

- (iii) The reversal of the zinc arc line at 2138 Å. As explained in Experiment II a reversed line appears when there is absorption by cold metallic vapour surrounding the arc.
- (iv) The reversal of the magnesium line 2853 Å. in the flame and arc.
- (v) The continuous emission in the magnesium flame from incandescent solid particles.

A Course in Chemical Spectroscopy

H. W. Thompson, Oxford Press 1938

EXPERIMENT IV

THE GENERAL FEATURES OF AN ELECTRONIC- BANDED MOLECULAR SPECTRUM

Theory. It is simplest in considering the spectra of molecules to confine attention in the first place to diatomic systems which are to a first approximation like elastic dumb-bells. Whereas an atom can take up energy of one kind only—electronic energy—a molecule can absorb energy of three kinds: electronic energy, vibrational energy of the nuclei, and rotational energy of the molecule as a whole. Thus, in theory at least, any single electronic transition might be accompanied by simultaneous changes in vibrational energy or rotational energy or both. In practice, various circumstances and limitations of the changes in energy of the different types diminish the observed number of transitions involving a change in energy of the three kinds. The structure of the molecular spectrum is, nevertheless, in general very complex.

As a rule it is found that

$$E_{el} \gg E_{vib} \gg E_{rot}$$

that is,

$$v_{el} \gg v_{vib} \gg v_{rot}.$$

The energy levels of a molecule are then built up qualitatively as shown in Diagram 9.

For a transition, we have,†

$$\nu = (v'_{el} - v''_{el}) + (v'_{vib} - v''_{vib}) + (v'_{rot} - v''_{rot}).$$

For a diatomic perfect harmonic oscillator in the older quantum theory, $E_{vib} = \nu_{00} / \omega_0$ being the fundamental vibration frequency and ν an integer, the vibrational quantum number. In the new quantum theory

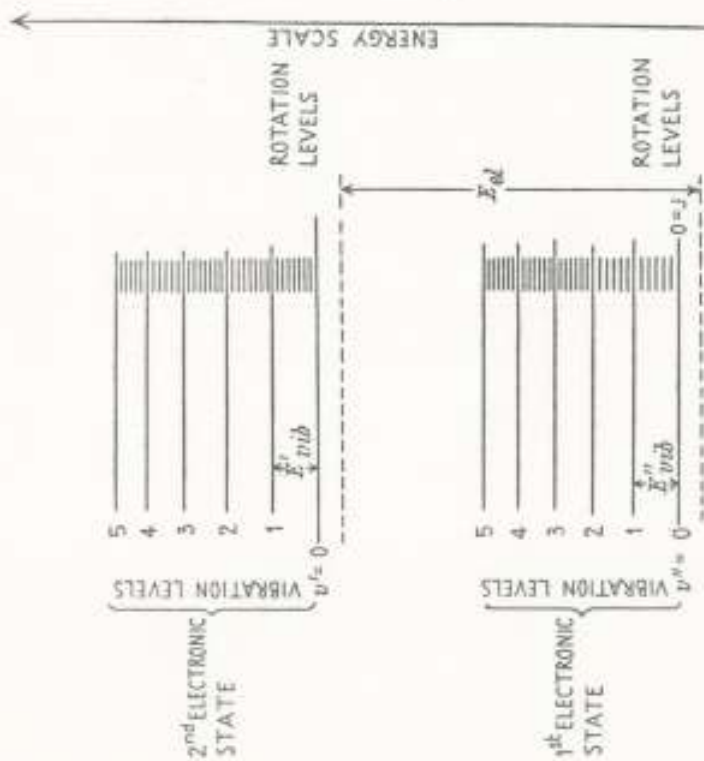
$$E_{vib} = (v + \frac{1}{2})\omega_0.$$

† The conventions taken here and subsequently for the indices are 'for the upper state', and 'for the lower'.

(so as to include the zero point energy). Actually, however, the anharmonicity of a real molecule makes it necessary to introduce at least one correction term, so that

$$E_{vib} = (v + \frac{1}{2})\omega_0 - (v + \frac{1}{2})^2 x_0 \omega_0 + \dots$$

and the terms after the second are generally negligible. The



energy of rotation of the dumb-bell is given by the new quantum theory by $E_{rot} = J(J+1)\hbar^2/(8\pi^2I) = J(J+1)B$. Owing to slight stretching under centrifugal force, it is sometimes necessary to add a small correction term, so that

$$E_{rot} = J(J+1)B + J^2(J+1)^2D,$$

but D is as a rule very small compared with B . A group of emitted or absorbed lines associated with the same change

in electronic and vibrational energy and differing only in the rotational energy change involved in the transition is called a **BAND**. Such a group is as a rule distinguished by a concentration of lines at one side—the 'head'. This somewhat clarifies the overall appearance of the spectrum, and helps in separating the different bands.

The detailed structure of individual rotation bands will be considered in Experiment V.

A group of bands associated with the same electronic energy change but with different vibrational energy changes is called a **BAND SYSTEM**. The set of two or more such systems is called a **BAND SPECTRUM**. A single molecule may give rise to many band systems, which may in addition overlap each other, leading to a very complex spectrum.

The arrangement of band origins (or for our present purpose the heads) in a given band system should be more closely examined. The fundamental vibrational frequencies in the two electronic states will not in general be the same. Despite this, a transition from $v' = 0$ (upper state) to $v'' = 0$ (lower state) will involve an energy change very close to that involved in the changes $v' = 1$ to $v'' = 1$, or $v' = 2$ to $v'' = 2$. The groups of bands with equal values of Δv are called **sequences**. A succession of bands with v' or v'' the same and v'' or v' changing steadily by unity is called a **progression**. Thus $v' = 0 \rightarrow v'' = 0, 1, 2, \dots$ is called a $v' = 0$ progression. Then, disregarding rotational energy changes,

$$E'_{vib} = (v' + \frac{1}{2})\omega'_0 - (v' + \frac{1}{2})^2 x'_0 \omega'_0$$

$$E''_{vib} = (v'' + \frac{1}{2})\omega''_0 - (v'' + \frac{1}{2})^2 x''_0 \omega''_0,$$

and for a sequence in which, say, $(v' - v'') = -1$,

$$\begin{aligned} \Delta E_{vib} &= (v'' - \frac{1}{2})\omega''_0 - x''_0 \omega''_0 (v'' - \frac{1}{2})^2 - (v'' + \frac{1}{2})\omega'_0 + (v'' + \frac{1}{2})^2 x'_0 \omega'_0 \\ &= v''(\omega''_0 - \omega'_0) - \frac{1}{2}(\omega''_0 + \omega'_0) - (v'' - \frac{1}{2})^2(x''_0 \omega''_0 - x'_0 \omega'_0) + \\ &\quad + 2v'' x'_0 \omega'_0. \end{aligned}$$

Thus the difference in the frequencies of the band origins arises both from the difference in the fundamental frequency

in the two electronic states, and also from the difference in their respective anharmonicity factors.

For a progression in which there is only a change in the vibrational quantum number of one of the electronic states,

$$\begin{aligned}\Delta E_{v_1 v_2} &= (v_1 + \frac{1}{2})\omega_0 - (v_1 + \frac{1}{2})^2 x_0 \omega_0 - (v_2 + \frac{1}{2})\omega_0 + (v_2 + \frac{1}{2})^2 x_0 \omega_0 \\ &= (v_1 - v_2)\{\omega_0 - x_0 \omega_0 (v_1 + v_2 + 1)\}\end{aligned}$$

in which $(v_1 - v_2) = 0, 1, 2, 3, \dots$

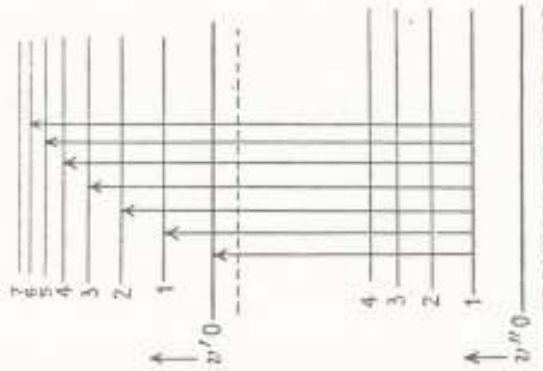


DIAGRAM 10.

Thus if $x_0 \omega_0$ were zero, i.e. harmonic vibrations, the progression would consist of equidistant bands. Actually, $x_0 \omega_0$ is finite and if we are dealing with a v'' progression the band origins (and for our purposes the heads) converge steadily towards higher frequencies as $(v_1 - v_2)$ increases. (Diagram 10.) For a v' progression the convergence will clearly be towards lower frequencies, with decreasing $(v_1 - v_2)$.

Apparatus. It is convenient to photograph some of the common band systems of nitrogen and carbon monoxide when a discharge is passed through air or carbon dioxide at

low pressure. The discharge tube, which must be fitted with a quartz window (fitted with sealing-wax or cement) can be of the simple form shown in Diagram 11. The carbon dioxide can be stored in a holder or glass bottle fitted with a tap, and connectable to the discharge tube with rubber pressure tubing. Air will be used to obtain the nitrogen bands. An

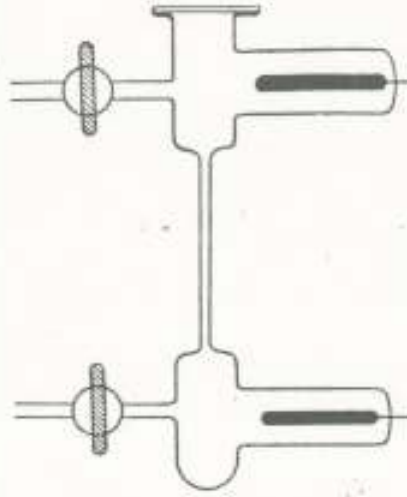


DIAGRAM 11.

induction coil or small transformer, and small oil pump are also required. The most suitable spectrograph is a quartz instrument such as those described for use in Experiments II and III, using a panchromatic plate or film.

Method. Photographs should be taken on the same plate of the following:†

- (i) The iron arc.
- (ii) The spectrum emitted when the discharge is passed through air at a pressure of a few mm.; the glow should be reddish purple.
- (iii) The spectrum emitted when the discharge is passed through about 1 mm., or less, of carbon dioxide; the bands are those of carbon monoxide. The tube should be washed out several times with carbon dioxide, and

† If desired the bands of CH and C₂ may be seen in the methane discharge.

evacuated. The washing-out process should be repeated at intervals, the slit of the spectroscope being covered during the process. The glow should be bluish green or livid.

The exposures required will depend naturally on the intensity of the source and the instrument used, but are generally of the order of 10 minutes with a small discharge tube and the Hilger E 315 instrument.

Typical photographs are shown.

The following main features of the photographs should be noticed:

(a) In the air spectrum there are two distinct systems of bands due to nitrogen, the 'First Positive' system in the yellow and red, i.e. 5000 Å. to longer wave-lengths, and the 'Second Positive' system from 5400-2700 Å. With the low dispersion of the quartz instrument in the visible, the structure of the First Positive system is seen hardly at all.

In the air spectrum there are also prominently to be seen the 'γ' bands of nitric oxide in the far ultra-violet; and other less intense systems due to either nitrogen or nitric oxide may be seen.†

(b) In the spectrum of carbon monoxide (upon which traces of the above spectra may well appear if the tube has not been adequately washed out) the Ångström bands in the blue, green, and red, from 4000-6000 Å., as well as other systems in the ultra-violet, especially the Fourth Positive system from 2800 Å. to shorter wave-lengths.

In a previous experiment the general principles which are followed in analysing a line spectrum were briefly outlined. It may be profitable, here too, to refer to the corresponding methods in the case of a molecular spectrum which has been photographed but about which little is known. The analysis can perhaps be best separated into the following stages: (i) the discovery of the molecule responsible for the spectrum;

† See Jevons, *Band Spectra of Diatomic Molecules*.

(ii) the separation of the band spectrum into band systems, if more than one system is present; (iii) the analysis of the bands of a system into sequences and progressions, the assignment of the appropriate vibrational quantum numbers involved, and the determination of the system origin, and (iv) the analysis of the rotational structure of individual bands. If an accurate and self-consistent analysis of all these matters can be made, all the molecular data involved will follow.

(i) The experimental conditions and methods of production of a given emission or absorption spectrum will naturally in itself suggest the molecule which is probably involved. This is not, however, always obvious, as experience has shown.† Small amounts of impurities may sometimes prove serious in this respect. Further, in the case of simple diatomic molecules it may not be immediately obvious whether the neutral or ionized molecule is involved. These empirical methods are, on the other hand, supplemented by the more recent theoretical considerations based on the interpretation of spectra in terms of quantum theory, which may at least indicate that the spectrum cannot arise from some of the molecules which might be experimentally plausible.

(ii) Transitions from one electron level of a given molecule to a series of other electron levels will lead to a series of band systems. These systems may, or may not, overlap each other. In the latter case their separation becomes more difficult, but usually the appearance of the bands of the different systems is sufficiently different to suggest a tentative classification of the main bands of each system. Moreover, the different band systems may not always be excited to the same degree under different experimental conditions. Application of the quantum theoretical interpretations again may carry the analysis further. The study of the rotational fine structure of the bands is also very helpful, since there

† Jevons, *op. cit.*, pp. 4-6; Finckelburg, *Hand. and Jahrb. Chem. Physik*, 9, ii, 200.

will be interval relationships in the rotational structure which remain constant throughout a band system, but differ in different band systems.

(iii) The determination of the system origin and the assignment of different bands to specific $v' \rightarrow v''$ transitions is more difficult. To some extent it is empirical, and ascertained after various trial and error assignments have been examined from the point of view of the quantum theoretical interpretation of the spectrum as a whole. There are, however, some definite systematic rules for testing the various tentative assignments. These have been fully discussed by Jevons.[†] One valuable guide in many cases is the effect of temperature upon the spectrum, especially if an absorption spectrum is involved, since the temperature will determine the distribution of molecules among the vibration levels, and hence to some extent the observed intensity distribution among the bands.

(iv) The analysis of the rotational fine structure of an individual band will be studied in Experiment V.

Problem. By reference to the known data, analyse the main central part of the Second Positive system of nitrogen into sequences and progressions. The method of exhibiting the analysis is seen in Diagram 12, placed alongside the plate of this system.

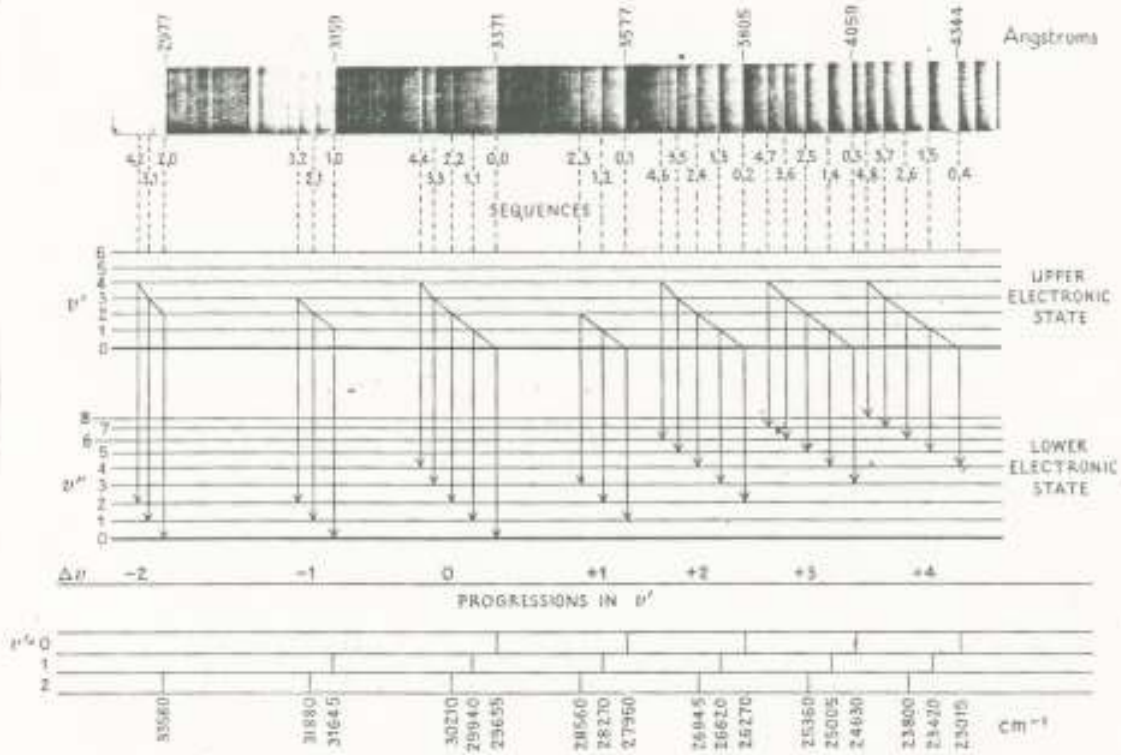
The relative intensities of the bands in this system are known to be given roughly by the figures in the following table:[‡]



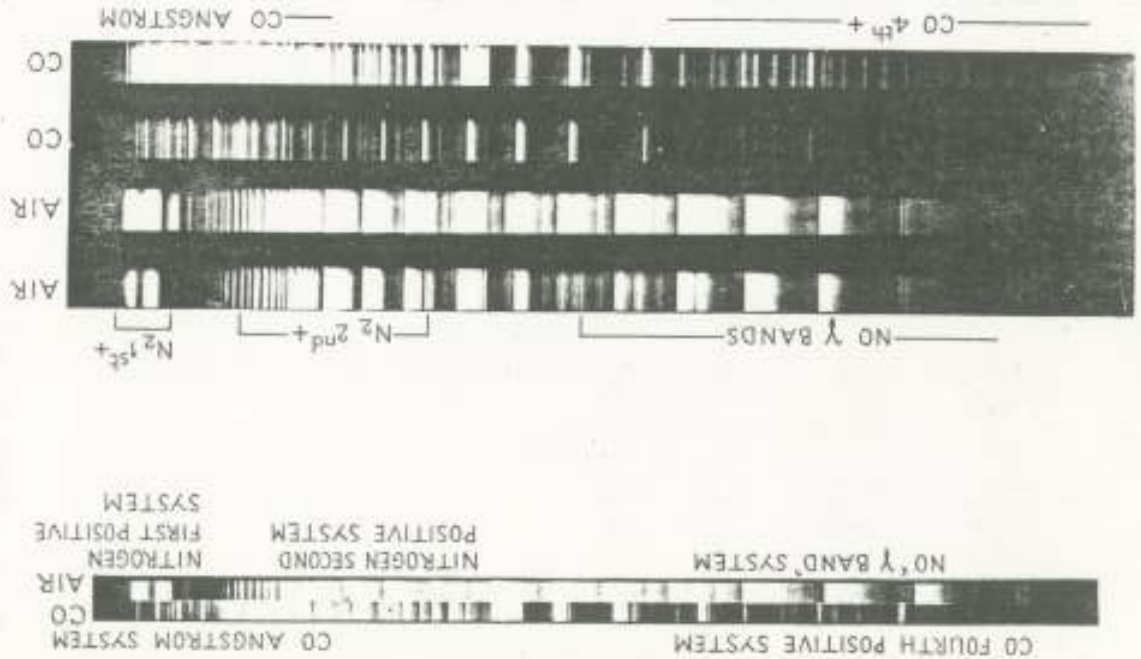
Assuming the sensitivity of the plate used to be uniform over the range involved, notice that the relative intensities

[†] Jevons, *op. cit.*, p. 60.

[‡] Rudy, *Bandenspektren*, p. 99.



Sequences and Progressions in the Second Positive System of Nitrogen



The Band Spectra of Molecules

of the bands follow the tabled figures. It will be seen that of the transitions from any given v' level, two (or perhaps three) are in general more favoured than the rest. Thus for a $v' = 1$ progression the strongest transitions are from $v'' = 1$ to $v'' = 0$ or 3. This result, taken together with the Franck Principle that the electronic transition occurs so rapidly as to leave the nuclear separation unaltered,† is very significant in deducing information about the potential energy curves of the two electronic states.

The meaning of this may be illustrated by two simple examples. First, however, it is necessary to be clear about what is meant by the potential energy curve of a molecule. When two atoms approach each other from infinity there is a repulsion between the nuclei which leads to an increase of the potential energy of the system. In Diagram 13 this is represented by some such curve as (i). Two other effects may simultaneously occur during this approach, arising from the interactions of the electronic configurations of the respective atoms. If there is a 'sympathetic fluctuation of the electron space clouds' there will be a tendency for union and bond formation leading to a decrease in potential energy represented by curve (ii). If the 'fluctuation' is not 'sympathetic', there will be a tendency for repulsion, represented by curve (iii). When each of the two curves (ii) and (iii) is in turn superposed upon the curve representing nuclear repulsion, the two curves *A* and *B* are obtained. *A* has a minimum and describes the potential energy curve of a stable molecule formed by the two atoms; *B* represents the potential energy curve of a physically unrealizable molecule, but while the molecule has no reality the curve has a very considerable significance, since any point on it represents an unstable configuration of the two nuclei involved.

If the molecule were an ideal simple harmonic oscillator

† The period of a nuclear vibration will be generally much less than the time for electronic excitation.

obeying Hooke's law, curve *A* would be a simple parabola. Actually, curve *A* describes the relationships for a 'real' molecule from its stable position to the state of dissociation. There will be a curve of type *A* for every separate electronic

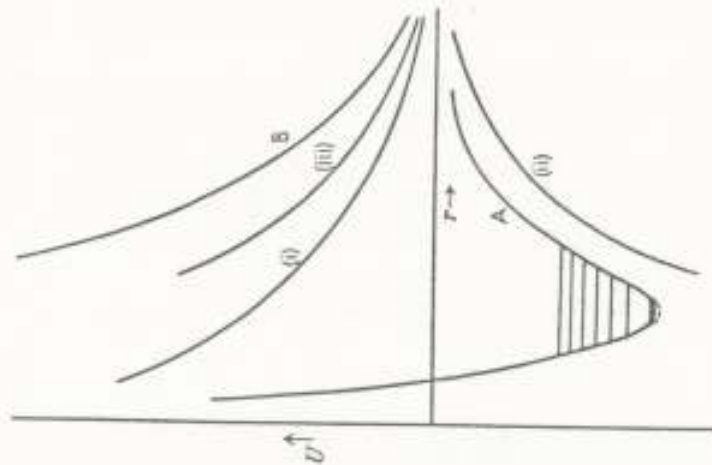
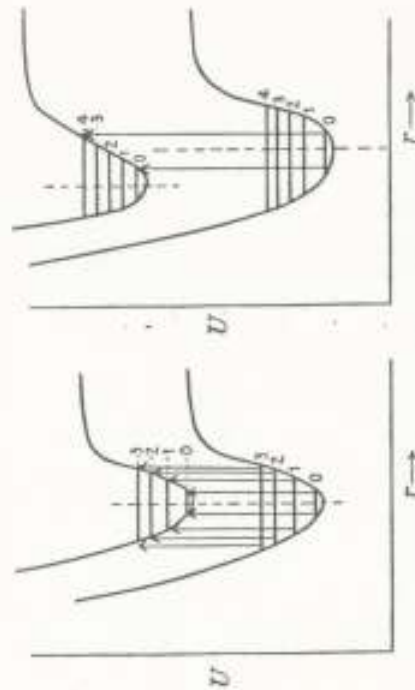


DIAGRAM 13.

state of the molecule with minima at values of the energy corresponding to the several electronic levels. The vibrational levels of the stable molecule are represented as horizontal lines, and the amplitudes in the various levels are given by the distances between the points of intersection of the lines with the curve.

In Diagram 14*a* it is supposed that there is no change in nuclear binding on electronic excitation, i.e. that the nuclear

separation remains unchanged. Further, let us suppose that the molecule is in the lower electronic state *A* and that the temperature is such that the lowest vibrational levels are the most populated. Now in the molecular vibration the nuclei are moving most slowly at the extremities of their vibrations, and therefore in considering an absorption of energy we shall

DIAGRAM 14*a* and *b*.

expect it to occur most frequently from configurations corresponding to these extremities. If this occurs, then according to the Franck Principle the nuclei will still have the same separation when the upper electronic state is reached, and this configuration will correspond to an extremity of a vibration in the upper state since the molecule will tend to its equilibrium configuration. In case 14*a* this means that absorption from the $v'' = 0$ level will lead primarily to the $v' = 0$ level, and this applies for absorption from either extremity of the vibration in the lower state. Similarly, absorption from the $v'' = 1$ level will lead primarily to the $v' = 1$ level, but since the population of the $v'' = 1$ level is less than that of the $v'' = 0$ level, the $v'' = 1 \rightarrow v' = 1$ band will appear weaker than the $v'' = 0 \rightarrow v' = 0$ band.

If, on the other hand, the potential energy curves are as in

Diagram 14*b* the strongest bands in absorption will be $v'' = 0$ to $v' = 0$ and $v'' = 0$ to $v' = 4$. The case of nitrogen examined experimentally above falls between the two extremes of 14*a* and 14*b*, and the intensity distribution in this case indicates that there is little change in nuclear binding on electronic excitation. This will, as a matter of fact, also be revealed by a study of the rotational structure of the individual bands.

The above elementary account of the significance of the Franck Principle has been regarded from a 'classical' standpoint. A consideration of the whole matter in terms of the new quantum theory, which enables a more accurate treatment of the various transition probabilities, leads to more detailed agreement between theory and experiment. This has been examined by Condon, and the principle enunciated above is now termed the Franck-Condon Principle. The considerable significance of this principle will become clear in later experiments.

EXPERIMENT V

THE ROTATIONAL STRUCTURE OF A BAND IN A MOLECULAR SPECTRUM

Theory. This experiment is designed to illustrate the details of the rotational structure of a band, which arises from a series of transitions in which the changes in electronic and vibrational energy are the same, but the change in rotational energy is different from one line to the next. The frequencies of the lines in such a band will be given by

$$\nu = \nu_{el} + \nu_{vib} + (\nu'_{rot} - \nu''_{rot}),$$

where ν_{el} is the change in electronic energy in the transition, ν_{vib} is the change in vibrational energy in the transition, and ν'_{rot} is the energy of rotation in the upper state,

and ν''_{rot} is the energy of rotation in the lower state.

Let $\nu_{el} + \nu_{vib} = \nu_0$.

Now, according to classical mechanics, the energy of rotation of a model with moment of inertia I and angular velocity ω is $\frac{1}{2}I\omega^2$. According to the older quantum theory, the angular momentum $I\omega = Jh/2\pi$, J being the rotational quantum number. Then,

$$E_{rot} = \frac{1}{2}I\omega^2 = \frac{h^2}{8\pi^2I}J^2,$$

or in wave number units

$$\nu_{rot} = \frac{h}{8\pi^2I}J^2.$$

This expression becomes modified by the new quantum theory, which gives angular momentum = $\sqrt{J(J+1)}h/2\pi$, and we have

$$\nu_{rot} = \frac{h}{8\pi^2I}J(J+1) = BJ(J+1).$$

Actually, owing to the slight stretching under centrifugal force, we should write

$$\nu_{\text{rot}} = B'J(J+1) + DJ^2(J+1)^2,$$

but D is as a rule very small compared with B .

Then for transitions from $J = J'$ to $J = J''$ the frequency is given by

$$\nu = \nu_0 + B'J'(J'+1) - B''J''(J''+1).$$

B' and B'' will differ, since the moments of inertia in the two states will not be the same by virtue of the change in binding and internuclear separation.

Three types of rotational energy change will be possible:

$$J \rightarrow J+1$$

$$J \rightarrow J$$

$$J \rightarrow J-1.$$

A selection rule limits the change in J to 0 or ± 1 .

If $J' = J'' + 1$ we speak of the Positive or R branch; if $J' = J'' - 1$ we have the Negative or P branch, and if $J' = J''$ we have the Zero or Q branch.

For the positive branch we have

$$\nu = \nu_0 + B'J'(J'+1) - B''(J'-1)J',$$

and in this expression J' will have possible values $+1, +2, +3, \dots$ since J'' starts at 0. This gives for the lines of the branch

$$\nu = \nu_0 + (B' + B'')J' + (B' - B'')J'^2,$$

in which

$$J' = +1, +2, +3, \dots$$

For the negative branch, we have, similarly,

$$\nu = \nu_0 - (B' + B'')J'' + (B' - B'')J''^2,$$

in which $J'' = +1, +2, +3, \dots$ since $J' = 0 \rightarrow J'' = -1$ is not possible. It is thus seen that the R and P branches are given by the formula

$$\nu = \nu_0 + XJ + YJ^2,$$

in which $J = +1, +2, +3, \dots$ for the R branch and $J = -1, -2, -3, \dots$ for the P branch.

Further, suppose $B' > B''$. Then both X and Y will be positive and, in the equation for the P branch, the square term will, as J increases, gradually outweigh the first power negative term in J and cause ν to start increasing again after an initial decrease from $J = 1$. Thus the P branch will show a 'head'. The R branch, on the other hand, will have lines the frequency of which steadily increases as J increases. Finally, the head of the P branch will lie on the low frequency side, i.e. the band will 'degrade to the violet'.

If $B' < B''$ the converse relationships hold, the R branch showing the head and the band degrading to the red.

This raises a point of some interest. The infra-red absorption spectra of molecules involve transitions between two vibration levels of the same (ground) electronic state. In all cases the mean moment of inertia in the upper state will be greater than that in the lower state, i.e. $B' < B''$. For this reason all the bands will degrade to the red. In the case of the electronic bands, however, we may have $B' < B''$, or $B' > B''$, or $B' \approx B''$. These bands may therefore either degrade to the red or violet or even fail to show a definite degrading at all (headless bands).

For the Q branch,

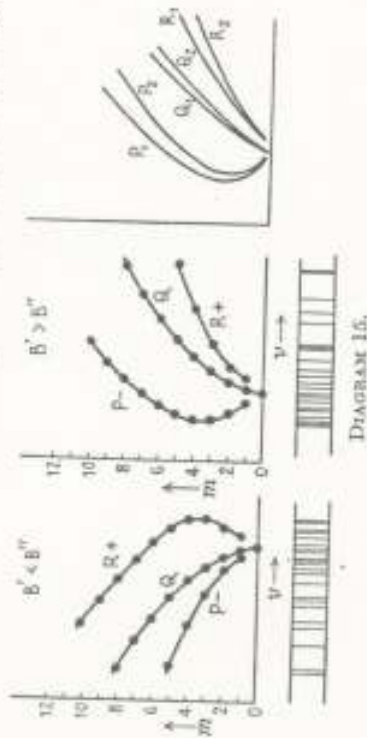
$$\begin{aligned} \nu &= \nu_0 + B'J'(J'+1) - B''J''(J''+1) \\ &= \nu_0 + (B' - B'')J + (B' - B'')J^2, \end{aligned}$$

in which $J = 0, 1, 2, 3, \dots$

These various relationships should be made clear by the so-called Fortrat diagrams of Diagram 15*a* and *b*.

It might then be expected that, in theory at least, any band should show a group of P , Q , and R branches, with the P or R branch showing the head according to the relative values of B' and B'' . This is not so. The interaction between the electronic rotational properties of the molecule and the overall molecular rotation leads to complexities in the simple P , Q , and R branch structure. First, selection rules deter-

mined by the electronic quantum numbers of the two combining states may forbid the occurrence of a Q branch. This occurs in the ${}^1\Sigma \rightarrow {}^1\Sigma$ transitions.† Also the possible rotational energy levels in each of the two combining electron levels may be by no means so simple as just described. Then again, each single P , Q , and R branch may in reality be doublet or triplet, the multiplet separation of the lines



increasing steadily as higher rotation quantum numbers are reached. The Fortrat diagram then has some such form as that of Diagram 15c. There are, however, many other subsidiary complications and details. These can be found by reference to the standard works such as that of Jevons. One main point to be remembered is that the nature of the rotational fine structure is a valuable indication of the electronic structures of the combining levels.

In a later experiment a band with simple P and R branch structure will be considered (${}^1\Sigma \rightarrow {}^1\Sigma$). In the present experiment a band with the next simplest structure, corresponding to a ${}^1\Sigma \rightarrow {}^1\Pi$ transition, will be examined. A suitable band is one of the Angström bands of carbon monoxide, which were photographed in Experiment IV. The green band at

† A ${}^1\Sigma$ level is one in which the component along the molecule axis of the resultant orbital momentum is zero, and the resultant spin momentum is also zero.

5198 Å. or the violet band at 4835 Å. may be chosen. These bands have apparently single P , Q , and R branches, although actually the higher members of the branches show a slight splitting. A closer analysis of this so-called Λ doubling would, however, lead to a much more detailed treatment of the problem than is desirable here, and for this reason it will be omitted.‡

Apparatus. The spectrum of carbon monoxide required can be excited in a discharge tube containing carbon dioxide

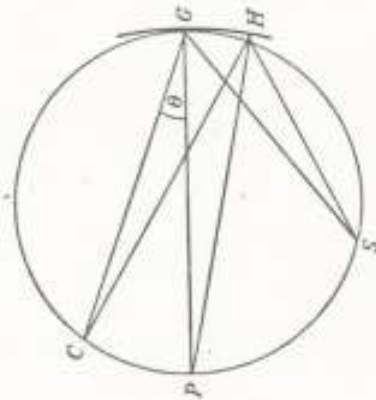


DIAGRAM 16.

in the same manner as described in Experiment IV. Two types of spectrograph are suitable, either a large glass Littrow instrument with optical system similar to that mentioned in Experiment III, or a grating spectrograph. A common form of grating instrument is a concave grating with Eagle mounting.† The theory of the concave grating is briefly as follows. Suppose GH is the grating (Diagram 16), placed with its centre on the circumference of a circle the diameter of which is the radius of the grating. Consider rays of light striking the

† See Jevons, *op. cit.*, pp. 125-8.

‡ See R. W. Wood, *Physical Optics*, 3rd edn., p. 263; Houston, *A Treatise on Light*, 6th edn., p. 179, or other standard works.

grating after emerging from the slit S . Suppose that the ray SG is diffracted at an angle θ to the normal GP giving a ray GC . Consider now a second ray from S striking the grating at H . Join HC and HP . Now GH is very small

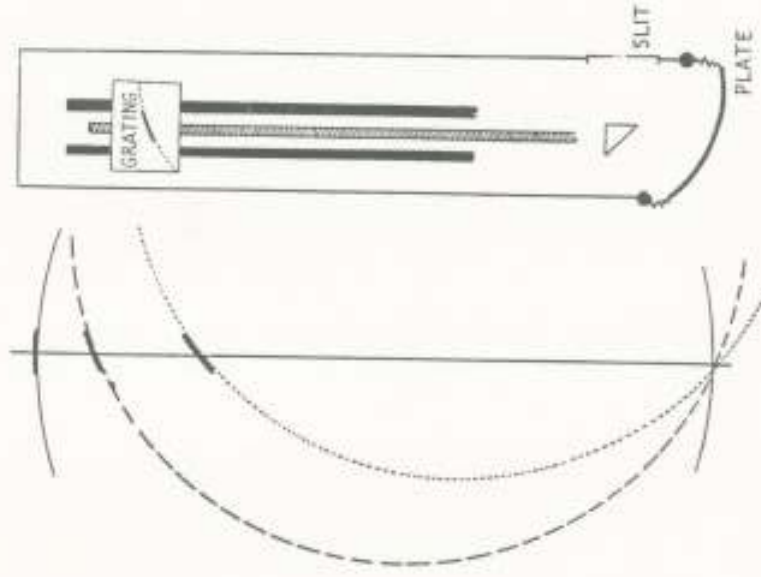


DIAGRAM 17.

compared with the circumference of the circle, and hence we can assume that H lies on this circumference. Thus, being angles on the same arc of the circle, we have

$$\angle PHC = \angle PGC = \theta.$$

But PH is normal to the grating. Thus no matter which rays from S to the grating are considered, all rays diffracted at an

angle θ to the normal pass through P . It will be seen that no lenses are required. The essentials are that the slit, camera, and grating shall be mounted on the circumference of the circle of diameter equal to the radius of curvature of the grating. By movement of the camera along this circumference (keeping the grating and slit fixed), different regions of the spectrum and different orders will be brought into view. A description of the different forms of mounting designed with this object would be out of place here. Perhaps the most convenient and compact arrangement is that of Eagle. In this the grating and camera are placed on a straight girder with some screw attachment suitable for altering the distance between them. Each is capable of rotation about a vertical axis through its centre (Diagram 17). The slit is placed at one side of the girder in front of a reflecting prism and in such a position as to cause a virtual image of the source to be just above (or below) the centre of the plate holder.

For further details the works referred to should be consulted. It may, however, be remarked that the resolving power of the grating depends upon its total number of rulings, and not, for example, upon their separation.

Method. The instrument to be used should be focused for the region required by taking suitable photographs of the iron arc. In the case of the concave grating it may be convenient to focus it for the second order spectrum, centre at about 5000 Å., i.e. first order centre 10,000 Å. A photograph should then be taken of the carbon monoxide bands in the green and blue. A panchromatic or Ilford Soft Gradation plate should be used. The plate will not be sensitive to the first order overlapping spectrum, while interposition of a glass plate either separately or as window for the discharge tube will eliminate the lower orders. The exposure required will, of course, depend upon the intensity of the source, but will in any case be longer than with the smaller instruments used in the previous experiments.

An iron arc should be superposed by means of the comparison shutter.

Problem. From the plate obtained, or an enlarged reproduction of it, the lines of one band should be identified with the help of known data,[†] and the band thus analysed into its three branches. At the same time a rough estimate should be made of the relative intensities of the lines.

From the analysis thus carried out the values of B' and B'' should be determined, and hence the values of v_0' and v_0'' .

The photograph shown reproduces the 4835 Å. band of carbon monoxide, taken in the second order of a concave grating of the above type, with Eagle mounting. The grating radius was 3 m., resolving power about 40,000 in the first order, and dispersion in the first order 5.8 Å. per mm. This band, as already explained, involves a transition between the two electronic states ${}^1\Sigma$ (upper) and ${}^1\Pi$ (lower), with change in vibrational quantum number $v = 0$ (upper) to $v = 1$ (lower). In the ${}^1\Pi$ level there are single (really very close doublet) levels of rotation with $J = 1, 2, 3, \dots$ but no $J = 0$ level.[‡] In the ${}^1\Sigma$ state the rotation levels have $J = 0, 1, 2, 3, \dots$. In the ${}^1\Sigma \rightarrow {}^1\Pi$ transition the lines start with $J'' = 1$. Thus we get $P(1), Q(1),$ and $R(1)$. There is no $Q(0)$ line. The intensity of the lines in the band is given by $\text{const.}(J' + J'' + 1)e^{-E_{rot}/kT}$, in which E_{rot} is the rotational energy of the initial state (${}^1\Sigma$).

The analysis of the band into its $P, Q,$ and R branches is best undertaken by the use of 'combination' rules by means of which hypothetical arrangements of the lines can be quickly tested. Thus, if the energy of a molecular level is given by $v = v_0 + v_{vib} + v_{rot}$, we can write $v = v_0 + v_{rot} = v_0 + F$ in which $F = B'J(J+1) + D'J^2(J+1)^2$. For the lines of the

[†] Hultbén, *Ann. d. Phys.*, **1**, 72 (1922).

[‡] For a detailed explanation compare Jevons, *op. cit.*, chap. viii; Spenser, *Molekulärspektren*, pp. 81-84.

three branches we can then write

$$R(J) = v_0 + F'(J+1) - F''(J),$$

$$P(J) = v_0 + F'(J-1) - F''(J),$$

$$Q(J) = v_0 + F'(J) - F''(J),$$

in which v_0 is written for $(v' - v'')$. We therefore have the following relationships:

$$R(J) - Q(J) = Q(J+1) - P(J+1),$$

$$\text{and } R(J) - Q(J+1) = Q(J) - P(J+1), \text{ etc.}$$

If D is neglected in comparison with B ,

$$R(J) - P(J) = F'(J+1) - F'(J-1)$$

$$= B'(J+1)(J+2) - B'J(J-1) = B'(4J+2)$$

and

$$R(J-1) - P(J+1) = F''(J+1) - F''(J-1) = 4B''(J+1).$$

The wave numbers of the lines of the carbon monoxide band at 4835 Å. are given in the following table:[†]

Carbon monoxide 4835 Å. band.

Wave numbers in cm.^{-1}

| J | $P(J)$ | $Q(J)$ | $R(J)$ |
|-----|---------|---------|---------|
| 1 | 20679.6 | 20683.4 | 20690.8 |
| 2 | 20677.6 | 20685.2 | 20703.2 |
| 3 | 20676.2 | 20687.7 | 20710.4 |
| 4 | 20675.8 | 20691.0 | 20718.3 |
| 5 | 20675.3 | 20694.9 | 20726.9 |
| 6 | 20676.4 | 20699.7 | 20736.3 |
| 7 | 20677.8 | 20705.2 | 20746.4 |
| 8 | 20680.1 | 20711.4 | 20757.1 |
| 9 | 20683.2 | 20718.2 | 20768.6 |
| 10 | 20686.9 | 20725.8 | 20780.8 |
| 11 | 20691.3 | 20734.1 | 20793.7 |
| 12 | 20696.4 | 20743.1 | 20807.3 |
| 13 | 20702.2 | 20752.8 | 20821.6 |
| 14 | 20708.8 | 20763.2 | 20836.6 |
| 15 | 20716.0 | 20774.3 | 20852.3 |
| 16 | 20723.9 | 20786.1 | 20868.7 |
| 17 | 20732.6 | 20798.7 | 20885.9 |
| 18 | 20742.0 | 20812.1 | 20903.8 |
| 19 | 20752.2 | 20826.1 | 20922.4 |
| 20 | 20763.1 | 20840.9 | |

[†] In the diagram shown, and for all other purposes, the splitting of the lines at higher rotational quantum numbers is ignored.

Using the values of this table and the relationships given above, the following results are obtained:

| J | $R_0(J) - P_0(J)$ | B' cm. ⁻¹ | J | $R_0(J-1) - P_0(J+1)$ | B'' cm. ⁻¹ |
|-----|-------------------|------------------------|-----|-----------------------|-------------------------|
| 1 | ... | ... | 1 | ... | ... |
| 2 | 19.2 | 1.92 | 2 | ... | ... |
| 3 | 27.0 | 1.93 | 3 | 21.0 | 1.50 |
| 4 | 34.6 | 1.92 | 4 | 27.9 | 1.55 |
| 5 | 43.0 | 1.95 | 5 | 34.0 | 1.55 |
| 6 | 50.5 | 1.94 | 6 | 40.5 | 1.54 |
| 7 | 58.5 | 1.95 | 7 | 46.8 | 1.56 |
| 8 | 66.3 | 1.95 | 8 | 53.1 | 1.56 |

$$\text{Hence, since } B = \frac{h}{8\pi^2 I} = \frac{27.66 \times 10^{-40}}{I},$$

we find, taking mean values for B' and B'' , that

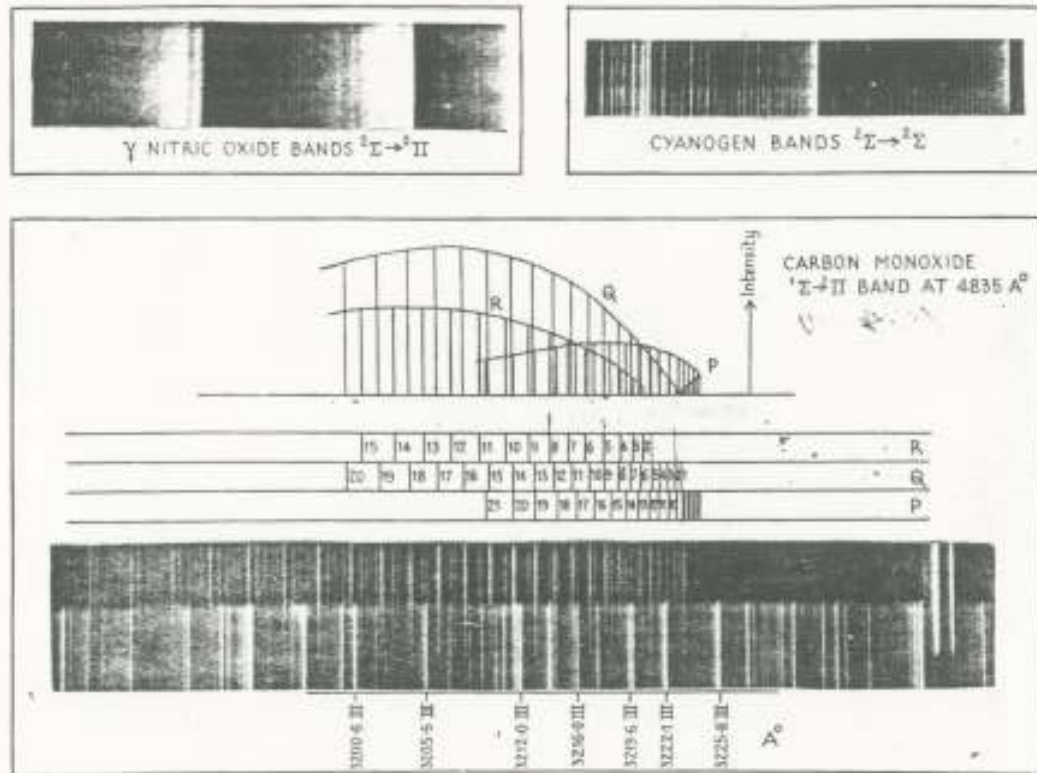
$$I' = 14.4 \times 10^{-40} \text{ gm. cm.}^2$$

and $I'' = 17.85 \times 10^{-40} \text{ gm. cm.}^2$. Remembering that

$$I = \mu r^2 = \frac{m_1 m_2}{m_1 + m_2} r^2,$$

we find $r'_0 = 1.12 \times 10^{-8} \text{ cm.}$ and $r''_0 = 1.26 \times 10^{-8} \text{ cm.}$ Thus in the higher (${}^1\Sigma$) state there is an increased binding, which could incidentally have been observed from the fact that the band degrades to the violet.

The relative simplicity of the band just described is not common. The nitric oxide ' γ ' bands photographed in Experiment IV and corresponding to a ${}^2\Pi \rightarrow {}^2\Pi$ transition are much more complicated in structure, as also the cyanogen bands (${}^2\Sigma \rightarrow {}^2\Sigma$) seen in Experiment II.



The Rotational Structure of a Band