

BAND SPECTRA AND CHEMISTRY

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I. INTRODUCTION

The study of the spectra of individual atoms, the so-called line spectra, with the help of the quantum theory has been of the greatest value in giving us an understanding of the electronic structure and properties of atoms (1). In the last few years, the center of interest in spectroscopic investigation seems to have shifted from line spectra to the spectra of molecules, the so-called band spectra. At present most of our available information on molecular spectra has to do with diatomic molecules in the vapor state, but as time goes on we shall doubtless slowly learn more about the spectra of polyatomic molecules. The progress from atoms to diatomic molecules to polyatomic molecules is associated with a steadily increasing complexity of the corresponding spectra, and a steadily increasing difficulty in the analysis. Although from the standpoint of chemistry diatomic molecules in the vapor state constitute a very limited class, they are nevertheless molecules, and a knowledge of their structure as obtained from the analysis of band spectra and from the quantum theory can take us a long way toward a fundamental understanding of molecular structure in general.

The ways in which molecular spectra can be put to use in problems of chemical interest may be placed under the following headings: (a) We may use the presence of various bands in an absorption or emission spectrum as a means of determining the presence or concentration of various molecules. (b) By accurate measurement and quantum analysis of the spectrum of a particular kind of molecule, we can obtain knowledge of many important numerical properties of that molecule. By generalization of such results and with the help of the new

quantum mechanics, rapid progress is now being made toward the solution of the problems of valence and molecular structure. We shall now consider in turn these two uses of band spectra, the first in section II, the second in sections III-V.

II. DIAGNOSTIC USES OF BAND SPECTRA IN CHEMICAL PROBLEMS

Spectra of polyatomic molecules

A great deal of work has been done in mapping the absorption spectra of liquids, solutions, and (to a less extent) vapors of polyatomic molecules, especially of organic compounds and of inorganic compounds containing complex ions. Although comparatively very little has as yet been done, on account of their complexity, toward a detailed analysis of such spectra, their general nature from the theoretical standpoint may be said to be understood (see section IIIc below). Such spectra are of use in qualitative and quantitative analysis and in the study of chemical equilibria. They are also often useful in establishing the presence of various groups or bonds in molecules, even though very little is as yet known of the theoretical relations involved.

Spectra of diatomic molecules

Turning now to simpler molecules, we encounter a large number of band spectra, which are commonly obtained by passing electrical discharges of one kind or another, and most of which have been known for a number of years (2). Until recently the origin of most of these spectra has been in dispute. The Swan bands, for example, now definitely known to be emitted by the C_2 molecule, were by various investigators attributed to CH, C_2H_2 , etc. But the detailed application of the quantum theory has now made it possible to determine with certainty the emitters of practically all known band spectra of the diatomic type. Table 1 contains a list of some of the diatomic molecules whose band spectra are known (3) (4).

Table 1 is of interest in two ways. First, it shows the existence of a number of molecules which are not ordinarily known in chemistry, but which certainly exist as intermediate products

TABLE 1
Some molecules of which band spectra are known†

MOLECULE	OCCURRENCE OF SPECTRUM	MOLECULE	OCCURRENCE OF SPECTRUM
CH	Flames; sun*; A.H. or A.N. + C compounds	ZrO	Stars*
NH	Sun*; A.N. + C ₂ H ₅ I, etc.	PbO	Pb arc in air
OH	Flames; sun*; very hot H ₂ O vapor*; A.H.	H ₂	Geissler tubes
MgH	Sun-spots*; cooler stars*; Mg arc in H ₂	He ₂	High-current discharges in pure helium at low pressure
HgH	Hg + A.H.; Geissler tubes	C ₂	Flames; sun*; comets; A.H. or A.N. + C compounds
CaH	Sun-spots*; cooler stars*; Ca arc in H ₂	N ₂	Sparks in air; Geissler tubes; A.N.
LiH, AlH, CuH, AgH, AuH	Metal arcs in H ₂ ; also vapor of hot metal in contact with H ₂ *	N ₂ ⁺	Sparks; aurora; comets
HCl ⁺	Sparks	O ₂	Air*; electrical discharges
BO	Sun-spots*; cooler stars*; A.N. + BCl ₃ + O ₂	O ₂ ⁺	Geissler tubes
CO	Geissler tubes, etc.	S ₂	Geissler tubes; vapor*
CO ⁺	Comets; Geissler tubes, etc.	Cl ₂	Geissler tubes; vapor*
CN	C arc in air; sun*; hot-tish stars*; comets; A.N. + C compounds	I ₂	Geissler tubes; vapor*; and recombination of I atoms
CS	Geissler tubes, etc.	ICl	Vapor*
NO	Cu and other arcs in air; sparks in air; A.N. + O compounds; NO gas*	Na ₂	Vapor*
AlO	Al arc in air	NaK	Vapor*
SiO	Si arc in air; C + SiO ₂ vapor	K ₂	Vapor*
SiN	A.N. + SiCl ₄	MgF, CaF	Fluorides in carbon arc
MgO	Burning Mg	CaCl, MgBr, SrI, etc.	Excess of alkaline earth metal in presence of halogens*
CuO	Cu arc in air	CuF, CuCl, CuBr, CuI	Vapor of Cu ₂ Cl ₂ , CuCl ₂ , etc. (* or in A.N.)
TiO	Sun-spots*; cooler stars*; Ti arc in air	SnCl	Discharge in SnCl ₄ ; A.N. + SnCl ₄
		AgCl, AgBr, AgI	Vapor*
		AuCl	A.N. + AuCl ₃

† This list is not exhaustive in respect either to molecules or to occurrence of spectra. The spectra given occur as emission spectra, except as indicated by an asterisk (*), which denotes absorption spectra. The abbreviations A.H. and A.N. denote active hydrogen and active nitrogen respectively.

in chemical reactions, or as equilibrium products at high temperatures; and second, it shows where such molecules are found. For example, band spectra show the existence of large numbers of the diatomic molecules CH, OH, and C₂ in ordinary flames, the CH and C₂ molecules respectively being responsible for the bluish and greenish colors of such flames. In a similar way, the presence of CO⁺, CN, and N₂⁺ molecules in the tails of comets is demonstrated, as well as the presence of various molecules in the sun and stars. Again, band spectra have shown that the vapors of the alkali metals are not strictly monatomic, as had long been supposed, but contain considerable percentages of diatomic molecules, and that in mixed alkali metal vapors, mixed molecules occur. A study of the OH absorption band spectrum in highly heated water vapor (5) has disclosed the importance of OH, hitherto neglected, in the equilibrium of H₂ and O₂. Likewise, the high intensity of the CN bands in the carbon arc burning in air, and in the sun, indicates that the equilibrium of carbon and nitrogen at high temperatures favors this molecule (6). Chemical reactions occurring in active nitrogen are a source of many interesting band spectra disclosing various intermediate reaction products. For example, when any hydrocarbon vapor is introduced into active nitrogen, the CN, C₂, and CH bands appear; certain compounds such as C₂H₅I give also the NH bands (7); oxygen-containing molecules give NO spectra, and so on.

III. BAND SPECTRA, ENERGY LEVELS, AND MOLECULAR PROPERTIES

a. Introduction

There are two basic rules, first proposed by Bohr and since established by many experiments, which are essential in line and band spectra. These are (a) the energy of an atom or molecule is capable of taking on only a discrete set of values, corresponding to a set of so-called energy levels, and (b) whenever the molecule gains or loses energy in the form of light, the quantity of energy gained or lost is proportional to the frequency of vibration ν of the light waves: $h\nu = E' - E''$ (E' and E'' are the energy values for two energy levels out of the dis-

crete set which the molecule possesses; E' is by definition greater than E'' ; h is Planck's constant).

In the study of the spectrum of an atom or molecule, one first obtains a knowledge of the wave-lengths and their relative intensities. This knowledge in itself has many useful applications, but it is less fundamental than the knowledge of energy levels (and their quantum numbers) which can be obtained from it. For when one knows the energy levels E of a molecule, one can compute all possible spectrum frequencies from the relation $h\nu = E' - E''$. A precise knowledge of the energy levels also has many important applications to problems of reaction mechanisms and of chemical equilibria. But we can go farther: from the numerical values of the energy levels, and their spectroscopic behavior, we can get various other important numerical data about the molecule (moments of inertia, vibration frequencies, angular momentum of electrons and of nuclei, law of force acting between the atoms, etc.), and can obtain a great deal of insight into its physical and chemical behavior. This we can do not merely for its lowest or normal state of energy, but also for its various excited or activated states.

In the next section (III*b*) we shall consider the main features of the energy level diagram for a diatomic molecule in the vapor state. In section III*c* we consider briefly the various types of molecular spectra for diatomic and polyatomic molecules, keeping in view their relation to chemical problems. Section III*d* contains a discussion of the energy levels of some actual molecules (H_2 , O_2 , I_2 , NO). The object of this section is to give some idea, by means of examples, of the numerical magnitudes involved and of the varied kinds of information which can be obtained from a study of the energy levels.

b. Energy levels of diatomic vapor molecules; general relations (8)

For a diatomic molecule we have energy of the electrons, energy of vibration of the nuclei along the line joining them, and energy of rotation of the nuclei about their center of gravity. All of these are capable of taking on only discrete values, so long as the molecule remains undissociated. The energy levels of a

diatomic molecule are accordingly subject to a threefold classification, each level being characterized by three kinds of quantum numbers. One group of quantum numbers specifies the condition or configuration of the electrons, a vibrational quantum number (n) determines the amplitude of vibration, and a rotational quantum number (K) fixes the rate of rotation.

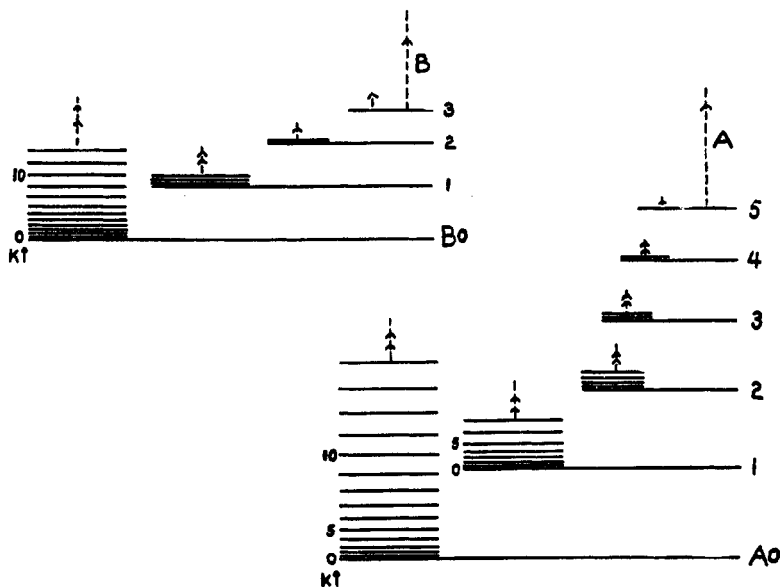


FIG. 1. SCHEMATIC ENERGY LEVEL DIAGRAM FOR DIATOMIC MOLECULE

The diagram shows two electron levels (A and B), each with a set of vibrational levels (A_0, A_1, \dots , and B_0, B_1, \dots), and each vibrational level having a set of rotational levels. The spacings are qualitatively correct, but the quantitative spacing of the rotational levels is relatively much too large.

Figure 1 is a qualitatively correct, but quantitatively impossible, diagram of energy levels for a diatomic molecule. In the figure, the ordinates represent energy, commonly measured from the lowest level as zero, while the abscissas have no significance. Two "electron levels," A and B , are shown, with each of which is associated a family of vibrational levels; the vibrational quantum numbers (n) are given on the right (A_0, A_1, A_2, \dots ; B_0, B_1, B_2, \dots). The amplitude of vibration is

a minimum (not quite zero, see section III*d*, p. 517) for $n = 0$, and increases with n . It will be noted that the vibrational levels (*a*) are more closely spaced than the electron levels, as can for example be seen by comparing the energy interval between A_0 and A_1 with the interval A_0 to B_0 (this relation is usually but not always true in practice); (*b*) differ in spacing for different electron levels (here A and B); (*c*) decrease, slowly, in spacing as n increases (in figure 1 the rate of decrease of spacing has been exaggerated). Now for every vibrational level there is a family of rotational levels, characterized by different values of the rotational quantum number K . The rotational levels show the following characteristics: (*a*) they are much more closely spaced than the electron or vibrational levels (in practice, their relative spacing is always much smaller than in figure 1); (*b*) they differ in spacing for different electron levels and, to a lesser extent, for different vibrational levels; (*c*) their spacing increases with K , approximately in proportion to K^2 . In figure 1, only a part of the vibrational and rotational levels is shown; the existence of the others is indicated by arrows.

The impressions given by figure 1 will be clarified in section III*d* by a discussion of the energy levels of some actual molecules (figures 2-5).

The effect of liquefaction or solidification on the energy levels of a diatomic gas, and the energy levels of polyatomic molecules are discussed in section III*c*.

c. Energy levels and band spectra (8)

Absorption and emission spectra; origin, classification, and structure. In the space available, it is not possible to discuss how one can determine energy levels and quantum numbers from an analysis of band spectra, but a brief description can be given of the various types of band spectra and their relation to molecular energy levels.

In an emission spectrum line, a molecule which has by some means been excited to a more or less high energy level makes a quantum jump to one of its lower energy levels, giving out the corresponding energy in the form of light. In an absorption

spectrum line, a molecule, ordinarily starting from one of the lower rotational levels of its lowest vibrational and electronic state (thermal equilibrium near room temperature), is carried by the absorption of a light quantum to a higher energy level. Resonance and fluorescence spectra are emission spectra of molecules which have been excited by light absorption. Chemiluminescence spectra are emission spectra of molecules which have been excited in the course of a chemical reaction. Raman spectra will be discussed below.

Molecular spectra can also be divided into three classes according to the type of energy change in the molecule: (a) pure rotation band spectra, (b) oscillation-rotation band spectra, (c) electronic band spectra. In pure rotation bands, the molecule goes from one rotational energy level to another, without any change in its vibrational or electronic state (for example, from $K = 4$ to $K = 5$ of the level A_0 in figure 1). Since the spacing of the rotational energy levels of a molecule is always comparatively small (see figure 1), and since the rotational quantum number never changes by more than one unit, the energy changes and so the frequencies involved in such spectra are very small, so that they lie exclusively in the far infra-red. In vibration-rotation bands, the molecule goes from one vibrational and rotational level to another, but without any change in its electronic state (for example, from $K = 3$ of level A_0 to $K = 2$ of A_1 in figure 1). The frequency here is approximately proportional to the interval between two vibrational levels, since the rotational quantum number changes only by 0 or ± 1 units, which represents only a very small energy change. Since, furthermore, the vibrational quantum number rarely changes by more than one or two units in vibration-rotation bands, the corresponding frequencies are rather small and such spectra lie almost exclusively in the near infra-red. In electronic bands, the molecule undergoes a change in its electronic state as well as in its vibrational and rotational states. Since electronic energy levels are in general widely spaced, electronic bands generally correspond to large energy changes and large frequencies and lie in the visible or ultra-violet part of the spectrum; but infra-red

electronic bands are also possible. In electronic band spectra, the rotational quantum number never changes by more than one unit, but the vibrational quantum number may change by large amounts.

The fact that rotational quantum numbers never change by more than one unit as a result of light absorption is important, in a negative sense, for photochemical theory, since it shows that light can rarely, if ever, seriously influence chemical reactions through its effect on the state of rotation of a molecule. Also important is the fact that the vibrational quantum number practically never (i.e. with only a very small probability) changes by more than one or two units as a result of the absorption of infra-red wave-lengths, unless they belong to an electronic band spectrum. Thus, absorption of infra-red light corresponding to the pure rotation or rotation-vibration spectrum of a molecule can hardly be expected to have much effect on its chemical activity, unless perchance the molecule is already on the verge of instability. But the absorption of wave-lengths (usually ultra-violet) belonging to an electronic band spectrum can—but need not necessarily—profoundly influence the activity of a molecule, either directly by producing an alteration in the electronic structure, or indirectly by setting the molecule into a violent state of vibration which in many cases goes so far as direct dissociation (see section IV below).

The foregoing remarks should hold for polyatomic as well as for diatomic molecule spectra, although the systems of rotational and especially of vibrational and electronic levels are more complicated and more closely spaced in the former case, because of the greater number of degrees of freedom.

In structure, the spectra of all the types mentioned above, for polyatomic as well as diatomic molecules, consist in general of a great number of sharply defined wave-lengths, but in those electronic band-systems¹ where dissociation of a molecule results

¹ A band system is a set of bands all of which correspond to the same electron jump, i.e., in an absorption spectrum, to the same electron configuration in the activated state. A complete band spectrum consists of a number of band-systems.

from light absorption (or conversely, where association is accompanied by light emission), part or all of the spectrum is continuous.

Raman spectra. Raman spectra are emission spectra of a type somewhat related to fluorescence spectra (9); a light quantum of frequency ν_1 (say, from a mercury lamp) strikes a molecule and bounces off with a somewhat smaller frequency ν_2 , the energy $h(\nu_1 - \nu_2)$ being imparted to the molecule, taking it to a higher energy level. Or sometimes ν_2 is somewhat greater than ν_1 , the energy $h(\nu_2 - \nu_1)$ being abstracted from the molecule. Raman spectra, although their position in the scale of wavelengths is mainly determined by the exciting frequency ν_1 , may be classified under the same three headings as ordinary band spectra—pure rotation, oscillation-rotation, and electronic Raman spectra—according to the nature of the energy change in the molecule.

The rules which govern the possible energy level changes in a molecule in Raman spectra are very different from those for ordinary band spectra; in fact, it is the rule that changes which could not occur at all in ordinary processes of light emission or absorption are the usual changes with Raman spectra (9). For example, the rotational quantum number generally changes by 0 or ± 2 in Raman spectra where it would usually change by ± 1 with ordinary spectra. Again, changes in the rotational and vibrational quantum numbers without change in the electronic state are possible in Raman spectra for homopolar diatomic molecules (i.e. molecules like H_2 and O_2 , composed of two equal atoms), whereas in ordinary emission and absorption spectra such molecules have only electronic bands.² Similarly, in the pure rotation and oscillation-rotation spectra of polyatomic molecules, changes commonly occur, in Raman spectra, in quantum numbers which never change in the case of ordinary emission or absorption bands. These various peculiarities make

² Of the diatomic molecules, only those which have an electric moment (heteropolar molecules) are capable of absorbing or emitting pure rotation and vibration-rotation bands as well as electronic bands. Homopolar molecules have only electronic bands.

the Raman effect very valuable as a means of supplementing the information which we can obtain about molecular energy levels from infra-red absorption spectra; just those facts which are withheld from us by the latter are disclosed by the Raman spectra.

Liquids, solids, and polyatomic molecules. It is of interest to consider how the energy levels of a diatomic molecule are altered when the vapor is condensed to form a liquid or solid. In the case of liquid H_2 , we know from band spectrum evidence (Raman effect) that the rotational and vibrational energy levels are practically the same as in the gas (10), and from other evidence that they persist even in the solid state (11). In the case of other non-polar molecules, (N_2 , O_2 , CO) the vibrational levels are practically the same in liquid and vapor (presumably also in the solid), but the rotational levels are probably destroyed (11) and replaced by some sort of a continuous energy distribution, so that the corresponding band spectra must consist of diffuse bands, instead of being composed of sharp lines like those of the vapor. It is probably safe to say that the electron levels of non-polar molecules are practically the same in position in the solid or liquid as in the vapor. Of course if the liquid contains molecular species not present in the vapor, as O_4 is probably present (12) in liquid O_2 , these may give new spectra. Also, spectra which are weak in the gas may become relatively strong in the liquid. For polar molecules (e.g. HCl) the changes in the energy levels on condensation are doubtless more radical than for non-polar molecules, especially in cases where the liquid is ionized or the solid is an ionic lattice (e.g. $NaCl$).

In gases at very high pressure, the rotational energy levels tend, as in liquids, to be obliterated, because of the frequency of collisions. All band spectra become more diffuse as the pressure is increased.

The absorption spectra of many organic molecules have been studied in both liquid and vapor states, especially by Henri and his students. The spectra are in general very nearly the same in the two cases, except for a greater diffuseness of the bands in the liquids, indicating that the rotational levels which are present in the vapor molecule are suppressed in the liquid.

Our knowledge, based on band spectra, of the structure and properties of polyatomic molecules is at the present time less than that of diatomic molecules, in spite of the large amount of empirical spectroscopic material on the former. The reason for this lies in the complexity of the energy levels and spectra of polyatomic molecules. In such spectra, the band lines in ordinary electronic bands are usually too numerous and too closely packed to be properly measured with the usual instruments; and even if a complete set of measurements were at hand for such a spectrum, the task of analysis and interpretation would be likely to be exceedingly difficult. A beginning has, however, been made in the work of Henri and Schou on formaldehyde vapor (13). Much progress has also been made in infra-red absorption bands of the vibration-rotation type where, although the complexity and the difficulties of interpretation are still formidable, they are much less than for the electronic bands. In the future a study of such infra-red bands, in conjunction with Raman effect data, will probably lead to a great deal of information about the normal states of the simpler polyatomic molecules. But it will probably be some time before we begin to obtain such a large amount of detailed information from the band spectra of polyatomic molecules as we have been getting from those of diatomic molecules. A good understanding, from a study of band spectra, of the higher (activated) electron states of polyatomic molecules, important especially for photochemical and electron-impact reactions, will probably come about especially slowly, since it depends on the interpretation of the very complicated (visible and ultra-violet) electronic band spectra. It may be that by the time this is possible, the mathematical technique of the new quantum mechanics will have developed to such an extent that it will be easier to determine what we want to know about polyatomic molecules by pure calculation.

d. Energy levels of H_2 , N_2 , O_2 , NO , and their interpretation

Electron levels. Keeping in mind the general scheme of figure 1, let us now examine the arrangement of the energy levels of some familiar molecules as revealed by band spectra, and see

what we can learn from them. In figure 2 are plotted the best known electron levels of the molecules H_2 , O_2 , and I_2 (4) (14). Each plotted level is of course only the lowest of a whole family of levels corresponding to a variety of states of vibration and of rotation of the molecule, i.e., the levels shown here are those one would get if the energy of vibration and rotation of the nuclei were omitted from consideration. On the right is a scale of calories per mol, on the left a scale of absolute temperatures such that RT is equal to the number of calories given on the right. This gives a rough idea of the temperatures needed to excite the molecules to the various levels. The horizontal dotted line for each molecule indicates the dissociation energy (in the case of oxygen, there is an uncertainty of about $\pm 13,000$ calories).³ From the positions of these lines one can see at once that it is possible for a molecule to have temporarily, stored up in its electron configuration, much more energy than would suffice to dissociate it. Such highly energized molecules are, however, capable of dissociating under certain conditions, such as collisions with other molecules, or (see below) often spontaneously. An H_2 molecule in its lowest excited electron level has, in fact, enough energy to dissociate both itself and another H_2 molecule if they should collide. We do not yet know whether this particular process actually occurs in nature, but we do have evidence that molecules which have been excited from their normal state to higher electron levels are chemically very reactive. (For the meaning of the symbols $^3\Sigma$, $^1\Sigma$, $^1\Pi$, etc. in figure 2, see section V, p. 532.)

Returning to the H_2 molecule, it is of interest to consider what may happen to an excited molecule if it does not collide with another molecule, or if it escapes intact from one or more such collisions, as is not unlikely. If it is in one of the excited states

³ The heat of dissociation will be accurately known from band spectrum data as soon as we know the energy X required to excite the O atom from its normal (3P) state to its low 1D state. The heat of dissociation is $163,000 - X$ calories. X probably lies between 25,000 and 50,000 calories; in figure 2 the value $X = 36,000$ has been assumed. See Herzberg, G.: *Z. physik. Chem.* **4B**, 1223 (1929).

${}^1\Sigma(B)$ or ${}^1\Pi(C)$ of figure 2, we know that it must almost certainly, after a short time, make a quantum jump to the normal state of H_2 , giving out its excess energy as a quantum of short wave-length ultra-violet light ($h\nu = E' - E''$). If it is the lowest state marked, ${}^3\Sigma$, it very probably makes another kind of

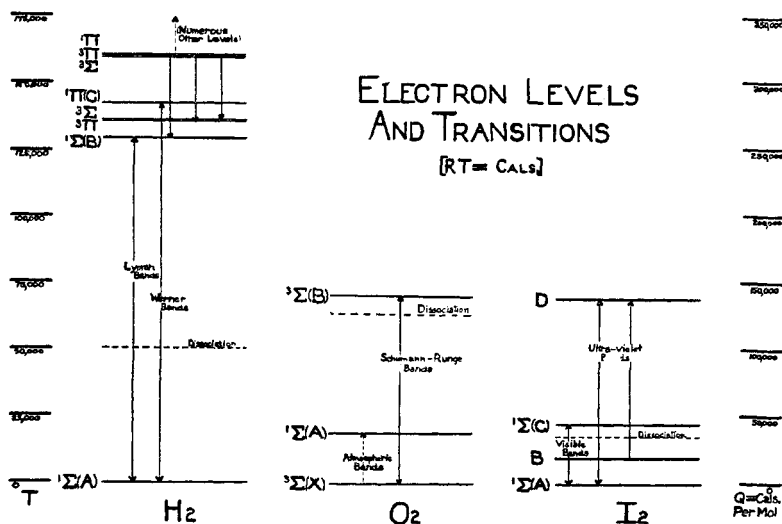


FIG. 2. MOST IMPORTANT KNOWN ELECTRON LEVELS (FULL HORIZONTAL LINES), AND DISSOCIATION ENERGY (DOTTED HORIZONTAL LINES), OF H_2 , O_2 , and I_2

(See reference (4), where additional excited levels of H_2 will be found. The existence of the B level of I_2 is not certain.) The designations of the levels are partly empirical and without general significance (A, B, C, D, X) and partly systematic (${}^1\Sigma, {}^3\Sigma, {}^3\Pi$, etc.); for the significance of the latter, see Part V below. The important band spectra corresponding to transitions between these levels are shown by vertical lines; arrow heads at the top of the lines indicate spectra which are known as absorption spectra; arrow heads at the bottom indicate known emission spectra. The energy scale is given on the right in calories per mol (Q), on the left in terms of absolute temperature (T), in such a way that $RT = Q$.

quantum jump; while, as it were, jumping towards a certain very unstable lower ${}^3\Sigma$ state not shown on the diagram (this is the $1s\sigma 2p\sigma, {}^3\Sigma$ state discussed in section V, p. 532), it spontaneously dissociates into atoms, which fly apart at high speed (15). In the process (a variable) part of the energy appears as light of a frequency equal to $1/h$ times the original energy minus the energy of dissociation and the kinetic energy of the retreating

atoms.⁴ The whole process is of interest as an example of a unimolecular reaction whose mechanism is understood. This and analogous processes are also of interest from the fact that they yield the chemically active atomic hydrogen.

The reader may wonder at this point how the H_2 molecule originally got up into the excited levels just under discussion. This may have happened in various ways, as by bombardment with fast electrons or with α particles, or by collision with excited or fast-moving or ionized atoms or molecules, or by absorption of short wave-length ultra-violet light. If the activation is produced by light, the subsequent chemical reactions of the activated molecules would be classed as photochemical. The problem of reaction mechanisms will be further discussed in section IV.

Vibrational levels. Returning now to the energy level diagrams of the three molecules, we see in figure 3 the lowest portion of the diagram of figure 2 on a larger scale (14). This time we have not merely the electron levels, but also, and principally, some of the associated vibrational levels. Figure 3 makes clear how greatly the spacings of the energy levels depend on the molecular weight. The equation which describes the vibrational energy levels of any molecule is

$$E^v = (n + \frac{1}{2})hc\omega_e - (n + \frac{1}{2})^2 hc x\omega_e + \dots \quad (1)$$

In this equation the first term is the principal one, and in it $c\omega_e$ is the frequency of vibration, which is, generally speaking, greater the smaller the molecule and the lighter its atoms; n is the quantum number of vibration, whose lowest value is zero. For $T = 0$ all molecules would be in the lowest vibrational state ($n = 0$). But since the energy is given by $(n + \frac{1}{2})hc\omega_e$, there is still a residual vibrational energy $\frac{1}{2}hc\omega_e$ when $n = 0$; this may be called the zero-point vibrational energy. The existence of this energy is demanded by the new quantum theory and is shown experimentally by a study of the isotope effect in band spectra.

⁴ This, aided by other similar processes, is very probably the origin of the well-known and useful continuous band spectrum which is obtained by passing a suitable electrical discharge through hydrogen gas at low pressures.

One of the most interesting results of band spectrum analysis has been the recent discovery (16) of the existence of oxygen isotopes of atomic weights 17 and 18, in respective amounts about 1/10,000 and 1/1250 that of O^{16} . The spectrum in which the oxygen isotopes have been found is the system known as the atmospheric absorption bands, which corresponds to a transition

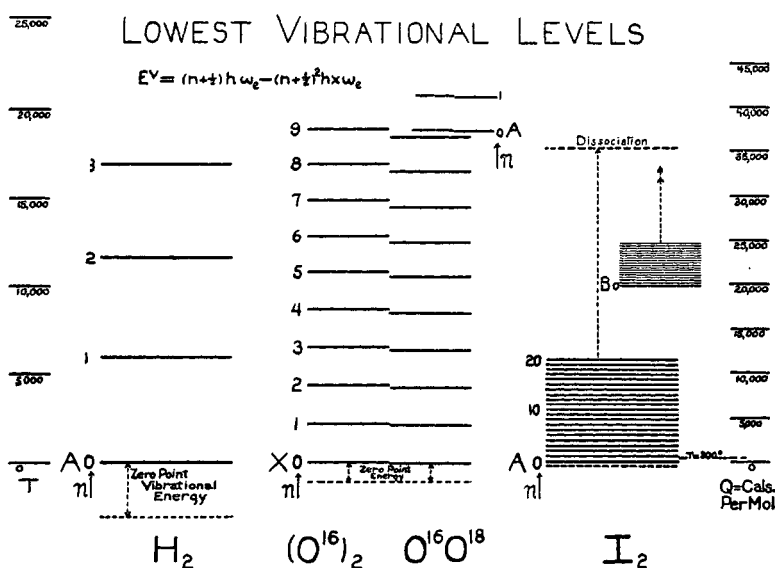


FIG. 3. LOWEST VIBRATIONAL LEVELS OF H_2 , O_2 , AND I_2

The Q and T scales are related as in figure 2. The energy is called zero for $n = 0$, although when $n = 0$ there is still some vibrational energy ("zero-point energy") which, however, cannot be removed; the dotted horizontal lines at the bottom of the diagrams show the amount of this zero-point energy. The O_2 diagram is not quite in agreement with the convention of zero energy for $n = 0$, but instead, in order more clearly to bring out the difference between the isotopes, has been drawn in accordance with the convention that the isotopes would have equal energy if the zero-point energy could be removed.

between the electron levels X and A of figures 2 and 3. These bands appear as Fraunhofer lines at the red end of the solar spectrum, being absorbed out of the sunlight in its passage through the earth's atmosphere. The very strong $(O^{16})_2$ bands are accompanied by very faint bands slightly displaced in precisely the way predicted by the theory for $O^{16}O^{17}$ and $O^{16}O^{18}$.

There should also be other bands due to $(\text{O}^{17})_2$, $\text{O}^{17}\text{O}^{18}$ and $(\text{O}^{18})_2$, but these are surely too faint to be observed. Another interesting result of band spectrum analysis is the discovery of the carbon isotope C^{13} in the C_2 , CN , and CO bands (17).

The vibrational levels of $(\text{O}^{16})_2$ and $\text{O}^{16}\text{O}^{18}$ are shown in figure 3. So far only the levels (X0 and A0) with $n = 0$, and the level A1, are known for $\text{O}^{16}\text{O}^{18}$. The positions of the $\text{O}^{16}\text{O}^{18}$ levels shown in figure 3 have been calculated from those of $(\text{O}^{16})_2$, as can be done exactly by means of the quantum theory. The observed interval between the levels X0 and A0 differs for $(\text{O}^{16})_2$ and $\text{O}^{16}\text{O}^{18}$ by exactly the theoretical amount; the result gives a confirmation of the predicted zero-point energy of $(\frac{1}{2})hc\omega_e^5$. The observed interval X0 to A1 also differs for the two isotopes by exactly the theoretical amount.

Accurate measurements on band spectra offer a possibility of very accurate determinations of the atomic weights of C^{13} with reference to C^{12} and of O^{17} and O^{18} with reference to O^{16} .

Returning now to an examination of the spacing of the vibrational levels in figure 3, it is easy to see why in the cases of H_2 and O_2 the vibrational energy does not contribute at ordinary temperatures to the specific heat, since for ordinary temperatures the level $n = 1$ lies far above the quantity $RT/2$ which, for the vibrational degree of freedom, represents the equipartition value of the energy per mol. In the case of I_2 , however, the spacing of the levels is so small that the energy of the level $n = 1$ is approximately equal at room temperature to $RT/2$. Hence in I_2 there is a vibrational specific heat, the molecules being distributed at room temperature over several vibrational levels in such a way as to give an average vibrational energy of approximately $RT/2$ (in excess of the zero-point energy).

Rotational levels. We turn now to figure 4, which shows on a still larger scale the lowest energy levels of our three molecules.

⁵ The isotope effect here does not give a direct test of the presence of the energy $(\frac{1}{2})hc\omega_e$ for the X0 and A0 states individually, but only shows that the *difference* between the values of this quantity for the X and A states (which is due to the fact that ω_e is different for the X and A states) differs in the calculated way for the two isotopes.

This time we see the rotational levels, which in figures 2 and 3 were omitted. On the scale used, the vibrational level $n = 1$ would come far above the top of the present diagram in the cases of H_2 and O_2 , but in the case of I_2 , where the vibrational levels are relatively close together, $n = 1$ appears in the figure. The rotational levels of the three molecules show the

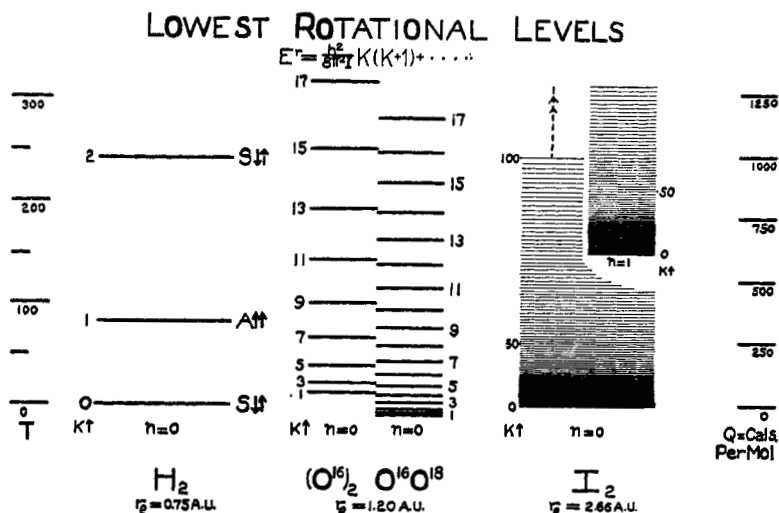


FIG. 4. LOWEST ROTATIONAL LEVELS OF LOWEST ELECTRON LEVEL OF H_2 , O_2 , I_2

In the case of I_2 , the lowest of the rotational levels are too closely spaced to be shown separately on the scale used. The Q and T scales are related as in figures 2 and 3. The energy is called zero for $K = 0$ in each case, except that in the O_2 diagram, the same convention has been adopted as in figure 3. The values of the equilibrium distance between the nuclei (r_e) are given in Angstrom units ($1 \text{ A.U.} = 10^{-8} \text{ cm.}$). In the case of H_2 , the symmetric and antisymmetric levels are labeled S and A , respectively, and the arrangement of the proton spins (parallel $\uparrow \uparrow$, or antiparallel $\uparrow \downarrow$) is indicated.

same sort of differences in scale as the vibrational levels. The rotational energy is given by formulas of the type

$$E^r = (h^2/8\pi^2 I)K(K + 1) + \dots \quad (2)$$

where I is the moment of inertia and K is the rotational quantum number. I is much larger for I_2 than for H_2 , both because of the larger mass and because of the larger equilibrium distance r_e between its nuclei ($r_e = 0.75 \times 10^{-8} \text{ cm.}$ for H_2 and $2.66 \times$

10^{-8} cm. for I_2). This distance is known from the spacing of the rotational levels, from which (see equation (2)) I can be calculated, and so r_e , since the masses of the nuclei are known. (For a molecule composed of equal atoms each of mass M , $I = Mr_e^2/2$.)

The spacing of the rotational levels is important in connection with the rotational specific heats. In the cases of I_2 and O_2 the spacing of the levels is small enough so that the rotational specific heat has nearly the ordinary equipartition value R except at the very lowest temperatures. (Since the rotational energy of a diatomic molecule corresponds to two degrees of freedom, its equipartition value per mol is RT , which gives a specific heat R per mol.) But in the case of H_2 the spacing is quite large, so that below about $200^\circ K$. the rotational specific heat falls rapidly, and becomes practically zero at $50^\circ K$.

A number of other facts can be learned from a careful study of the rotational levels, or rather, of the band spectra from which these levels are determined. Thus a study of the hydrogen band spectra shows that in each band, alternate band lines have intensities differing in a ratio of about 3:1. The interpretation is that half the rotational levels, namely, in the case of the lowest electron level, those with odd values of K , have a statistical weight or *a priori* probability three times as great as for the even levels. (For the even levels, the statistical weight is $2K + 1$). The explanation of this peculiarity, and of analogous relations in other homopolar molecules, is found in a combination of two factors, namely, the fact that the molecule is composed of two like atoms, and the fact that the nuclei, or protons in the case of H_2 , have an internal angular momentum.

The effect of the first factor, i.e. symmetry, alone, can be seen in the case of the rotational levels of $(O^{16})_2$. Here every other level is completely missing. Only the so-called antisymmetric rotational levels, namely those with odd values of K , are present in the case of the normal electron state. This is explained by the postulate, closely related to the Pauli exclusion principle for atoms, that in homopolar molecules only antisymmetrical states exist. To explain the difference between H_2 and O_2 , we

suppose that in $(\text{O}^{16})_2$, the O^{16} nuclei have no internal angular momentum, but that in H_2 each proton has a unit of spin. These proton spins are then able to arrange themselves in H_2 in such a way as to make possible all values of the rotational quantum number. (In $(\text{O}^{16})_2$, although each nucleus contains numerous protons and electrons, each presumably with a spin, these are evidently so arranged as to neutralize one another.) In the normal state of H_2 the antisymmetric rotational levels ($K = 1, 3, 5, \dots$) are present just as in $(\text{O}^{16})_2$; for these levels, the proton spins are arranged symmetrically, i.e. roughly speaking parallel (see figure 4), and do not affect the symmetry of the molecule as a whole. The symmetric rotational levels ($K = 0, 2, 4, \dots$) are, however, also present; this is made possible by an antisymmetrical, i.e. an antiparallel, arrangement of the proton spins (see figure 4), which makes the state of the molecule as a whole antisymmetrical, hence permitted. But the odd levels now have three times as great a statistical weight as the even levels, because a parallel orientation of the proton spins has three times as great a weight as an antiparallel orientation.⁶

There is another very curious and interesting fact about these odd and even levels in hydrogen, namely that it is extremely difficult to reverse the orientation of the proton spins, even in collisions, so that hydrogen behaves almost like a mixture of two different gases, or isotopes. At high temperatures we should expect about one-fourth of the molecules to be distributed among the symmetric states ($K = 0, 2, 4, \dots$) and about three-fourths among the antisymmetric states ($K = 1, 3, 5, \dots$). If now we cool the gas to a low temperature, all the symmetric molecules accumulate in the level $K = 0$, and the antisymmetric molecules in the level $K = 1$. Only in the course of long periods of time, in gas at atmospheric pressure, can one expect the final equilibrium to be established in which all molecules are in the state $K = 0$, because of the resistance of the proton spins to having their orientation reversed. Equilibrium is, however, rapidly

⁶ The explanation just given is too brief to be accurate. For a detailed review of the subject, see Mulliken's paper given at the September 1929 meeting of the Faraday Society.

established by the catalytic action of coconut charcoal at the temperature of liquid hydrogen (18). The slowness of attainment of equilibrium under ordinary conditions serves to explain some of the anomalous behavior of the specific heat of hydrogen at low temperatures (18) (19).

Relations similar to those in H_2 and O_2 have been found in other homopolar molecules. The ratio of statistical weights of alternate levels is in some cases (He_2 , C_2) 1:0 as in O_2 , in others (F_2) it is 3:1 as in H_2 , while in others it has other values. In each case, this ratio enables us to determine the internal angular momentum of the nucleus; this turns out to have a variety of values in different atoms (20).

Turning now to oxygen, the considerable differences in spacing of the energy levels of $(O^{16})_2$ and $O^{16}O^{18}$ are of interest. These differences are verified experimentally in the atmospheric oxygen bands. There is also the very striking difference that in $O^{16}O^{18}$ all the rotational levels are present, and without any alternation in statistical weight. This is exactly as expected, because the difference in mass of the two atoms in O^{16} and O^{18} is enough to destroy the symmetry which exists in the case of $(O^{16})_2$. An analogous phenomenon is found in the case of Cl_2 when the rotational levels of $(Cl^{35})_2$ and $Cl^{35}Cl^{37}$ are compared.

There are other facts about the oxygen molecule which can be deduced from its rotational energy levels. One of these is that its normal electronic state is a $^3\Sigma$ (triplet sigma) state, i.e. a state in which the electron spins give a resultant angular momentum $h/2\pi$, but in which the average orbital angular momentum of the electrons is zero. The triplet character is shown by the fact that each rotational level is a close group of three. This is not shown in figure 4, but it is very important, since it accounts for the fact that O_2 is paramagnetic. As Van Vleck has shown (21), the observed paramagnetic susceptibility corresponds exactly to that of a $^3\Sigma$ state. The triplet character of the levels is important in that it multiplies the statistical weight by three, giving the weight $3(2K + 1)$ for each K value which is present. The existence of a triplet normal level is also of interest in that it shows, according to London's theory of valence, which is mainly

a translation of Lewis' theory into quantum theory terms (see section V) that each O atom in O_2 is exerting only one of its valences; in other words, that the bond between the O atoms is a single and not a double bond. The existence of paramagnetism here and elsewhere is directly connected with the existence

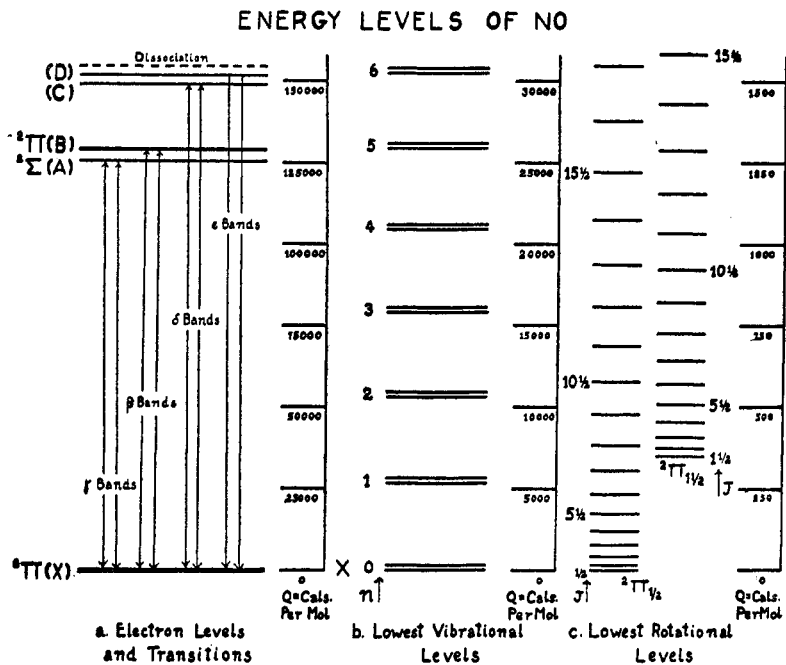


FIG. 5. ENERGY LEVELS OF NO

Figure 5a is analogous to figure 2, figure 5b to figure 3, and figure 5c to figure 4. In figure 5a the ${}^2\Pi$ electron levels appear as very narrow doublets; in figure 5b the $X^2\Pi$ level appears as a wider doublet (because of the larger scale), which is repeated for each vibrational level; in figure 5c the two sets of rotational levels corresponding to the two components (${}^2\Pi_{1/2}$ and ${}^2\Pi_{3/2}$) of the $X^2\Pi$ electron level for $n = 0$ are shown.

of unsatisfied valence, although this does not imply that valence forces are magnetic in character. The paramagnetism is rather a symptom than a driving force in valence.

Energy levels of NO (example of ${}^2\Pi$ state). The normal electron states of H_2 , O_2 , and I_2 are all Σ levels, i.e. levels for which the average orbital angular momentum of the electrons is zero.

The rotational levels associated with such electron levels are of a particularly simple type, especially when they are $^1\Sigma$ levels, as in H_2 and I_2 . It will be of interest to consider briefly a molecule whose normal state is of a different type. The paramagnetic molecule NO, whose energy levels are well known from band spectra, has a $^2\Pi$ normal state. Figures 5a, 5b, and 5c show, in the same manner as figures 2, 3, and 4 for H_2 , O_2 , and I_2 , the electron levels, the lowest vibrational levels, and the lowest rotational levels for NO. The $^2\Pi$ normal electron state consists of two sub-states, $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$, of which $^2\Pi_{1/2}$ is slightly lower. Each of these electron sub-states has a complete set of vibrational and rotational levels (see figures 5b, 5c). The spacing of the vibrational levels is about fifteen times as great as the interval between the $^2\Pi_{1/2}$ and the $^2\Pi_{3/2}$ levels, so that the vibrational level diagram appears as a series of narrow doublets (figure 5b). In $^2\Pi$ states, every rotational level, in both the $^2\Pi_{1/2}$ and the $^2\Pi_{3/2}$ set, has a statistical weight $2(2J + 1)$, where J is the rotational quantum number (this differs from K of figure 4 in the fact that it includes the electron spin) (22). The $^2\Pi_{1/2}$ levels are non-magnetic or nearly so for small values of J , while the $^2\Pi_{3/2}$ levels are paramagnetic. At room temperature, many molecules exist in both sets of levels, so the gas as a whole is paramagnetic; Van Vleck has shown (21) that the observed paramagnetic susceptibility at room temperature is in excellent agreement with that calculated from the band spectrum data by means of the quantum theory. At low temperatures, however, the paramagnetism decreases (23), and should finally disappear with the crowding of the molecules into the lowest levels of the $^2\Pi_{1/2}$ set. The specific heat of NO should also show interesting peculiarities on account of the double electron level (24).

Band spectra and entropy of gases. From a knowledge of the energy levels of a molecule and of their statistical weights, as determined from band spectra, it is possible to calculate not only the specific heat of the gas, but also (making use of the Sackur-Tetrode equation) its absolute entropy. Giaque and Wiebe have made such entropy calculations for HCl, HBr, HI, and O_2 , and have compared the results with those obtained from

direct calorimetric measurements, assuming the correctness of the third law of thermodynamics. In all cases, the agreement is excellent. Giaouque and Wiebe (25) conclude that calculations based on spectroscopic data are to be preferred to those based on calorimetric data. Corrections must, however, be made for deviations of the gas from the state of an ideal gas.

IV. BAND SPECTRA AND THE MECHANISM OF CHEMICAL REACTIONS

The most important types of homogeneous chemical reactions (26) for the present discussion are perhaps as follows:

1. Reactions produced by electron impact or by the absorption of light. It is well known that the effect of electrons of given energy is similar to that of light quanta of corresponding energy ($h\nu$), except that the conditions which the electrons must fulfil are less rigorous than those for light quanta. To produce a definite change in a molecule, a light quantum must have exactly the right frequency, while an electron can accomplish the same effect even if its energy is considerably more than the exact amount needed. Another difference is that there are no such rigorous selection rules governing electron impact as there are for light absorption; nevertheless it is true in a general way that processes which are impossible or improbable (i.e. infrequent) in the case of light absorption are also improbable for electron impact. In reactions produced by light or electron impact, the initial effect is always the activation, ionization, or dissociation of a molecule as a result, direct or indirect, of a disturbance of its electron configuration. (As already noted in section IIIc, absorption of infra-red light corresponding to pure rotation or vibration-rotation spectra is not likely to produce photochemical action.)

2. Reactions produced by collisions of the second kind, in which energy of excitation or ionization is transferred from one excited atom or molecule to another (examples: $\text{Hg}' + \text{H}_2 \rightarrow \text{Hg} + 2\text{H}$; $\text{N}_2' + \text{Hg} \rightarrow \text{N}_2 + \text{Hg}'(?)$; $\text{Ne}^+ + \text{CO} \rightarrow \text{CO}^+ + \text{Ne}$).

3. Reactions produced by the impact of fast moving atoms or molecules. These include thermal reactions. Here one may often expect large changes in vibrational and rotational energy

as a result of collisions; or sometimes rearrangements of the atoms in a complex molecule; or also often, as above, changes in the electron configuration.

A knowledge of the energy levels of a molecule, such as can be derived from band spectrum data, is obviously of value in understanding reactions of any of the above types, but we shall consider here mainly reactions produced by light absorption or electron impact.

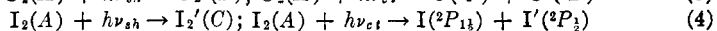
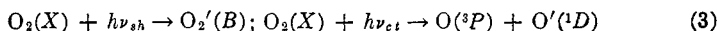
The first step in a photochemical reaction is a change in the electron state of a reacting molecule as a result of the absorption of light, nearly always of visible or ultra-violet light. There are then two possibilities: either (*a*) the activated molecule may dissociate spontaneously, the dissociation products thereafter often reacting further, or (*b*) the activated molecule may remain unchanged until, on collision with another molecule, it reacts, or until, if collision is too long delayed, it makes a quantum jump to a lower energy level, giving out radiation (fluorescence). The same possibilities exist in the case of electron impact.

The most general type of band-system¹ in the spectrum of a diatomic molecule consists of two parts; the one composed of numerous bands generally made up of sharp lines and corresponding to the transfer of the molecule from one quantum state to another, the other a continuous region of wave-lengths corresponding, in an absorption spectrum, to the transfer of the molecule from one of its lower energy levels directly to a state of dissociation, the latter being unquantized. This last process may be considered as caused by an unusually large change in vibrational energy. Such changes occur whenever, roughly speaking, the activated electron state is much less stable than the unactivated state. The theory of these phenomena was first developed by Franck (27). In many band-systems (or in most band-systems, in diatomic molecules), one finds with measurable intensity either the separate bands only, or the continuous region only. In some band-systems, however, as for example the Schumann bands of O₂ and the visible absorption bands of I₂, and pretty generally in polyatomic molecules, both regions are strong. In such cases, a determination of the value of the

frequency for the boundary between the two regions makes possible an accurate spectroscopic measurement of the heat of dissociation, provided one knows in what electron states the dissociation products are. In cases where only the continuous region is present, an upper limit for the heat of dissociation can often be set, while in cases where only the separate bands are present, the heat of dissociation can very often be estimated fairly accurately by extrapolation (27).

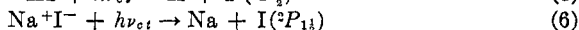
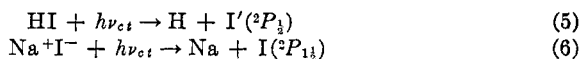
In many, especially polyatomic, molecules the part of any band-system which consists of separate bands must be further differentiated. It has been noted, especially by Henri (28), that many absorption spectra contain a region of bands composed of sharp lines, and another region (usually at shorter wave-lengths) in which the bands, while still individually distinguishable, are diffuse. In the latter case, according to Henri, the activated molecule is in a "state of predissociation," in which the rotational motions are no longer sharply quantized. The explanation of this lack of sharp quantization is probably that the activated molecule makes, after an extremely short interval (of the order of 10^{-11} sec.), a quantum jump in which it dissociates spontaneously without the emission of light (29) (30). For all practical purposes this is the same as if the dissociation had occurred simultaneously with the absorption, as in the case of the true continuous region of the band-system. Theoretically, however, the two cases are quite different. Intermediate stages between simple activation and predissociation apparently often exist, as would be expected theoretically.

The following equations represent known or probable examples of the various types of photochemical activation and dissociation. In these equations the subscripts "ct," "df," and "sh" in ν_{ct} , ν_{df} , and ν_{sh} refer to the type of band spectrum (continuous, diffuse, or sharp-line) which produces the given reaction. The symbols X , A , B , C , etc. refer to certain electron states of O_2 and I_2 which appear in figure 2. When no symbol is given for the initial state, the normal state is usually meant.



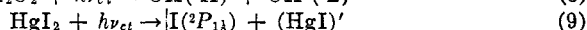
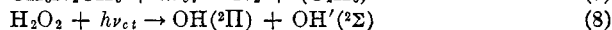
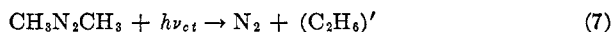
Following photochemical activation according to equation (3), ozone is formed; this probably occurs both for the sharp-line and for the continuous absorption; apparently either O_2' molecules or O atoms are capable of forming O_3 as a result of collision with unexcited O_2 molecules. In the case of I_2 (and similarly for the other halogens), photochemical action results mainly, if not entirely, from the formation of dissociated atoms.

In the cases of the alkali and hydrogen halides, only the continuous parts of the absorption band-system appear under ordinary conditions. For example (31) (32),

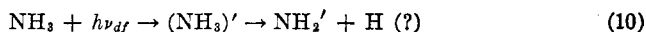


Bonhoeffer and Farkas (31) have shown that equation (5) holds probably not only for gaseous HI, but also in the case of solid HI.

Also, probably (33) (34) (35)



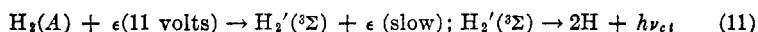
In the case of NH_3 there is a predissociation spectrum (29):



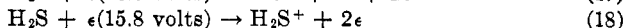
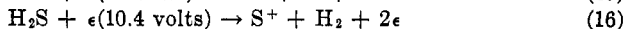
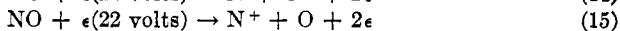
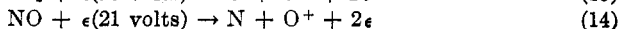
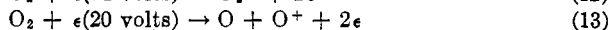
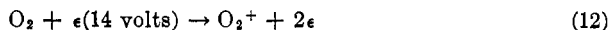
The examples given are among those which have been most carefully studied; large numbers of analogous cases undoubtedly exist. In connection with the above equations it should be remarked that the indicated dissociation products usually are those for the absorption region of longest wave-length in the spectrum. In general the absorption spectrum consists of a number of regions, each of which produces dissociation products in different excited states, or sometimes different dissociation products.

In addition to the two types of photochemical dissociation discussed above, a third type is conceivable; namely, one in which the activated molecule makes a quantum jump in which it dissociates spontaneously (after a time of the order of 10^{-8} sec.) *with light emission*. An example of this (15), except for the fact that the activation was produced by electron impact,

has already been given above in section III*d* in discussing the electron levels of H_2 (see p. 514). The same type of reaction should also sometimes occur photochemically, although not in this particular case (ϵ indicates an electron):



Besides photochemical processes involving activation of molecules, there should be others involving ionization, or simultaneous ionization and dissociation, or simultaneous ionization and activation, the latter sometimes followed by dissociation. The occurrence of such processes as a result of electron impact is well known; some examples (36) (37) (38) are given in equations (12) to (18). The only assignable reason why such processes are not yet known in photochemical work with molecules is the fact that such work is ordinarily done with wave-lengths longer than 1800 Å.U., whereas the longest wave-length capable of ionizing a molecule probably in no case that has been tried exceeds about 1700 Å.U. (The process $N_2 + h\nu \rightarrow N_2^{+'}$ has been studied, to be sure (39), but it is not known that any chemical action follows.)



It is safe to predict that processes analogous to those of equations (12) to (18) can be produced by ultra-violet light of sufficiently short wave-length.

V. MOLECULAR QUANTUM NUMBERS, DISSOCIATION, AND VALENCE THEORY

Quantum numbers, electron configurations, and structure principle

The various electron states of a molecule, like those of an atom, can be classified by giving quantum numbers for the individual electrons and, in addition, certain electron quantum numbers for the molecule as a whole. The system of electronic quantum

numbers is more complicated for diatomic molecules, to which we shall mainly confine ourselves here, than for atoms. For polyatomic molecules very little has as yet been done on the problem of electronic quantum numbers.

The electron state of an atom is fully described by such a formula as the following, which is that for the normal state of the Si atom:



The *configuration* formula, $1s^2 \dots 3p^2$, means that the atom contains two $1s$ electrons ($1s^2$), two $2s$ electrons, six $2p$ electrons ($2p^6$), two $3s$ and two $3p$ electrons, a total of fourteen electrons. In the symbols $1s$, $2p$, etc., the number is the principal quantum number n (not be confused with the molecular vibrational quantum number n), while the letter denotes the value of the azimuthal quantum number l (s , p , d , ... mean $l = 0$, 1 , 2 , ...). The order in which the symbols are written is the order of decreasing firmness of binding; the $1s$ electrons are the most, the $3p$ the least, firmly bound ("firmly bound" = difficultly ionized). Each electron has, in addition to n and l , also a spin quantum number s , which is not especially indicated in the formula, since it always has the same value $s = \frac{1}{2}$. (This use of s has no relation to the use of s to denote $l = 0$.) Each electron has an angular momentum of $\sqrt{l(l+1)} h/2\pi$ due to its motion in its orbit and in addition an amount $\sqrt{s(s+1)} h/2\pi = \sqrt{3}h/4\pi$ due to its spin.

The term formula 3P_0 has the following significance. The letter denotes the value of the quantum number L , which is a sort of resultant azimuthal quantum number (resultant of the l 's of those electrons which are not in closed shells,—see below). The superscript number on the left (3 in 3P_0) denotes the multiplicity M , which is a number such that $M = 2S + 1$, where S is the resultant spin quantum number; S is the resultant of the individual spins of those electrons which are not in closed shells. The subscript number on the right (0 in 3P_0) denotes the value of the "inner" quantum number J , which represents the resultant of L and S ; $\sqrt{J(J+1)}h/2\pi$ is the resultant angular momentum of the atom as a whole (40) (41).

The electron state of a diatomic molecule (41) (42) is described as in the following two examples. The first of these is the formula for the normal state of the molecules N_2 , CO, and NO^+ , all of which have fourteen electrons like the Si atom. The second is the corresponding formula for the normal state of NO. The third is that for the normal state of O_2 .⁷

$$N_2, CO, NO^+: 1s\sigma^2 2p\sigma^2 2s\sigma^2 3p\sigma^2 2p\pi^4 3s\sigma^2, {}^1\Sigma \quad (20)$$

$$NO: 1s\sigma^2 2p\sigma^2 2s\sigma^2 3p\sigma^2 2p\pi^4 3s\sigma^2 3p\pi, {}^2\Pi_{\frac{1}{2}} \quad (21)$$

$$O_2: 1s\sigma^2 2p\sigma^2 2s\sigma^2 3p\sigma^2 2p\pi^4 3s\sigma^2 3p\pi^2, {}^3\Sigma \quad (22)$$

The configuration formula means that the molecule contains two $1s\sigma$ electrons ($1s\sigma^2$), two $2p\sigma$, two $2s\sigma$, two $3p\sigma$, four $2p\pi$, and two $3s\sigma$ electrons, and (in NO and O_2) one or two $3p\pi$ electrons⁷ (42). The number and the first letter have essentially the same significance as for an atom, while the second (Greek) letter gives the value of a quantum number λ which does not exist for the atom, ($\sigma, \pi, \delta, \dots$ mean $\lambda = 0, 1, 2, \dots$). (Instead of the symbol λ , the symbols $i_{l\tau}$ and $\sigma_{l\tau}$ have hitherto been usual.) In the term formula ${}^1\Sigma$ or ${}^2\Pi_{\frac{1}{2}}$ or ${}^3\Sigma$, the Greek letter gives the value of a quantum number Λ ($\Sigma, \Pi, \Delta, \dots$ mean $\Lambda = 0, 1, 2, \dots$) which is, here and in general, equal to the sum of the individual λ 's, some of the latter taken with a positive and some with a negative sign; the superscript on the left gives the multiplicity M and implicitly the resultant spin S ($M = 2S + 1$) just as for an atom. (Instead of the symbols $\Sigma, \Pi, \Delta, \dots$ the symbols S, P, D, \dots have until recently been commonly used, although the meaning of these symbols is quite different from that of S, P, D, \dots in atoms; instead of Λ, i_i or σ_k or σ_l has hitherto been usual.) The meaning of the quantum number λ is as follows: when an atomic electron orbit with azimuthal quantum number l is placed in an electric field of suitable strength, or when the atom is replaced by a diatomic molecule, a new quantum number λ comes into existence; this corresponds to the projection of l on the electric axis (in the molecule, this axis is the line

⁷ It should be emphasized that the exact electron configurations given here for various molecules (equations (20), (21), and (22), table 2, etc.) may be subject to correction. But this possible uncertainty does not involve any essential doubt as to the principles involved.

joining the nuclei); λ is capable of taking on the integral values from l to 0, e.g. any p electron orbit ($l = 1$) gives the two cases $\lambda = 0$ ($p\sigma$ orbit) and $\lambda = 1$ ($p\pi$ orbit), while an s electron ($l = 0$) gives only the one case $\lambda = 0$ ($s\sigma$ orbit).

If one compares the electron configurations given above for Si and N_2 , it will be evident that the latter is the same as the former except for some changes in the relative order of binding of different orbits and the subdivision of the group of six $2p$ electrons in Si into two $2p\sigma$ and four $2p\pi$ electrons in N_2 ; also, the $3p$ electrons of Si are $3p\sigma$ electrons in N_2 . In a molecule, $\lambda h/2\pi$ is, for any electron, the component of electronic orbital angular momentum around the electric axis, while $\Delta h/2\pi$ is the total angular momentum of this kind for the molecule as a whole (41) (42).

In Bohr's theory of the periodic system of the atoms (40), the idea of closed shells of electrons is of the utmost importance. The existence of closed shells depends on the empirical fact that there is a limit to the number of electrons which can simultaneously occupy the same kind of orbit (Pauli principle). Two s electrons with the same value of n make a closed shell (e.g. $1s^2$ or $2s^2$ or $3s^2$), likewise six equivalent p electrons (e.g. $2p^6$), or ten equivalent d electrons, and so on. An important peculiarity of every closed shell is that the motions of the electrons are so ordered that it has a resultant orbital angular momentum L of zero, also a resultant spin momentum S , of zero. In the case of the spins, this results from a pairing off of all the spins, each pair containing the spins of two electrons with their spin axes antiparallel (\rightleftharpoons). Since every closed shell has $L = 0$ and $S = 0$, the resultant L and S of an atom, (hence the term type, as 3P_0 in the normal state of Si), are determined exclusively by those electrons—usually the outermost ones—which are not in closed shells. In the Si atom, these are the two $3p$ electrons.

The resultant spin S , as we shall see later, is important in chemistry because $2S$ is the value V of the non-polar valence according to the theory of London and Heitler. This number $2S$ is merely the number of individual spins which are not paired off, and which have their axes parallel. (Each individual spin

has the quantum number $s = \frac{1}{2}$. Spins always set themselves with their axes either parallel or antiparallel. Two antiparallel spins give $S = 0$. Two parallel spins give $S = 1$; three, $S = 1\frac{1}{2}$; and so on. Hence $2S$ is the number of spins whose axes are parallel.) Electrons whose spins are parallel are available for valence purposes, while those whose spins are paired off with their axes antiparallel are not so available.

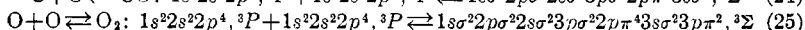
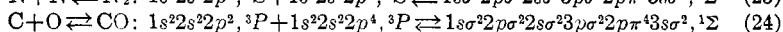
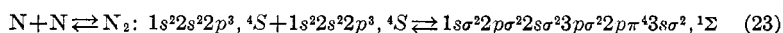
In predicting the electron configuration of the normal state of an atom, Bohr used the following structure principle ("Aufbauprinzip"). To the completely ionized atom, electrons are supposed to be added one by one, each electron being allowed to drop to the lowest available orbit; by "lowest orbit" is meant the orbit of lowest energy—the most firmly bound orbit. As successive electrons are added, successive shells become filled. The completed atom in its normal state ordinarily consists entirely of closed shells except for zero or more of the last-added electrons; these outermost electrons determine the term-type (see preceding paragraph). If one knows the relative strengths of binding of the different orbits, one can thus specify the electron configuration and (with the help of certain additional considerations) the term-type for any atom in its normal state. For light atoms the order of binding is $1s, 2s, 2p, 3s, 3p, 4s, 4p, 3d, \dots$; for heavier atoms it is $1s, 2s, 2p, 3s, 3p, 3d, 4s, 4p, 5s, 5p, 4d, \dots$ and so on. The shift in the relative strengths of binding of the $3d$ and other orbits with increasing atomic number, and analogous phenomena for heavier atoms, have important consequences for the periodic table and the properties of atoms (40).

In diatomic molecules (42), as in atoms, there are closed shells. One may also seek to set up a structure principle for determining the normal states of molecules, although the relations are more complicated than for atoms. In the first place, the closed shells are more numerous: the atomic closed shells have to be subdivided to obtain those of the molecule, as we have already seen in comparing Si and N_2 . Two σ electrons of any one kind ($1s\sigma^2, 2p\sigma^2, 2s\sigma^2$, etc.), or four π , or δ , electrons of any one kind (e.g., $2p\pi^4$, or $3d\pi^4$, or $3d\delta^4$) constitute a closed shell for a di-

atomic molecule. Such a closed shell has the value zero for the total electronic orbital angular momentum ($\Lambda h/2\pi$) around the electric axis, and also has a zero resultant spin ($Sh/2\pi$). In the normal state of N_2 , CO, NO^+ , all the electrons are in closed shells, hence $\Lambda = 0$, $S = 0$ for the molecule as a whole. In the second place, the order of binding of the different closed shells varies not only with the atomic numbers of the atoms, but also with the equilibrium distance between the nuclei, and furthermore depends on the degree of disparity between the charges on the two nuclei. There is, however, a fairly definite order of binding if one limits oneself to any group of molecules which are reasonably similar in respect to the position of their atoms in the periodic table (e.g., C_2 , CN, CO, N_2 , NO, O_2). The order of binding which is probably typical for the first fourteen to sixteen electrons in such molecules is that which appears in equations (20), (21), and (22). The fact that the three molecules, N_2 , CO, and NO^+ , have the same type of normal state is an example of the truth of the statement that the order of binding of electrons is fairly definite within a group of similar molecules. The fact that the normal state of NO is obtained from that of NO^+ merely by adding one more electron in a higher orbit, without disturbing those already present, is a further example of the applicability of the structure principle in molecules.

Electron states of molecules and their atomic dissociation products

A consideration of the relationship between the electron state of a molecule and those of its component atoms on dissociation (42) raises interesting questions. It is known, for example, from band spectrum data, that CO or N_2 or O_2 in their normal states, if their vibrational energy were steadily increased up to the point of dissociation, would give two normal atoms ($C + O$ or $N + N$ or $O + O$). This dissociation and the converse process of formation of a normal molecule from two atoms can be formulated as follows:



It is evident that in the formation of such molecules, radical changes, other than merely the assignment of λ values, are required in the quantum numbers of the atomic electrons. Thus, in $N + N$ or $C + O$ one has four $1s$, four $2s$, and six $2p$ electrons, while in N_2 or CO one has two $1s$ (i.e., $1s\sigma$), two $2s$, six $2p$ (two $2p\sigma$ and four $2p\pi$), two $3s$, and two $3p\sigma$ electrons. Thus some of the atomic electrons are promoted in the formation of the molecule, i.e. their principal quantum number n is increased, while l is often also changed. If it were not for this promotion, there would be in the molecule too many $1s$ and $2s$ electrons, namely four of each, whereas only two of each are permitted according to the Pauli principle. The way in which promotion is possible is made clear only by the new quantum mechanics (42). The relations between the atomic electrons and the corresponding molecular electrons are further discussed below.

Valence theory

Equations (23) to (25) illustrate an important relation which is general: in the formation of the normal state of a stable molecule from the corresponding atoms, the multiplicity M and the resultant spin S of the molecule ($M = 2S + 1$) usually assume a low value, ordinarily the lowest possible value. This comes about through a (\rightleftharpoons) pairing off (see p. 533) of spins originally unpaired and belonging to electrons in the separate atoms. Thus in the case $N + N \rightarrow N_2$, we have in each 4S nitrogen atom three unpaired spins ($M = 4$, hence $S = 1\frac{1}{2}$, for each atom, corresponding to three individual spins, $s = \frac{1}{2}$, all parallel, hence unpaired). These evidently belong to the $2p$ electrons, since the $1s$ and $2s$ electrons are in closed shells (see equation (23)). But in the resulting N_2 molecule (${}^1\Sigma$ state, $M = 1$, $S = 0$) all the electrons are in closed shells and the six originally unpaired electron spins are all paired off.

In general, when two atoms a and b with respective spins S_a and S_b unite, the possible values of the spin S_{ab} for the molecule (if we choose the designations a and b so that $S_a \geq S_b$) are $S_a + S_b, S_a + S_b - 1, \dots, S_a - S_b$. In the case of $N + N$

just discussed, we have $S_a = S_b = 1\frac{1}{2}$, giving 3, 2, 1, and 0 as possible values of S_{ab} , of which actually we find $S_{ab} = 0$ for the normal state of N_2 . According to the valence theory of London and Heitler (43), the valence V of any atom (or molecule) is equal to the number $2S$ ($= M - 1$) of unpaired spins,

$$V = 2S = M - 1 \quad (26)$$

while the number B of valence bonds established in the formation of a molecule from two atoms (or molecules) a and b is equal to the number of spin-pairs formed in this union. Evidently

$$2B = 2S_a + 2S_b - 2S_{ab}, \text{ or, } B = (M_a + M_b - M_{ab} - 1)/2 = (V_a + V_b - M_{ab} + 1)/2 \quad (27)$$

If two atoms with equal valence unite ($V_a = 2S_a = M_a - 1$, $= V_b = 2S_b = M_b - 1$), the maximum possible number of valence bonds is given by $B_{max} = V_a = V_b$. Other possibilities are given by $B = 0, 1, \dots, V_a$, but the most stable state of the molecule is usually, at least when the atoms are in S states, that in which B has its maximum possible value. Thus for two normal (4S) N atoms, we have $V_a = V_b = 3$, and in the normal N_2 molecule we have $B = 3$. Similarly in the case of C + O (both in 3P states) we have $M_a = M_b = 3$ and $V_a = V_b = 2$, while in the resulting normal state of CO we have $B = 2$ (see equation (24)). But (see equation (25)) in the case of two normal oxygen atoms (both 3P), with $V_a = V_b = 2$, we get an O_2 molecule whose normal state is a $^3\Sigma$ state ($M_{ab} = 3$), showing according to equation (27) that only one of the two valences of each atom has been saturated, i.e. $B = 1$ (single bond) instead of the possible value 2. When two atoms with unequal valences V_a and V_b unite, then if $V_a > V_b$, the maximum value of B is equal to V_b , and the molecule has still $V_a - V_b$ unsaturated valences. London and Heitler's valence theory applies also to polyatomic molecules, but since there is as yet little or no information for such molecules from band spectrum data and bearing on valence theory, we shall not consider them here.

According to London and Heitler's theory, the heat of dissociation of a non-polar diatomic molecule in a given state is usually greater the larger the number of valence bonds involved in its

formation. (Examples, normal states of CO and N₂; exception, normal O₂). As a result of this, it often happens that the normal state of such a molecule gives on dissociation one excited and one normal atom, instead of two normal atoms, in cases where the excited atom has a larger V than the same atom in its normal state. A good example of this is found in the case of the CN molecule (44). For this we know, from band spectra, three electron levels. These are given, together with their probable⁸ dissociation products, in table 2.⁷ The lowest state

TABLE 2
States of CN and of C + N

C ATOM		N ATOM		CN MOLECULE	
State	Energy	State	Energy	State	Energy*
	<i>cal.</i>		<i>cal.</i>		<i>cal.</i>
$1s^2 2s^2 2p^3, {}^5S$	+37,000	$1s^2 2s^2 2p^3, {}^4S$	0	$1s\sigma^2 2p\sigma^2 2s\sigma^2 3p\sigma^2 2p\pi^4 - 3s\sigma, {}^2\Sigma$	-186,000
$1s^2 2s^2 2p^2, {}^3P$	0	4S	0	$1s\sigma^2 2p\sigma^2 2s\sigma^2 3p\sigma^2 2p\pi^3 - 3s\sigma^2, {}^2\Pi$	-145,000
3P	0	4S	0	$1s\sigma^2 2p\sigma^2 2s\sigma^2 3p\sigma 2p\pi^4 - 3s\sigma^2, {}^2\Sigma$	-113,000

* The energy values (calories) are only approximate; they are measured from the normal state of C + N (C, 3P and N, 4S) as zero. The electron configurations given for the various states of the CN molecule are not yet entirely certain (in particular, it may be that $3s\sigma$ and $3p\sigma$ should be interchanged).

of CN is formed by the union of a normal (4S) nitrogen atom ($V = 3$) and an excited (5S) carbon atom ($V = 4$). Three valence bonds are formed ($B = 3$), leaving one free valence so that the CN molecule in its chemical behavior resembles a Cl atom, which also has $V = 1$. In the formation of the normal state of CN from C(5S) + N(4S), about 223,000 calories are given out per mol of CN; after deducting about 37,000 calories as the energy per mol required to excite C atoms from their 3P normal state to their 5S state, we still have 186,000 calories as the net energy of formation of normal CN from two normal atoms by this method.

⁸ The correlation between atomic and molecular states given in table 2 and elsewhere is very probable, but not absolutely certain.

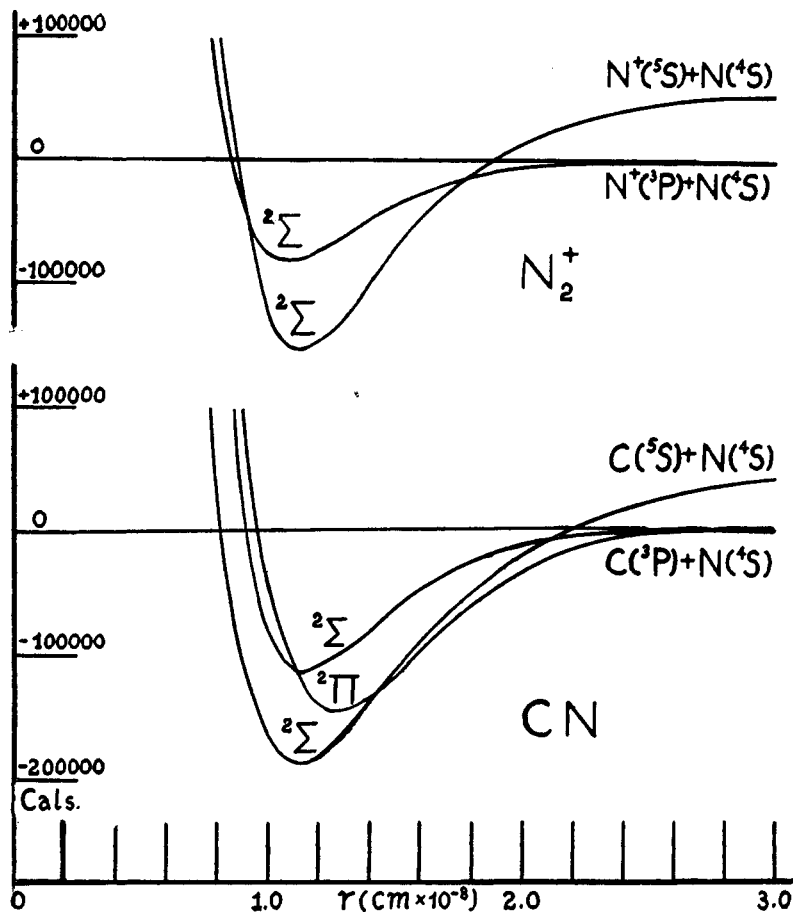


FIG. 6. CURVES REPRESENTING THE POTENTIAL ENERGY $U(r)$ OF THE TWO ATOMS AS A FUNCTION OF THE DISTANCE r BETWEEN THEM

The minimum in each curve is the equilibrium value (r_e) of r ; r_e is the distance between the nuclei for a molecule which is neither vibrating nor rotating. In a vibrating molecule, the vibrations take place between two values of r which correspond to two points of equal energy on the $U(r)$ curve. The exact forms of the $U(r)$ curves are not known except near $r = r_e$ and for $r \gg r_e$; the curves have been merely sketched in a plausible way for other values of r , but must not be considered as accurate. The curves shown represent only the known states of the molecule. Many other curves must exist, some of which must coincide asymptotically for large r_e with those shown in figure 6, but most of these doubtless represent unstable molecular states (shallow $U(r)$ curves with large r_e), or highly excited states.

Through an error, the position of the arrow heads in the case of the ϵ bands has been reversed. They should be at the top instead of at the bottom of the vertical lines indicating the ϵ band transitions.

The two other known states of CN are both formed from a normal nitrogen atom ($V = 3$) and a normal (3P) carbon atom ($V = 2$). Here only two valence bonds are formed, and the heats of formation (145,000 and 113,000 calories for the two states) are much less than for the normal state of CN. Comparing the two cases ($^3P + ^4S$ with $B = 2$ and $^5S + ^4S$ with $B = 3$), we see that the energy lost by exciting the carbon atom from its bivalent 3P to its quadrivalent 5S state is more than compensated by the additional energy gained in the formation of CN. Various other similar cases are known (45). In N_2^+ (44), for example, two $^2\Sigma$ states are known which are exactly analogous to those of CN, the lower (normal) state being derived from 5S excited N^+ plus normal N , the upper from normal (3P) N^+ plus normal N . The relations which are found in CN and N_2^+ are shown graphically in figure 6.

*Relations between atomic and molecular electron configurations;
bonding electrons*

A comparison of the electron configurations of various electron states of molecules with those of their atomic dissociation products suggests some interesting conclusions. Thus in the formation of normal N_2 from $N + N$ (see equation (23)), the correlation between atomic and molecular electrons is probably as follows (45):

$1s^2 + 1s^2$ (closed shells) of $N + N \rightarrow 1s\sigma^2 2p\sigma^2$ of N_2 (closed shells; the $2p\sigma$ electrons are promoted electrons)

$2s^2 + 2s^2$ (closed shells) of $N + N \rightarrow 2s\sigma^2 3s\sigma^2$ of N_2 (closed shells; the $3s\sigma$ electrons are promoted electrons)

$2p^3 + 2p^3$ (valence electrons) of $N + N \rightarrow 3p\sigma^2 2p\pi^4$ of N_2 (closed shells; the $3p\sigma$ electrons are promoted electrons)

The $3p\sigma$ and $2p\pi$ electrons in N_2 may according to this correlation be regarded as the bonding electrons (45), since they are electrons whose spins become paired off when the atoms unite.

In the formation of normal CO from $C + O$, the same relations as for N_2 hold in respect to the $1s^2$ and $2s^2$ atomic electrons ($1s\sigma^2$, $2p\sigma^2$, $2s\sigma^2$, $3s\sigma^2$ in CO). Of the atomic $2p$ electrons the

C atom has two which are valence electrons, while the O atom has four, of which two are valence electrons, while the other two already have their spins paired. These paired $2p$ electrons of the O atom perhaps give the $3p\sigma^2$ closed shell in CO, while the four valence electrons of C + O give the closed shell $2p\pi^4$ of CO (double bond).

In the various states of C + N (see table 2) we have again largely the same correlations, beginning with $1s^2 + 1s^2 \rightarrow 1s\sigma^2 2p\sigma^2$. In $C(^5S) + N(^4S) \rightarrow CN(^2\Sigma)$, we have the $2s$ valence electron of $C(^5S)$ appearing as a still unsatisfied $3s\sigma$ electron in CN, while the $2s^2$ closed shell of $N(^4S)$ appears as $2s\sigma^2$ in CN. The three $2p$ valence electrons in each atom give, as in the case of normal N_2 from $N + N$, the closed shells $3p\sigma^2 2p\pi^4$ (bonding electrons, triple bond). For the two excited states of CN formed from normal C + N ($^3P + ^4S$), we have in the one case ($^2\Pi$) $2p^2(C) + 2p^3(N) \rightarrow 3p\sigma^2 2p\pi^3$ and in the other ($^2\Sigma$) $2p^2 + 2p^3 \rightarrow 3p\sigma 2p\pi^4$. In the former case, two $3p\sigma$ and two $2p\pi$ electrons are the bonding electrons, the third $2p\pi$ electron being an unsatisfied valence electron corresponding to the third $2p$ electron of N. In the latter case, four $2p\pi$ electrons are the bonding electrons, while the one $3p\sigma$ electron is now derived from the third $2p$ electron of N.

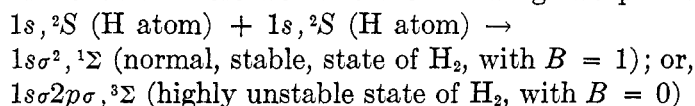
Possible molecular states, and stable molecular states

When two atoms in specified states unite, there are in general several different molecular states which may result. The number and nature of these can be predicted⁹ (42). Of these theoretically possible molecular states, however, in general only one or a few are stable enough to be observed chemically or even spectroscopically. Of the remaining unstable states, some could probably be observed under favorable conditions, while others may have only a momentary existence.

⁹ The possible molecular states resulting from the union of any two atoms in specified states can be definitely predicted (42) at present only in regard to the values of Λ and S , but not in regard to the detailed electron configuration. The problem of the determination of electron configurations has been considered by Hund and the writer (42) and by Herzberg (45), but is not yet finally solved.

Some examples will be helpful. In the union of a carbon atom and a nitrogen atom, each in its normal state (3P and 4S respectively) the theoretically possible states are a $^2\Sigma$, a $^2\Pi$, a $^4\Sigma$, a $^4\Pi$, a $^6\Sigma$, and a $^6\Pi$ state.⁹ Of these the first two are known from band spectra (see table 2 and figure 6); in these two we have $B = 2$, while in the quartet states ($^4\Sigma$ and $^4\Pi$) $B = 1$ and in the sextet states ($^6\Sigma$ and $^6\Pi$), $B = 0$ (see equation (27)). Thus the observed states, which are doubtless the most stable states, are just those in which the number of valence bonds is greatest, in agreement with the London and Heitler theory. In the case of $C(^5S) + N(^4S)$ —see table 2—the possible states are $^2\Sigma$, $^4\Sigma$, $^6\Sigma$, $^8\Sigma$.⁹ Of these, the first, with $B = 3$, is the normal state of the CN molecule; none of the others is as yet known, although it seems likely that the $^4\Sigma$ state, having $B = 2$, is fairly stable and may later be found.

A very simple example is that of two hydrogen atoms each in its normal state. This was the first case considered by Heitler and London. Here we have the following two possibilities:



As Heitler and London showed in their first paper (43) (14), two normal H atoms approaching each other in the manner required to give normal H_2 exert on each other a strong attraction until the two nuclei have approached to a small distance r_e (0.76×10^{-8} cm. for normal H_2) which corresponds to equilibrium.¹⁰ But if the two H atoms approach each other in the manner required to give the unstable $^3\Sigma$ state, they repel each other strongly at all distances, except for a slight van der Waals attraction at large distances. This van der Waals attraction should lead to an equilibrium at some large distance r_e , but the energy of formation for this state of H_2 is doubtless so small that this $^3\Sigma$ state is of negligible stability.

¹⁰ A normal H_2 molecule cannot, however, be directly formed as a result of a collision of two atoms, since it cannot radiate any part of its excess energy (energy of formation). For the actual formation of H_2 , some kind of a collision involving a third body is necessary. This limitation does not, however, apply to all molecules.

In more complex molecules analogous relations hold, except that in general there are a number of molecular states—some stable, some very unstable, others of intermediate stability, as in the example of C + N already discussed (42) (45). In the special case of two atoms, one of which is in a singlet state (as 1S , or 1P , or 1D), we have necessarily $B = 0$, corresponding to an unstable molecular state according to London and Heitler. Thus two normal helium atoms (both $1s^2, ^1S$) should give theoretically one molecular state (14) with $B = 0$ ($1s\sigma^2 2p\sigma^2, ^1\Sigma$), which, however, is without doubt very unstable, so that such molecules are not present in any appreciable numbers in helium gas. In many cases where $B = 0$, however, especially when only one atom is in a singlet state, we know experimentally that molecules of considerable stability can be formed. This may be attributed to the van der Waals forces, which apparently can be of decided importance in cases where the quantum valence forces of Heitler and London are lacking. (In polar molecules, of course, ionic attraction is of primary importance.) Thus normal Zn(1S) unites with normal H(2S) to give a normal ZnH molecule ($^2\Sigma$) with a heat of formation, according to band spectrum data, of 21,000 calories. Similar relations, in some cases with even larger heats of formation, exist for the diatomic hydrides of Be, Mg, Ca, Cd, Hg, etc. (46).

The simple theory of non-polar valence as developed by London and Heitler, according to which the stability of a molecule depends on the number of spin pairs formed, is the quantum equivalent of the Lewis theory of valence, but like the latter, is only a first approximation to a complete theory of the energy or stability relations which govern the formation of molecules.

Very much more might be said here about the applications of band spectra to chemical problems, but the object of this paper has been to give an illustrative and suggestive rather than an exhaustive treatment.

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