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ABSORPTION SPECTRA OF POLYATOMIC MOLECULES.

Predissociation and Dissociation of these Molecules.

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The study of the absorption spectrum is much more complicated in the case of polyatomic molecules than in that of diatomic; it is in fact not possible to give a complete analysis of the electronic configurations for a molecule formed by more than two atoms. Any state would be represented by about one hundred or more letters.

For the vibration spectra also, the complete solution of the problem is complicated by the mutual influence of different vibrations. But, in this case, we can now obtain for several spectra an approximate representation of the vibration spectra.

Generally, we may observe that, for complicated molecules like benzene and derivatives, the vibrations are very nearly harmonics; the correction for non-harmonicity is very small.

The formula of the vibration spectrum can be represented at a first approximation by the formula :

$$\nu = \nu_0 + p'\alpha'(1 - x'p') + q'\beta'(1 - y'q') + r'\gamma'(1 - z' \cdot r') + \dots + p_0\alpha_0(1 - x_0p_0) - q_0\beta_0(1 - \gamma_0q_0) - r_0\gamma_0(1 - z_0r_0) - \dots$$

In this formula α' , α_0 , β' , β_0 , γ' , γ_0 , ... are the different vibration frequencies in the activated and normal molecule, and p', p_0 , q', q_0 , r', r_0 ... are the corresponding vibration quantum numbers.

By studying the absorption spectrum of a great number of different molecules (more than 40), we have found that there is a common feature in the structure of the spectrum, which in every case appears on the ultra-violet side of the spectrum. Those bands which for lower frequencies have a fine structure with quite definite edges and sometimes a well-developed rotation spectrum, become for higher frequencies broad, diffuse; the edges are not very sharp and there are no more rotation lines.

As an example, there is given in Fig. 1 the absorption spectrum in the far ultra-violet of NO₂ vapour; the photographic reproduction shows first, two vibration bands $\lambda = 2491$ and 2459 with many very fine rotation lines, which correspond to a double rotation of this triangular molecule, that we have studied with Louis Harris. There are similar bands with fine structure towards the visible corresponding to different vibration states of the molecule. But the next bands towards the ultra-violet

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side change abruptly in their structure; this is quite visible for the bands 2447 and 2425, and there are about ten bands of this sort in the far ultra-violet.

The upper microphotometric registration shows very clearly the abrupt change in the structure of the bands.

The bands are diffuse, without any fine structure; the quantisation of the rotation movements of the molecule has disappeared totally, but the vibrations are quantised: the bands are distributed at nearly regular intervals.

A second example is that of sulphur vapour, S_2 , given in Figs. 2 and 3. The vapour was at the temperature of 600° C. One-tenth of milligram of sulphur is enclosed in a quartz tube of volume 16 c.c. and length 10 cm. In this condition, the vapour consists practically of S_2 molecules. There is a series of about 20 vibration bands with a period of 397 cm.⁻¹ in the first part and of 365 to 350 cm.⁻¹ in the second ultra-violet part. These bands are formed by a large number of fine rotation lines (Fig. 3 to the left).

But exactly at the limit 2792 Å., all fine structure disappears suddenly and the bands are then diffuse with only vibration bands without any rotation line.

The photomicrograph of Fig. 3 shows this abrupt change in the absorption spectrum. There are two curves corresponding to two different points of the same spectrum; and the third lowest curve corresponds to the iron spark.

In Fig. 2, the absorption spectrum is given with less enlargement, so that one can see twelve successive vibration bands, as well as the two limits of predissociation. The same result is obtained for many other substances.

The physical signification of this modification in the absorption spectrum of any substance in vapour state could be analysed by different investigations.

We found following the general results for the properties of the molecule in the region of broad diffuse bands :---

(I) The vibration frequency in this region decreases, indicating an increase in the distance between the vibrating masses—the molecule becomes *labile*.

(2) The fluorescence excited by the light in the region of the diffuse bands is very feeble, or, indeed, entirely absent.

(3) The molecule becomes chemically active in this region of spectrum.

(4) The limit of the production of diffuse bands is displaced towards the red by raising of the temperature. This displacement is larger for substances with high molecular specific heat, than for those with low specific heat.

These results indicate a new state of the molecule, which is preparatory to the dissociation and we called it the "*predissociation of the mole*cule."¹

We are able to study this special chemical activity of the molecules in the region of diffuse bands by two examples. These are the photochemical decomposition by monochromatic light of benzaldehyde vapour, in which case we obtain quantitatively benzene and carbon monoxide :

 $C_6H_5COH \rightarrow C_6H_6 + CO$,





FIG. 3.—S₂ vap. (1) Predissociation. $t = 600^{\circ}$. [To face page 766.





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and the photochemical dissociation of acetaldehyde:

$$CH_3COH \rightarrow CH_4 + CO.$$

The first reaction was studied in my laboratory by M. de Hemptinne, and the second by James H. C. Smith. It was found that, in both cases, only light corresponding to the region of diffuse bands produces the dissociation of the molecule. The light from regions where the absorption bands have a fine structure has no action on these molecules.

But, when the vapour of benzaldehyde or acetaldehyde is heated to 200° C., the absorption spectrum changes. Thus, for benzaldehyde, the diffuse bands appear for $\lambda = 2750$ Å. at 200°, and only at 2550 Å. for 20°, and for acetaldehyde, the diffuse bands appear at 3200 Å. at 200°, and at 3050 Å. at room temperature. At the temperature of 200°, the photochemical dissociation is produced for benzaldehyde by rays of $\lambda = 2750$ and for acetaldehyde of $\lambda = 3200$ instead of $\lambda = 2550$ and 3000 at the temperature of 20°.

There is an exact parallelism between the structure of the absorption spectrum and the chemical activity of the molecules.

This change of the absorption spectrum with increase of temperature is a general result, which I studied especially with MM. de Hemptine and Almasy.

We give in Figs. 4, 5, 6, and 7 examples for the absorption spectrum of benzene vapour at different temperatures.

Fig. 4 corresponds to C_6H_6 at p = 5 mm., the tube length being 30 cm. The quartz tube was sealed and the absorption spectrum photographed at $t = 18^\circ$, then 325° , then 18° .

In Fig. 5 are given the absorption spectra at 18° and 325° with greater enlargement.

In Fig. 6 are three spectra at 19°, 188° and 332°.

And in Fig. 7 are photomicrographs of the absorption spectra given on Fig. 6.

We see, for example, in Fig. 6 that the temperature produces a change in the absorption spectrum. The bands are broadened and become diffuse. This influence of temperature begins on the ultra-violet side and progresses more and more towards the red by increase of temperature.

We see that the heating of any substance produces a predissociation of the molecules; we call this effect "*thermal predissociation*". There is an exact addition of thermal energy and light energy.

This result shows that increase of temperature has an effect on the stability of the molecule; the vibrations of the atoms are enhanced and the distances are increased. It gives an analysis of the influence of temperature on the velocity of chemical reactions.

We can directly see by studying the absorption spectrum that the temperature effect consists not only in the enhancement of the kinetic energy of the molecules, but also in the modification of the internal energy, which is followed by alteration in the internal structure of the molecules, the distances between different atoms being increased.

This temperature influence is especially high for molecules with great molecular specific heat, where we have a large number of degrees of free dom. It is, moreover, possible by the displacement of the predissociation limit corresponding to an elevation of 100° or 200° , to calculate the value of the molecular specific heat of the substance.