxide molecule the distance between the carbon and oxygen atom  $1.02$  Å.U.

For the activated molecule we find two values of the moments of inertia:  $J_1 = 1.56 \times 10^{-40}$  and  $J'_1 = 1.51 \times 10^{-40}$ . The branches  $R, P, Q$  correspond to the transitions from the normal energy level to the state with the moment  $J_1$ , and the branches  $R', P', Q'$  to the transitions from the same normal state to the energy level with the moment  $J'_1$ . The distance between the hydrogen atoms is increased by the activation from  $1.30$  to  $1.37$  Å.U.

This general structure of a rotational spectrum with two simultaneous quantifications has been observed by us for several other molecules belonging to the type of 'Y-molecules'; for example, phosgene and thiophosgene. Together with Prof. J. Errera, we have found the same type of absorption spectra for different para-derivatives of benzene.

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