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THE HEAT OF DISSOCIATION OF NON-POLAR MOLECULES[1]

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Abstract

Heat of dissociation from band spectra data.—The limiting amount of vibrational energy which a diatomic molecule can possess is given by

$$E_n = h\int_o^{n_o} \omega^n dn,$$

where ω^n is the frequency of vibration, as a function of the vibrational quantum number n, and n_o is the value of n for $\omega^n = 0$. For *non-polar* molecules n_o is finite, for polar molecules it is infinite. The $\omega^n:n$ curve for the normal state of each of the molecules here discussed is strictly linear, over the known range, and its linear extrapolation to $\omega^n = 0$, *for essentially non-polar molecules*, seems to give the true value of E_n to within half a volt. Since increasing the vibrational energy until the two nuclei dissociate, results in the formation of two normal atoms, $E_n = D$, the heat of dissociation. When a molecule dissociates, while excited by E_e units of electronic energy, the products of dissociation seem in some cases to include at least one excited atom. The total energy required for the dissociation thus exceeds the true heat of dissociation by the amount of the resulting atomic excitation. The $\omega^n:n$ curves, and the correlated sets of energy levels are shown for all known band systems of O_2, O_2^+, N_2, N_2^+, CO, CO^+, and NO.

Oxygen. The $\omega^n:n$ curve of one excited state can be followed almost to $\omega^n = 0$, and the resulting limiting energy is 7.05 ± 0.01 volts. The situation is similar to that found in iodine. From the known structure of the oxygen atom, the products of dissociation are either two normal atoms, or one or two atoms excited with 0.02 or 0.03 volts energy. Hence $D = 7.02 \pm 0.05$ volts. The linear $\omega^n:n$ curve of the normal state gives 6.65 volts. For O_2^+ the normal state curve gives 6.46 volts, and the only known excited state curve, 6.49 volts. Knowing the heat of dissociation of an ionized molecule (D') and of a neutral molecule (D), and the ionization potential of the constituent atom (I_a), one can calculate the ionization potential of the molecule (I_m), since from conservation of energy, $I_m + D' = D + I$. For oxygen this gives $I_m = 14.1$ volts. $D' = 6.5$ volts is however probably too low, and $I_m = 14.1$ volts too high, according to recent work on the spectrum of O_2^+.

Nitrogen. From the energy of active nitrogen, D for N_2 is 11.4 volts. This value can be checked approximately, but not accurately, from band spectra data. The normal state of the nitrogen molecule is not known. D' is found to be about 9.1 volts, and I_m is 16.5 volts, giving $I_a = 14.2$ volts, compared to Hopfield's observed value of 14.5 volts. These results for oxygen and nitrogen are in satisfactory agreement with the positive ray work of Hogness and Lunn.

Carbon monoxide. $D = 11.2$ volts, from the $\omega^n:n$ curve of the normal state. Assuming our value of D for O_2 and certain chemical data, D for CO can be calculated as 10.8 volts. $D' = 9.8$ volts, from the spectral data. I_m is known to be closely 14.2 volts, and if CO^+ dissociates into $C + O^+$, $I_a = 13.56$ volts. The equation $I_m + D' = D + I_a$ checks to 0.3 volts.

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[1] A brief account of this work has been presented to the Amer. Phys. Soc.,—Abstracts No. 13, 14, 15, 16, of the March 1926 meeting. Phys. Rev. **27**, 640 (1926).

Nitric oxide. $D=7.9$ volts, from the normal state curve. Assuming our value of D for O_2 and for N_2, and certain chemical data, D for NO is 8.3 volts. From one of the excited state curves, the total limiting energy is 17.2 volts, indicating dissociation into one normal nitrogen atom and one 9.1 volt ("resoanance" state) excited oxygen atom.

General considerations. The possibility of the dissociation of a molecule adiabatically, by means of light absorption, is discussed and a tentative explanation given of the difference in behavior found in the positive ray analysis for oxygen and nitrogen. The various possible processes resulting in dissociation from excited molecular states are considered in the light of the evidence presented by the known sets of vibrational energy levels.

HEAT OF DISSOCIATION FROM BAND SPECTRA DATA

THE heat of dissociation of a diatomic molecule is defined as the energy necessary to separate the normal molecule into two stable atoms. If the actual process of dissociation results in the formation of one or more excited atoms, the energy of excitation must be subtracted, in order to obtain the true heat of dissociation.

Franck in a recent paper[2] has discussed the possible types of nuclear binding, in the case of homopolar molecules. One possibility is that the atoms of the molecule are bound together by van der Waals, or secondary, forces. In these molecules the electron orbits of the individual atoms still exist, but in a more or less disturbed state. Such molecules can be separated adiabatically into normal atoms. When they are excited by light, an electron of one of the atoms passes to a higher quantum orbit and the corresponding absorption frequency will be almost identical with a frequency found in the spectrum of the constituent atom. The loosely bound molecules Na_2, Hg_2, etc., belong to this type, and the molecular bands attach themselves closely to the atomic lines.

The second type of binding in homopolar molecules results in the appearance of quite new types of electronic orbits. For instance, certain electrons may be held in common by the two atoms of the molecule. Such molecules when in the normal state can very likely not dissociate into two atoms by an adiabatic process. The electron transitions necessary for the dissociation of these molecules cannot be caused by light absorption, but only by collisions.

Franck explains the unusual energy distribution of the absorption bands of iodine[3] (belonging to the first type of homopolar molecules) in terms of the large change in the value of the moment of inertia accompanying the electron excitation. He assumes that the two nuclei, as a result of the sudden electronic jump, are left at the same separation as

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[2] Franck, Trans. Faraday Soc. **21**, part 3 (1925).

[3] See Report of the National Research Council on "Molecular Spectra" (in press), Chap. IV., Fig. 16. In the future, this publication will be referred to as "Report."

before the jump, and that because of the large change in the equilibrium position, they suddenly "find themselves" with a large amount of potential energy which starts a large vibration. It should be pointed out that the major aspects of the intensity distribution in every known band system can be explained in this manner. Thus, in addition to the iodine bands, the Schumann ultraviolet bands of oxygen, the first negative group of oxygen (due to O_2^+) and the β bands of nitrogen (due to NO) have in the initial state (emission) a much smaller frequency of vibration than in the final state. It is, however, known that this condition is always correlated with a moment of inertia in the initial state which is much larger than that in the final state, and in the case of each of these band systems there is in fact found the peculiar intensity distribution best typified by the iodine bands. This distribution is such that a change from the non-vibrating state, $n''=0$ (in the absorption process) to a large value of n' is very probable.

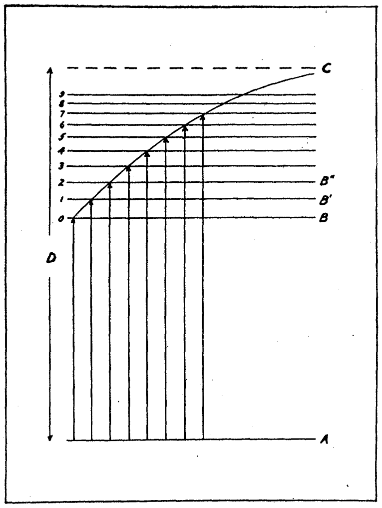

Fig. 1.

Dymond[4] has assumed that the result of the dissociation of iodine, when produced by light absorption, is one stable atom and one atom in a metastable P state, corresponding to about one volt of excitation. The details are as follows. The apparent value of the heat of dissociation D can be determined from the high frequency limit of a progression of absorption bands indicated on the usual energy level diagram in Fig. 1. In this figure A represents the stable (non-vibrating) state of the molecule, and B an electronic (but non-vibrating) excited state. B', B'', etc., represent the successive vibrational states for this same electronic excited state,

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[4] **Dymond, Zeits. f. Physik 34, 553 (1925).**

the values of the vibrational quantum number n being indicated at the left of the levels.

Now as is well known, the separation of any two energy levels, differing by one unit in a given quantum number, gives some mean value of the correlated classical frequency for the two energy states in question.[5] In the case of vibration the law of variation is such that this separation equals ω^n, the frequency of vibration corresponding to the arithmetic mean value of n for the initial and final levels. For an elastic vibrator the levels should be equally spaced. Actually the spacing decreases, and the bands can be followed, in the case of iodine, until the separation is too small for resolution, i.e., until ω^n is almost zero. Continuous absorption sets in for frequencies greater than AC where C is the energy level obtained by the actual extrapolation to $\omega^n=0$. Evidently at C the molecule is dissociated, and Dymond proved this by showing an absence of fluorescence for all portions of the region of continuous absorption, in contrast to its presence in the region of discontinuous absorption. The total energy required for the dissociation is represented by AC, and for iodine this equals 2.47 volts.[6] But the value of D as measured chemically is about 1.5 volts, and the difference is assumed by Franck and Dymond to represent the energy of excitation of one of the iodine atoms. This is probable since the valence level of the iodine atom should be a double P level of about one volt separation.[7]

In iodine the point of dissociation was obtained by a very short extrapolation of the observed progression of bands, and also by the beginning of continuous absorption (the two methods agreeing with great accuracy). But it seems possible to evaluate BC even with a rather long extrapolation of the vibrational energy levels. Kratzer's expression for ω^n as a function of n is

$$\omega^n=\omega^0-2\times\omega^0 n+\cdots \tag{1}$$

Now as shown by Fig. 4 ahead, in many progressions the $\omega^n : n$ curve is

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[5] This follows from Eq. (2) ahead, since ΔE_n $(=E_{n+1/2}-E_{n-1/2})$ is very closely $\partial E/\partial n$.

[6] Calculated from the limit of continuous absorption (20,020 cm^{-1}) as given by Mecke, Ann. d. Physik **71,** 104 (1923). One volt $=8100$ $\text{cm}^{-1}=$ 23, 070 gram calories per gram mol.

[7] Turner, Phys. Rev. **27,** 397 (1926) has recently obtained a recurring doublet separation in iodine of 7600 cm^{-1} $(=0.94$ volts) which he interprets as an accurate measure of this interval. This yields $2.47-0.94=1.53$ volts for the heat of dissociation. In this connection it might be noted that the chemical value of 1.5 volts is taken from the work of Starck and Bodenstein (Zeit. f. Elektrochem. 16, 961, 1910). Dr. E. Condon has called our attention to the fact that this work was performed at an average temperature of 1000°C, and that these investigators made no correction for the average amount of vibrational energy at this temperature (0.10 volts). Hence their true result is more correctly 1.6 volts.

strictly linear over the experimental range. In others the slope increases in absolute magnitude as n increases (corresponding to additional *negative* terms in Eq. (1)), while very rarely it decreases in magnitude. We call the first a negative deviation from linearity, the second a positive. ω^n is calculated from the very fundamental equation

$$\omega^n = \frac{1}{h} \frac{\partial E}{\partial n} \tag{2}$$

Hence the limiting value of the vibrational energy (BC of Fig. 1) is given by

$$E_n = h \int_0^{n_0} \omega^n \, dn \tag{3}$$

where $\omega^n = 0$ for $n = n_0$. Tartakowsky[8] attempted to get a theoretical expression for n_0. Kratzer[9] pointed out the error in his work, and obtained the following results. If the law of force (of the atomic binding) is a power series, in terms of the nuclear separation r, and if the first term in the region of large values of r is an inverse square or inverse third power, then E_n is finite, but n_0 is infinite. This is the situation in the case of polar molecules (inverse square law for very large nuclear separation). The $\omega^n : n$ curve becomes asymptotic to the n axis with increasing n. This is shown schematically in Fig. 2, curve (a). The slope may first decrease, but if so a point of inflection is reached and the curve then

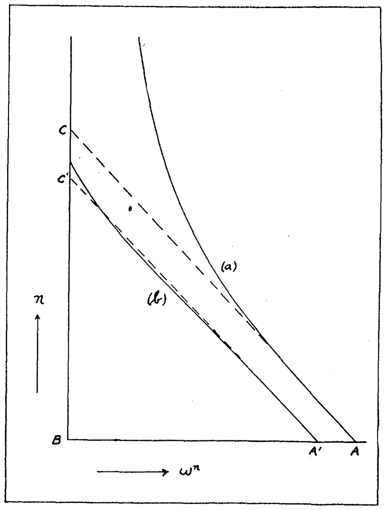

Fig. 2.

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[8] Tartakowsky, Zeits. f. Physik **24,** 98 (1924).

[9] Kratzer Zeits. f. Physik **26,** 40 (1925).

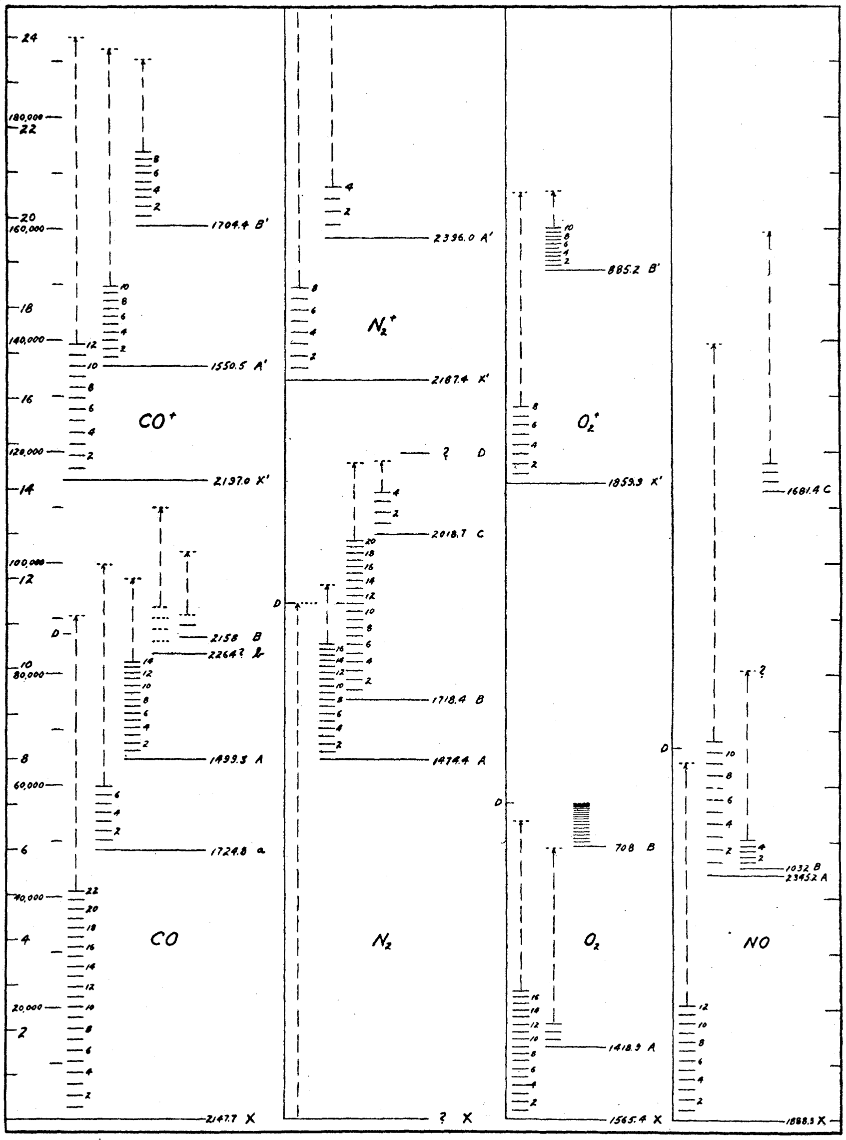

Fig. 3. Electronic and vibrational energy levels of certain molecules

The designations (X, A, B etc) of each electronic level are purely arbitrary. The probable true quantum designation according to Birge (Nature 117,300, 1926) and the curve of Fig. 4 giving the ω^n values for each of these levels are as follows.

CO $X = 1^1S$ = curve 21′, 22′.
$a = 1^3P$ = curve 11′, 22.
$A = 1^1P$ = curve 5′, 21.
$b = 1^3S$ = curve 11.
$B = 2^1S$ = curve 5.

CO^+ $X' = 1^2S$ = curve 6′, 7′.
$A' = 1^2P$ = curve 7, 8′.
$B' = 2^2S$ = curve 6, 8.

N_2 $X = 1^1S$ ω^n unknown.
$A = 1^3P$ = curve 14′.
$B = 1^1P$? = curve 13′, 14, 15′.
$C = 2^3P$ = curve 13.
$D = 3p^3$? no vibration known.

N_2^+ $X' = 1^2S$ = curve 16′.
$A' = 2^2S$ = curve 16

O_2 X = ? = curve 20′.
A = ? = curve 19.
B = ? = curve 20.

O_2^+ $X' = 1^2P$ = curve 18′.
$B' = 1^2D$ = curve 18.

NO $X = 1^2P$ = curve 1′, 2′.
$A = 1^2S$ = curve 2, 17′.
$B = 1^2D$ = curve 1.
C = ? = curve 17.

The known band systems connected with these electronic levels are

CO	$A - X$	Fourth positive group of C.
	$a - X$	Cameron CO bands
	$B - A$	Angstrom CO bands.
	$b - a$	Third positive group of C.
CO^+	$A' - X'$	Comet-tail bands.
	$B' - X'$	First negative group of C.
	$B' - A'$	"Combination" bands of Baldet-Johnson.
N_2	$A - X$	Predicted ultraviolet bands of N_2.
	$B - A$	First positive group of N_2.
	$C - B$	Second positive group of N_2
	$D - B$	Fourth positive group of N_2
N_2^+	$A' - X'$	First negative group of N_2.
O_2	$A - X$	Atmospheric bands of O.
	$B - X$	Schumann-Runge bands of O.
O_2^+	$B' - X'$	First negative (ultraviolet) bands of O.
NO	$A - X$	Third positive group (γ bands) of N_2.
	$B - X$	β bands of N_2.
	$C - A$	Ultraviolet (Lyman-Birge-Hopfield) bands of N_2.

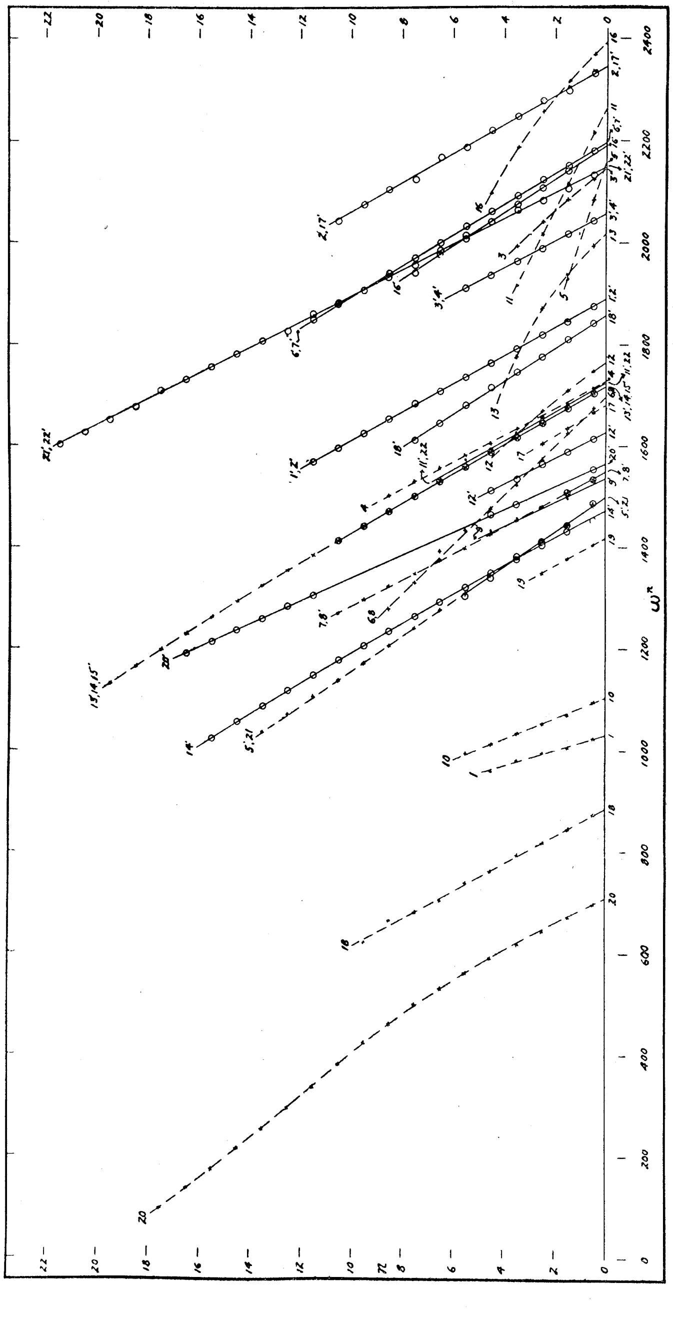

Fig. 4. Frequency of vibration of certain molecules. The frequency of vibration (ω^n) is plotted as a function of the vibrational quantum number n, for every known electronic state of all diatomic molecules composed of oxygen, nitrogen, and carbon, and their combinations. See caption of Fig. 3 for further details.

turns upward. If, however, the series begins with a fourth or higher power of the force, then both D and n_0 are finite. This means that even if the $\omega^n:n$ curve turns upward, it runs into the n axis. This is illustrated in Fig. 2, curve (*b*). Now a homopolar molecule, for which the forces at large nuclear separation are due largely to polarization effects, is likely to have as a law of force for such large separations one beginning with a high inverse power, such as possibly the ninth.

This theoretical work by Kratzer indicates that it is not possible to obtain from band spectra data any reliable estimate of the heat of dissociation, in the case of polar molecules which separate into two ions, such as HCl, but it holds out the possibility of obtaining such a result in the case of non-polar molecules, especially when the observed $\omega^n:n$ curve is strictly linear over a considerable observed range. The following experimental results support these deductions.

As an example of polar molecules, we may take HCl. Its $\omega^n:n$ curve is known only to $n=3$ but it has definitely a negative curvature. Even if this curvature is disregarded, and a linear extrapolation made, using the slope at $n=0$, a value of E_n of only 5 volts is obtained. Hund,[10] and Kemble,[11] considering the law of force for large nuclear separation, as well as the band spectra data, obtained much larger values (13.7 and 10.9 volts respectively).

OXYGEN

As an example of homopolar molecules, let us first consider oxygen. The known energy levels of this molecule as well as of other more or less non-polar molecules, are shown, plotted to scale, in Fig. 3. The $\omega^n:n$ curves for all of the sets of levels shown in Fig. 3, as well as certain others, are given in Fig. 4. This latter figure is taken from Chap. IV (Fig. 12) of the Report on Molecular Spectra, and gives all of the known $\omega^n:n$ curves for diatomic molecules consisting of carbon, oxygen, or nitrogen, and their combinations. Each electronic energy level in Fig. 3 is given an arbitrary designation, following the system used by Birge,[12] and the relation of the curves of Fig. 4 and the levels of Fig. 3 is given in the caption of Fig. 3, together with other information. The spectroscopic data used in the preparation of Fig. 3 are indicated briefly in the present communication. They will be given in detail in separate articles, in the

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[10] Hund, Zeits. f. Phys. **32,** 1 (1925).

[11] Kemble, Jour. Opt. Soc. Amer. **12,** 1 (1926).

[12] Birge, Nature **114,** 642 (1924), for N_2; Nature **117,** 229 (1926), for CO and CO^+.

near future.[13] The scale on the left side of Fig. 3 is in wave-numbers (cm^{-1}) running from 0 to 200,000, and in volts, running from 0 to 24. The level X in each case represents the stable (i.e., normal) state of the neutral molecule. The level X' represents the stable state of the ionized form, so that $X'-X$ equals the ionization potential of the molecule, which we designate I_m. The sources of information for these values will be given presently. Obviously the $X'-X$ interval is not known with any real accuracy in any case but all other intervals, such as $A'-X'$, or $A-X$, are known with considerable accuracy from band spectra data. Finally, at the right of each electronic level there is given, in addition to its letter designation, the value of ω^0, the frequency of vibration for infinitesimal amplitude for that particular electronic configuration.[14]

The most interesting band system in the case of oxygen is the Schumann[15] ultraviolet absorption bands. Hopfield and Leifson[16] have observed new bands for this system, and Leifson[17] has made fairly accurate measurements of these new bands. We have since found that these bands form a continuation of the $n''=0$ progression, using the recent interpretation of this system by Füchtbauer and Holm.[18] The distribution of intensity is, as already noted, precisely similar to that found in the iodine bands, and for that reason the intensity decreases as n' decreases, in the $n''=0$ progression. (n' refers to the excited, n'' to the less excited or normal state.) Hence it is difficult to decide, from observations merely on the absorption spectrum, what are the true values of n'. The question has now been answered by Dr. R. S. Mulliken (private communication) who finds that the Runge emission bands of oxygen[19] are merely a portion of this same band system. The bands actually measured by Runge correspond to $n'=0$, $n''=11$ to 17. There are, however, other bands on Runge's plates, stretching into the violet and evidently corresponding to smaller values of n'' of this same progression (the bands to be expected *in emission* for a source at low temperature).[20] This discovery shows that

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[13] For brief preliminary accounts see Birge, Phys. Rev. **23**, 294 (1924) and Nature **114,** 642 (1924) for N_2; Nature **117,** 229 (1926) for CO; Nature **116,** 171 and **207** (1925), for CO^+; Sponer, Nature **117**, 81 (1926), Sponer and Hopfield, Phys. Rev. **27,** 640, Abstract No. 10, (1926), and Birge and Hopfield, Nature **116,** 15 (1925), for NO; Ellsworth and Hopfield, **27,** 639, Abstract No. 9, (1926) for O_2^+.

[14] In the case of the B' level of CO^+, 1697.8 is a slightly better value than 1704.4. Similarly for A' of N_2^+, 2392.3 is better than 2396.0.

[15] Smithsonian Contributions to Knowledge, **29,** No. 1413 (1903).

[16] Hopfield and Leifson, Phys. Rev. **25,** 716 (1925).

[17] Leifson, Astrophys. J. **63,** 73 (1926).

[18] Füchtbauer and Holm, Phys. Zeits. **26,** 345 (1925).

[19] Runge, Physica 1, 254 (1921).

[20] See Report, Chap. IV. section 4, for further details.

the n' numbering used by Füchtbauer and Holm is actually two units too low. Using Runge's measurements of the emission bands, and also all available data on the absorption bands, we find that the entire system can be represented by[21]

$$\nu=49,359.3+(708n'-13n'^2-\cdots)-(1565.37n''-11.37n''^2) \qquad (4)$$

where Leifson's measured bands run to $n''=0$, $n'=18$, the bands from $n'=9$ to 18 being new. The $f(n')$ is given by curve 20 of Fig. 4, and as is immediately evident from the figure, a complex function would be needed for an accurate representation. A precisely similar curve occurs for the excited state of the iodine bands.

Assuming such an extended $f(n')$, Eq. (4) represents the above noted bands and also the $n''=1$ progression of Füchtbauer and Holm. The relative frequencies of their other progressions are also represented, but according to the above equation all are slightly displaced. This is due probably to the fact that another instrument was used for these additional (high-temperature) progressions.

In further analogy to iodine, there occurs on Leifson's plate a region of strong continuous absorption, at the head of the discontinuous progression of bands $n''=0$. Curve 20 of Fig. 4 indicates that the position of this point can be obtained with great accuracy, and in fact a smooth extrapolation of this curve to $\omega^n=0$ $(n=21)$, gives $E_n=0.81\pm0.01$ volts. The electronic excitation ($B-X$ of O_2, on Fig. 3) is 6.24 volts, and the total energy required for dissociation is therefore 7.05 ± 0.01 volts. In other words, the beginning of continuous absorption is at λ1751, five Angstrom units (or 0.02 volts) beyond the last measured band. These relations yield immediately a fairly accurate value of the true heat of dissociation of O_2, for in the case of the oxygen atom, we have exact information as to the energy levels. Hopfield[22] has shown that the valence level of oxygen consists of a triple P level, of spacing 0.01 and 0.02 volts. The next level represents 9.1 volts of energy. Hence we may assume, in analogy to iodine, that the electronic excited oxygen molecule, in state B, dissociates into one stable atom and one atom in a metastable P state. But whereas in iodine this metastable state is about one volt above the lowest level, in oxygen it is at the most 0.03 volts above. Hence the most probable value of the true heat of dissociation D of oxygen

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[21] In equation (4) all frequencies are expressed, as usual, in wave-numbers (cm^{-1}). The coefficient of the first power term in n equals ω^0, the frequency of vibration for infinitesimal amplitude, while the coefficient of the second power term in n equals $\omega^0 x$, or one-half the rate of variation of ω^n with n. (Compare Eq. (1)).

[22] Hopfield, Astrophys. J. **59**, 114 (1924). See also O. Laporte, Naturwiss. **12**, 598 (1924).

is $7.05-0.03$, or $7.05-0.02$ volts. If *both* atoms are excited the least possible value of D is $7.05-0.06$ volts. If both are stable, it is 7.05 volts. It would seem that we are certainly justified in assuming that D is 7.02 ± 0.05 volts.[23]

Let us now consider the stable state of the oxygen molecule. The $\omega^n:n$ curve is known from $n''=0$ to $n''=17$ (with certain points now missing, as already mentioned, and as shown in curve 20′ of Fig. 4). It is linear over this range and using the constants of Eq. (4), we obtain

$$n_0=\frac{1565.37}{2\times 11.37}=68.81, \text{ and } E_n=\frac{1565.37\times 68.81}{2}=53{,}856 \text{ cm}^{-1}, \quad \text{which}$$

divided by 8100 gives 6.65 volts.[24] This should be the true heat of dissociation, if the extrapolation is correct, and the discrepancy of 0.4 volts with the previous value may be taken as an indication of the probable error of such an extrapolation. From state A, a similar extrapolation gives $E_n=4.43$ volts, which added to the electronic energy $E_e=1.62$ volts (i.e., A-X) gives 6.05 volts, compared to the previous 7.05 volts. In this case, however, the known $\omega^n:n$ curve (No. 19 of Fig. 4) is so short that no reliance can well be placed on the result.

Turning now to O_2^+, we find but two known levels, both associated with the first negative group of oxygen. Johnson[25] has made the most extensive measurements of this system, and Mecke[26] and Birge[27] independently made quantum assignments which differed slightly from each other, and from Johnson's arrangement. The uncertainty is due to the intensity distribution which, as already noted, is similar to that for the iodine bands, and for the Schumann oxygen bands. The proportional change in ω^0 for this system is in fact greater than in any other known system. The energy levels of Fig. 3 and curves 18 and 18′ of Fig. 4 are based on the $n'n''$ assignment assumed by Birge, which leads to the equation

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[23] It is of interest to note that this new value of D checks the rough estimate of 7 volts, made by Born and Gerlach (Zeits. f. Physik. **5**, 433 (1921) from the observed long wave length limit of the photochemical formation of ozone from oxygen. On the other hand it disagrees with Eucken's estimate of 18.4 volts (Liebig's Ann. d. Chemie **440**, 111 (1924). Prof. Eucken has since changed this estimate to 9.1 volts. as Prof. Grimm has kindly informed one of us.

[24] Throughout the paper we record results such as this to 0.01 volt, even though they cannot be trusted, as far as a value of the heat of dissociation is concerned, to less than 0.5 volt.

[25] Johnson, Proc. Roy. Soc. **105A**, 683 (1924).

[26] Mecke, Phys. Zeits. **26**, 217 (1925).

[27] Birge, Phys. Rev. **25**, 240 (1925).

$$\nu = \left.\begin{matrix}38,308\\38,108\end{matrix}\right\} + (885.23n' - 13.7n'^2) - (1859.86n'' - 16.53n''^2) \qquad (5)$$

The $\omega^n : n$ curve of the stable (X') state is linear from $n''=0$ to 8 (No. 18′ of Fig. 4). Its linear extrapolation gives $D'=6.46$ volts, the heat of dissociation of the ionized oxygen molecule. The excited state B', in spite of the low value of ω^0, also gives a linear curve (No. 18) and from it we obtain $E_n=1.76$ volts, $E_e=4.73$ volts, and hence $D'=6.49$ volts. Evidently, as in the case of O_2, the products of dissociation, even from an excited molecule, may be two stable atoms, or at the most two but slightly excited atoms. The valence level of O^+ is probably an S level of the quartet system and therefore single.[28] The next level may safely be assumed as at least several volts higher. This is outside the limits of error, and we may therefore conclude that $D'=6.5$ volts, with a possible error of a few tenths of a volt.

Values for the heat of dissociation of a neutral and an ionized molecule may be correlated with ionization potentials in the following manner. If three of the following four quantities are known,

D = dissociation heat for the neutral molecule
D' = dissociation heat for the ionized molecule
I_m = ionization potential for the neutral molecule
I_a = ionization potential for the neutral atom;

the fourth can easily be calculated. Thus a process $O_2 \rightarrow O + O^+$ can theoretically occur in two ways, i.e., first by ionizing the molecule and then dissociating it, or first by dissociating the molecule and then ionizing one of the atoms. Hence by conservation of energy

$$I_m + D' = D + I_a \qquad (6)$$

With the value $I_a=13.56$, known from Hopfield's work, we obtain

$$I_m + 6.5 = 7.02 + 13.56 \qquad (7)$$

or $I_m=14.1$ volts. This gives the X'-X interval for oxygen, and was used in plotting Fig. 3.

Ellsworth and Hopfield[29] have recently measured a number of additional bands of the first negative group of oxygen. These new bands fit into the $n'n''$ assignments as given by Birge, but would be excluded by Mecke's assignment. In addition, however, they observe one more n' progression of bands, lying still further to the violet, and there are indications of additional progressions. All of these are too faint to measure. The addition of such new progressions, in Fig. 3, would not

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[28] See Fowler, Proc. Roy. Soc. **110A**, 476 (1926).
[29] Ellsworth and Hopfield, Phys. Rev. **27**, 639 (A) 1926.

affect any of the levels as now drawn, but would merely add one or more additional vibrational levels *below* level X' of O_2^+. In other words the present level marked X' does not correspond to $n''=0$, but rather to $n''=1$ or even several units higher. The true value of $\omega^{0''}$ is therefore somewhat higher than 1859.9.

This change would make D' *greater* and I_m *less*, by just these added levels (about 0.23 volts per added level). Therefore the true ionization potential of the neutral oxygen molecule may be several tenths of a volt less than 14 volts. Now Hogness and Lunn[30] have made the most recent measurements of the voltage at which O_2^+ ions and O^+ ions first appear, in the positive ray analysis of oxygen. They find that these two types of ions are produced each by a primary process, at 13 volts and 20 volts respectively. The limit of error is at most one volt in each case. Hence an O_2 molecule can be dissociated directly into O and O^+, and by Eq. (7) the required amount of energy is 20.58 volts, as compared to the Hogness and Lunn value of 20 ± 1, while an O_2^+ ion can be produced directly at 13 ± 1 volts, as compared to our value of 14.1 volts which as just noted is probably quite a little too high. The agreement is very satisfactory.[31]

NITROGEN

We next consider the nitrogen molecule. Three band systems of N_2 and one of N_2^+ are known, as stated in the caption of Fig. 3. But these systems determine only the levels A, B, C, D, X' and A'. The level X is evaluated from Sponer's[32] measurements of the excitation potentials of the various known band systems. This gives for the interval A-X, 8.0 ± 0.3 volts. The interval X'-X is known both by ionization potential measurements,[33] giving about 16.9 volts as the most probable value, and from Sponer's measurement of the excitation potential of the first negative bands of nitrogen (giving $B'=19.6 \pm 0.3$ volts, $X'=16.5 \pm 0.3$ volts). Sponer's value has been used for Fig. 3.

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[30] Hogness and Lunn, Phys. Rev. **27**, 642 (A) (1926) and **27**, 732 (1926).

[31] It is thus evident that these two critical potentials measured by positive ray analysis give I_m and I_m+D'. If then I_a is known from other sources, equation (6) can be used to determine D. This has been carried out by Grimm (Zeits. f. Elektrochem. **31**, 474 (1925) for oxygen and nitrogen, using for I_m+D' the older positive ray results of Smyth (Proc. Roy. Soc. **105A**, 116 (1923), and **104A**, 121 (1923), and independently by Sponer (Naturwiss. **14**, 275 (1926) for the same two molecules, using the newer values of Hogness and Lunn (see Phys. Rev. **26**, 786 (1925), for nitrogen).

[32] Sponer, Zeits. f. Phys. **34**, 622 (1925).

[33] See p. 119, Report on "Critical Potentials" of the National Research Council, by Compton and Mohler.

The strongest bands observed in the afterglow of "active nitrogen" correspond to transitions from the level $n=11$, of electronic level B of neutral nitrogen.[34] Sponer (loc. cit.) by assuming that active nitrogen is atomic nitrogen, has concluded that the energy value of this level (i.e., its height about level X) measures the true heat of dissociation of N_2. This value is 11.4 volts, and may be assumed as a fairly correct evaluation of D.[35] The limiting values of the electronic plus vibrational energy, for levels A, B, and C are shown on Fig. 3.

The vibrational levels of set A are given by

$$E=1474.37n-13.982n^2+0.02134n^3-0.001721n^4-0.000,0277n^5 \tag{8}$$

according to the analysis by Birge.[36] The analytic extrapolation of the corresponding $\omega^n:n$ curve (No. 14′ of Fig. 4) to $\omega^n=0$ gives $E_n=3.88$ volts. The total energy is therefore $8.0\pm3.9=11.9$ volts. Similarly set B is given by

$$E=1718.40n-14.437n^2-0.001,473n^3-0.000,0605n^4-0.000,0296n^5 \tag{9}$$

and the extrapolated energy is 5.27 volts, which added to the 9.35 volts of electronic energy gives 14.62 volts. Only five levels are known for set C and the great curvature of the $\omega^n:n$ graph (curve 13 of Fig. 4) can be represented only by using enough constants to pass the curve through every point. The resulting energy equation is

$$E=2018.67n'-26.047n'^2+0.9873n'^3-0.546n'^4 \tag{10}$$

and the extrapolated value of E_n is 1.64 volts, the total energy being 14.64 volts. Level D lies at 14.8 volts, and no actual vibration is known indicating an especially unstable state of the molecule. In fact it is possible to get the fourth positive group of nitrogen (D-B transition) only with certain limited experimental conditions.

In the case of N_2^+, the stable level is given by a linear $\omega^n:n$ curve (No. 16′ of Fig. 3) and the excited level A' by a slightly negative curve (No. 16). The entire system, using mainly the data of Merton and Pilley[37] is given by

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[34] See Birge, Nature **114,** 642 (1924), and **117,** 81 (1926).

[35] This disagrees with the value of 19.1 volts given by Eucken (loc. cit), obtained from specific heat data. He has since revised this value to 16.5 volts which agrees quite closely with the value of 15.9 volts obtained by Grimm (loc. cit) from positive ray analysis. In this work by Grimm, he used for I_a a value of 11.8 volts obtained by interpolation of the L_{III} Moseley diagram, (Fig. 14 of Report on "Critical Potentials") and for I_m+D' the results of Smyth, as already noted.

[36] Birge, Phys. Rev. **23,** 294 (1924).

[37] Merton and Pilley, Phil. Mag. **50,** 195 (1925).

$$\nu=25,565.9+(2392.3n'-22.8n'^2-\cdots)-(2187.4n''-16.3n''^2) \qquad (11)$$

The extrapolated value of the vibrational energy, from level X', is 9.06 volts and this may be a reasonably accurate determination of the heat of dissociation D' of N_2^+. The level A', because of the short and curved character of the $\omega^n:n$ graph yields a very uncertain value of the extrapolated energy. Assuming a parabola for curve 16, the value of $E_n=3.6$ volts. Using only the first two terms of the parabola, as given in Eq. (11), the value of E_n is 7.7 volts. These may be taken as upper and lower limits. The electronic energy is 3.16 volts, and $E_e+E_n=6.8$ or 10.9 volts, compared to 9.1 obtained from level X'.

Assuming that D is 11.4 volts, and D' is 9.1 volts, we may use Eq. (6) to determine I_a. For the sake of consistency we should use Sponer's value of 16.5 volts for I_m, rather than 16.9 volts, since $D=11.4$ volts is taken from the same measurements by Sponer. Hence

$$16.5+9.1=11.4+I_a \qquad (12)$$

or $I_a=14.2$ volts. Now Hopfield[38] has recently found the ionization potential of the nitrogen atom to be 14.49 volts. Considering the uncertainty in each of the figures of Eq. (12), this is a satisfactory agreement. These figures seem to show that, if N_2^+ and N^+ ions are each produced as a primary process, as in the case of O_2^+ and O^+ ions, the required potentials should be about 16.5 and 25.6 volts respectively. Hogness and Lunn[31], in their work on the positive ray analysis of nitrogen find these voltages to be 17 and 24, respectively (each ± one volt) but the formation of N^+ ions they find to be a *secondary* and not a primary process. A preliminary interpretation of these results has already been made by one of us[39] as already noted. With the new results of Hopfield for I_a we can give a more detailed discussion. The first value of 17 volts, for the production of N_2^+ ions agrees well with the previous direct observations of I_m already cited. Since the second critical voltage should give always I_m+D', the difference is a direct measure of D'. This difference is 7 volts, as compared to our value of 9 volts, and appears to be outside the limits of error. The *relative* values of I_m and D, used in Eq. (12), should be much more accurate than either one, since both are taken from Sponer's measurements. Hence

$$16.5-11.4=5.1=I_a-D'. \qquad (13)$$

If I_a is 14.5 volts as found by Hopfield, D' is 9.4 volts. If D' is only 7 volts, as results from the Hogness and Lunn values, I_a is 12.1 volts.

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[38] Hopfield, Phys. Rev. **27**, 801(A), 1926.

[39] Sponer, Naturwiss. **14**, 275 (1926).

Now the deepest level of the nitrogen atom found by Hopfield is an S level of the quartet system, at 14.49 volts, while the next level is the S level of the doublet system, at 12.1 volts. If there are *no* transitions between the quartet and the doublet system, there is a possibility that 12.1 volts represents one valence level, and that another type of electron lies in the 14.5 volt level, and may independently be removed. The reason why N^+ is formed as a secondary process, while O^+ is formed as a primary process, will be considered later. The discussion of the possible products of dissociation for the A, B, C, and D levels of N_2 is also best postponed in order that all available data may be considered collectively.

Carbon Monoxide

Taking up next the CO molecule, we find five known electronic levels. The facts regarding the X, A, and B levels are due to Birge[40] who gave the $n'n''$ assignments for the fourth positive group of carbon, and the Angstrom CO bands. The appearance of the expected portion of the fourth positive group, on Leifson's[17] absorption spectrum proves beyond question that X is the stable level of the CO molecule. R. C. Johnson[41] has recently been able to obtain the quantum interpretation of the new Cameron bands[42] and of the third positive group of carbon, thus establishing two additional electronic levels (a and b) for CO. In the case of the Cameron bands, the essential n' progressions for $n''=1$ and $n''=0$ were not observed, but by using the results of Birge for the fourth positive group, Johnson was able to show that in all probability the two band systems have a common final state. In this case the n' progression for $n''=0$, of the Cameron system (whose calculated wave-lengths are λλ2060.4, 1990.2, 1925.3, 1866.1, etc.) should appear on Leifson's absorption plates. They do not, however, appear and it is thus evident that the X-a transition is much less probable than the X-A transition. Johnson also proved beyond question that the excited state of the Cameron bands (level a) is identical with the final state, for emission, of the third positive group of carbon.

There is some doubt as to the number of vibrational levels known for states b and B. In the case of the Angstrom CO bands the n'' progression for $n'=0$ (λλ4511, 4835, 5198, 5610, etc.) and for $n'=1$ (λλ4123, 4393, 4698, 5016, etc.) certainly exist.[43] But the few faint bands assigned to

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[40] Birge, Nature **117**, 229 (1926).

[41] Johnson, Nature, **117**, 376 (1926).

[42] Cameron, Phil. Mag. (7) **1**, 405 (1926).

[43] See Kayser's Handbuch, Vol. V. pp. 227-228 for older list of wave-lengths, and Hulthén, Ann. d. Phys. **71**, 41 (1923) and McLennan and Smith, Trans. Roy. Soc. Canada (3) **19**, 39 (1925) for later measurements. Also spectra Nos. 269 and 279 of Hagenbach and Konen, Atlas der Emissions-spektren, for a good low dispersion photograph. The printed scale on 279 should be shifted 100A to the right.

the $n'=2$ progression (λλ4301, 4581, 4901, 5281, etc.) may be only accidental clusters of lines of other bands. Hence we mark this $n'=2$ level with a dashed line. Similarly the vibrational levels for set b are drawn from the data by Deslandres.[44] The work of Wolter[45] shows quite clearly, however, that only the $n'=0$ progression of the third positive group of carbon actually exists. We have accordingly indicated these spurious levels by dashed lines.

Turning now to the evaluation of the heat of dissociation, we find for level X a strictly linear $\omega^n:n$ curve known over the unusually long interval $n=0$ to 22. (Curve 21′, 22′, of Fig. 4.) Its extrapolated area equals 11.18 volts. This value of the heat of dissociation of carbon monoxide can be checked from other known data as follows.

Let C_g represent carbon in the gaseous state, and C_s carbon in the solid state. Then

$$C_s+O_2=CO_2+94{,}430 \text{ calories.}^{46} \tag{14}$$

$$CO+1/2\ O_2=CO_2+67{,}960^{46} \tag{15}$$

$$O_2=O+O-161{,}950^{47} \tag{16}$$

$$C_s=C_g-141{,}000^{48} \tag{17}$$

From these four equations, one obtains

$$CO=C_g+O-248{,}445 \text{ calories} \tag{18}$$

or $D=10.8$ volts.[49] This value should be fairly accurate and again shows that the extrapolation of the $\omega^n:n$ curve for the stable state is likely to give a result in error by several tenths of a volt.

As is shown in Fig. 3, the extrapolation of the $\omega^n:n$ curves from other levels gives values varying from 12.0 to 12.6 volts (excluding the b levels which as noted are undoubtedly spurious). But the extrapolation for the B level is possible only by assuming that $n'=2$ is a real level, and this seems doubtful. The $\omega^n:n$ curve for level a (No. 11′, 22) is very poor,

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[44] See p. 233, Vol. V, of Kayser's Handbuch for data.

[45] Wolter, Zeit. wiss. Phot. **9**, 36 (1911). See also Birge, Nature **116**, 170 (1925).

[46] Landolt-Börnstein p. 1497, 1923 (from Thomsen's investigations.)

[47] Assuming our value of the heat of dissociation of oxygen (7.02 volts = 161,950 calories).

[48] H. Kohn and M. Guckel, Naturwiss. **12**, 139 (1924). This value of the heat of sublimation of diamond is the final result of a long series of observations, and should be quite accurate.

[49] Eucken (loc. cit.) gives 18.0 volts for this quantity, and his corrected value is 14.3 volts.

and so the extrapolated energy of 12.3 volts is very uncertain. Only in the case of level A is there a trustworthy $\omega^n:n$ curve (No. 5′, 21), yielding 12.0 volts for the heat of dissociation, if the products of dissociation are stable atoms. We have no information as to the energy levels of the carbon atom, except that the valence level should theoretically be a triple P level of small separations, as in the case also of the oxygen atom, the other product of dissociation.

For CO^+ there are three known levels.[50] The stable X' level yields as usual a strictly linear $\omega^n:n$ curve (No. 6′, 7′) and a long extrapolation gives $D'=9.82$ volts. The B' level also has a linear $\omega^n: n$ curve (No. 6, 8), according to Johnson's[51] new data for the first negative group of carbon. These data give for the B' level

$$E=1697.8n-24.33n^2 \tag{19}$$

a somewhat more trustworthy representation than the third degree equation given previously by Birge (loc. cit.). The extrapolated area is 3.66 volts, which added to $E_e=5.64$ volts, gives $D'=9.30$ volts, in rather good agreement with 9.82 volts from the stable state data. Level A' is one of the very few to give a *positively* curved $\omega^n:n$ graph (7, 8′ of Fig. 4). The extrapolation is naturally very uncertain, but happens to give $D'=7.02$ (vibration) $+2.53$ (electronic) $=9.55$ volts.

Adopting 9.8 volts as the most trustworthy value of D', and 10.8 volts as undoubtedly the best value of D, we may test Eq. (6), since each member is known. The value of I_m for CO has been obtained by direct measurement, and also indirectly by Birge[52] from Duncan's measurements. The most probable value is 14.2 volts. If CO^+ dissociates into $C+O^+$, the value of I_a is 13.56 volts, as already used in the discussion of oxygen. Hence in Eq. (6)

$$\left.\begin{array}{l} 14.2+9.8=10.8+13.56 \\ \text{or} \quad 24.0=24.36 \end{array}\right\} \tag{20}$$

The value of D' involves the greatest uncertainty and the agreement shown is even more satisfactory than might have been anticipated.

Nitric Oxide

Only the neutral form of this molecule is known, from data on band spectra. The four electronic levels are evaluated from measurements

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[50] See Birge, Nature **116,** 170 (1925) and **116,** 207 (1925).

[51] Johnson, Proc. Roy. Soc. **108A,** 343 (1925).

[52] Birge, Nature **117,** 229 (1926).

of three different band systems. The recent work of Sponer[53] and of Sponer and Hopfield[54] shows unquestionably that the β bands and the third positive group (γ bands) of nitrogen have a common final level,— the normal level of NO,— and that the initial level of the γ bands is identical with the final level of the new ultra-violet system first found in nitrogen by Lyman,[55] and later extended and analyzed by Birge and Hopfield.[56] The electronic energy of state C (13.96 volts) is surprisingly large since electron impact measurements give about 9 volts for the ionization potential of NO.[57] Mulliken (private communication) has accordingly suggested that the C-A band system represents a double electron transition. On the other hand, Morton and Riding[58] from dispersion data conclude that the ionization potential is about 14 volts, and E. Condon (private communication) has independently reached a similar conclusion.

For the state level of NO one finds, as usual, a linear $\omega^n:n$ curve (No. 1′, 2′, of Fig. 4) with a corresponding energy equation

$$E = 1888.31n - 13.885n^2 \tag{21}$$

The extrapolated area is 7.93 volts, and this estimate of the heat of dissociation of nitric oxide can be checked from other data. Thus we know[59]

$$\mathrm{NO} = 1/2\ \mathrm{N_2} + 1/2\ \mathrm{O_2} + 21{,}570 \text{ calories} \tag{22}$$

Assuming our previous values of the heat of dissociation of oxygen (7.02 volts = 161,950 calories) and of nitrogen (11.4 volts = 263,000 calories), one obtains

$$\mathrm{NO} = \mathrm{N} + \mathrm{O} - 190{,}900 \text{ calories} \tag{23}$$

or a heat of dissociation of 8.3 volts.[60] This discrepancy of 0.4 volts again indicates the order of magnitude of the error introduced by the use of the $\omega^n:n$ curve for the normal state of the molecule.

Nitric oxide presents the interesting case of a normal level with a frequency of vibration much less than that for one of the known excited levels. In such a case it is obvious that the limiting energy, as obtained from the higher level (here level A) will be much greater than that

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[53] Sponer, Nature **117**, 81 (1926).

[54] Sponer and Hopfield, Phys. Rev. **27**, 640(A), (1926).

[55] Lyman "Spectroscopy of the Extreme Ultra-Violet," pp. 82 and 113.

[56] Birge and Hopfield, Nature **116**, 15 (1925).

[57] Report on "Critical Potentials" page 124. This result has since been verified by Hogness and Lunn (private communication) from positive ray analysis of NO.

[58] Morton and Riding Phil. Mag. (7) 1, 726 (1926).

[59] Landolt-Börnstein, p. 1495, (1923).

[60] Eucken (loc. cit.) gives 15.2 volts, since revised to 11.9 volts.

obtained from the normal level unless the *slope* of the $\omega^n : n$ curve of level A is much less than that of level X. The $\omega^n : n$ curve for this level (No. 2, 17′) is linear. The energy equation for level A as well as for level C has already been given by Birge and Hopfield (loc. cit). The limiting value of E_n is 11.75 volts, while E_e is 5.44 volts, a total of 17.19 volts. Assuming a true heat of dissociation of 8.3 volts, this leaves 8.9 volts of excess energy. But as already noted, the first level in the oxygen atom above the triple valence level represents 9.10 volts energy. It therefore seems very probable that in this case the products of dissociation are one stable nitrogen atom and one 9.1 volt excited oxygen atom.

The $\omega^n : n$ curve for state B is very uncertain (No. 1 of Fig. 4) and the limiting energy, 10.0 volts has therefore no significance. On the other hand, only four levels are known for state C, and the very long extrapolation of the $\omega^n : n$ curve (No. 17) gives about 19.6 volts for the total energy, a figure 2.4 volts higher than that obtained from level A.

This completes the various energy values obtained from spectroscopic sources, and with the data now available, we may consider in a more general way the possible processes involved in dissociation and ionization.

Some General Considerations

We have noted earlier in this paper that Franck draws a sharp distinction between molecules like I_2 which are held together by secondary forces and have a small heat of dissociation, and molecules like O_2 and N_2 which have a very high heat of dissociation. Franck considers that the second type cannot dissociate by an adiabatic process, and therefore the dissociation of such molecules cannot be caused by light absorption but only by collisions. We have seen, however, that oxygen dissociates by light absorption in a manner precisely similar to iodine, even though we cannot assume that this molecule is held together by van der Waals forces. The theory in the case of iodine has been given by Franck, as outlined in the first section of this paper. If a molecule possesses an electronic level in which the binding is much weaker than that for the stable level, the most probable transition between the two levels, when caused either by absorption of light or electron impact, is accompanied by a large change in the vibrational energy. It is quite possible to change from a state of zero vibration to one of so violent vibration that dissociation takes place. This occurs in the only known excited level of iodine, and in level B of oxygen. Similar considerations may be used to explain the difference in the behavior of oxygen and nitrogen in the Hogness and Lunn experiments on positive ray analysis. They found, as noted earlier, that O^+ ions are produced as a primary process, but N^+ ions only as a secondary process. As a result of electron impact, one electron may be ejected, producing the positive molecule ion. This is obviously a primary process, in the case of any molecule (ionization). It is, however, possible as a result of electron impact of sufficient energy to remove one electron entirely from the molecule, and simultaneously to displace another electron to an excited orbit. If now this excited orbit (of the ionized molecule) corresponds to a binding of the two nuclei much weaker than that for the initial state, then, just as in the case of light absorption, the molecule "finds itself" with a relatively large amount of vibrational energy, sufficient possibly to dissociate it.

In other words, the energy lost by the impacting electron goes partly into vibrational and partly into electronic energy. In previous interpretation of critical potential work the observed potentials have been taken as a measure of the separation of the various electronic energy levels. The new possibility of the acquirement also of vibrational energy will obviously make the observed critical potentials less sharp, and also too high in certain cases. Witmer[61] has very recently pointed this out in the case of the ionization potential of the hydrogen molecule, where it is possible that the molecular ion has quite a different strength of binding from the neutral molecule.

Now in O_2^+ we have an excited electronic level of very weak binding (level B') as compared to the binding in level X. But in N_2^+ the only excited level corresponds to a binding ($\omega^0=2396$) which is probably about equal to that of level X of N_2.[62] Therefore it is possible, as a result of a single electron impact, to ionize the oxygen molecule, and further to give it electronic excitation of such a character that it finds itself with sufficient vibrational energy to dissociate (into O and O^+). But in the case of nitrogen this is not possible, so far as the known spectroscopic data show. We may assume that there is an electronic level above A' of N_2^+ in which it is possible to place the molecule, by means of electron impact, and that if this excited N_2^+ molecule represents sufficient energy

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[61] Witmer Proc. Nat. Acad. Sci. **12,** 238 (1926).

This investigation by Witmer was carried out simultaneously with our own work, and was quite independent of it. Witmer finds a series of hydrogen bands on Lyman's spectrograms which have a common initial (excited) state, and so evaluate a set of final states. The resulting $\omega^n:n$ curve runs almost to $\omega^n=0$, and from it Witmer obtains a heat of dissociation of 4.3 volts, by the same process that we are using. We believe that this result is essentially correct, although there is no direct proof as yet that the $\omega^n:n$ curve used by Witmer represents the normal state of the hydrogen molecule, or that the lowest observed level corresponds to $n=0$.

[62] We may expect, in view of the many other analogies, that level X of N_2 and CO will have about the same ω^0, (i.e., about 2150).

to change N_2 into $N+N^+$, dissociation into these products may later occur as a result of collision, as found by Hogness and Lunn.

Let us consider now more closely the general question of the mechanism of dissociation. In the case of molecules like Hg_2 and Na_2, which are presumably held together by secondary forces, it is possible for the molecule, by addition of sufficient vibrational energy, to be separated by a continuous process into two atoms. For molecules like N_2, CO, and O_2 it does not seem possible to picture such a process, since there are in the molecules several electronic orbits of different quantum designation from those in the constituent atoms (Franck, loc. cit.). It may be, however, that as such molecules are given more and more quantum units of vibrational energy, the point is reached where the whole molecule *suddenly* becomes unstable and dissociates. This would mean a sudden ending of the $\omega^n : n$ curve, before it has reached the n axis. In the case of the B level of O_2 such a point, if it exists, must be very close to the value of $\omega^n = 0$, and the error introduced in the evaluation of the heat of dissociation, by extrapolating the $\omega^n : n$ curve to $\omega^n = 0$, is certainly less than 0.02 volts. Now in this case we are dealing with an excited molecule, but any reasonable assumptions as to the structure of the oxygen molecule seem to indicate the existence of at least four electron orbits in the molecule of different quantum designations from those in the atom. The excited state differs from the normal only by the displacement of a single electron, and hence any difficulty in visualizing the dissociation process applies equally to both of these states. The agreements which we have obtained, by extrapolating the $\omega^n : n$ curves for the normal state of the various molecules to $\omega^n = 0$ seem to indicate that any sudden break in these curves, if it exists, is within 0.5 volts of the limiting energy obtained by this smooth extrapolation. We believe, however, that the break in all such cases, if it exists, is very close to the $\omega^n = 0$ point, and that the discrepancies of a few tenths of a volt which have been found are to be ascribed to the error of the extrapolation.

In the case of many excited states of the molecule, the electronic energy is so large that the addition of a relatively small amount of vibrational energy will make the total energy equal to the heat of dissociation. Now it is known that *spontaneous* dissociation depends not on the total amount of energy, but upon the amount of vibrational energy. In fact it is possible for a molecule to absorb and re-emit energy greatly in excess of the heat of dissociation, due to the fact that most of the energy is not in the form of vibration. But we may assume that *collision* with another body *may* result in dissociation, if the molecule has a total amount of energy equal to the heat of dissociation. In this case the two resulting atoms must be in the normal condition. In the case of certain excited electronic states (such as level B of nitrogen) dissociation does *not* occur when this critical energy point is reached, with collisions occurring. We may explain this by assuming that for such cases, the products of dissociation include at least one excited atom. This predicts a break in the series of observed vibrational energy levels when the total energy equals the heat of dissociation plus a certain energy of atomic excitation.

Now the distribution of intensity in the band systems associated with the energy levels of Fig. 3 shows that in several cases the vibrational energy levels do break off sharply at a certain value of n. These cases include the C level of $N_2(n_{max}=4)$, the C level of $NO(n_{max}=3)$, and the B level of CO, where we have noted that state $n=1$ definitely occurs (with about the same probability as state $n=0$) but state $n=2$ is probably missing. In other cases, as level D in N_2, and level b in CO, no vibrational levels even exist. Let us consider these cases in more detail.

The b and B levels of CO both have a break at an energy virtually equal to the heat of dissociation. In this case we cannot decide whether the products of dissociation are two normal atoms, or whether they include one excited oxygen atom with 0.02 or 0.03 volts of energy. It should be noted that there is no known level in CO corresponding to energy greater than the heat of dissociation. In nitrogen the only known break occurs in the C level at $n=4$, for which the total energy is 13.94 volts. This is 2.5 volts above the heat of dissociation. Now Hopfield, as already noted, finds an S level of the doublet system, in the nitrogen atom, 2.4 volts above the S level of the quartet system. It is therefore possible that the products of dissociation in this case are two nitrogen atoms, one in each of these two electronic states. For level C of NO the break corresponds to 14.6 volts energy, or 6.3 volts above the heat of dissociation. The probable interpretation is that a collision causes dissociation into one normal (or essentially normal) oxygen atom, and one 6.3 volt excited nitrogen atom. The entire system of levels for the nitrogen atom is not yet sufficiently well known to preclude this possibility.

In other cases of band systems, the distribution of energy is such as to indicate that, with suitable experimental conditions, it would be possible to observe many higher vibrational levels than those indicated in the correlated sets of energy levels of Fig. 3. These cases may be analogous to level B of O_2 where, if a break occurs, it is close to the point for which $\omega^n=0$. In fact, by extrapolation the $\omega^n:n$ curves for these excited states one sometimes gets a total energy corresponding clearly to dissociation into one stable and one excited atom. A good example of this is level A of NO, which has already been discussed. A further example is level B of N_2 where the extrapolated total energy is about 2.5 volts higher than the extrapolated energy of state *A*. In this case the products of dissociation from state *A* may be two normal nitrogen atoms and for state *B*, the same two products as already suggested for state *C*. In the case of O_2^+, the products of dissociation for the *B'* level are evidently a normal neutral and a normal ionized atom, or a slightly excited neutral and a normal ionized atom. In the case of the other ionized molecules, we cannot yet draw definite conclusions.

CONCLUSIONS

It must not be thought that we have advanced the ideas of the last few pages as representing definite convictions on these matters. They are offered merely as tentative explanations of the facts indicated by the system of energy levels of Fig. 3. The actual evaluation of heats of dissociation does, however, seem possible. The $\omega^n:n$ curve for the normal state of the molecule is invariably linear, and its linear extrapolation to $\omega^n = 0$ seems to yield a value of D which is within at least 0.5 volts of the true value. In this case the corresponding physical process cannot be realized experimentally, but the result must give two normal atoms. In the case of dissociation from an excited molecular state the products of dissociation may be normal or excited atoms, and this uncertainty in general makes impossible the evaluation of the heat of dissociation from data on such states. If, however, the $\omega^n:n$ curve of an excited state can be followed almost to $\omega^n = 0$, as in the case of level *B* of O_2, and if the known energy levels of the resulting atoms are such as to closely limit the possible products of dissociation, we have a means of determining a really accurate value of the heat of dissociation. Thus far iodine and oxygen are the only known molecules for which such a condition exists.

By way of summary we give a table of the various heats of dissociation which we have obtained, together with the sources of each value.

TABLE

Molecule	D from band spectra	D from other sources
O_2	7.02 volts = 162,000 cal.	6.5 volts = 150,000 cal.[30] (from posit. ray analysis)
O_2^+	6.5 volts = 150,000 cal.	
N_2	11.9 volts = 274,000 cal.	11.4 volts = 263,000 cal.[32] (from active nitrogen)
N_2^+	9.1 volts = 210,000 cal.	
CO	11.2 volts = 258,000 cal.	10.8 volts = 249,000 cal. (from chem. data, using D_{O_2})
CO^+	9.8 volts = 226,000 cal.	
NO	7.9 volts = 182,000 cal.	8.3 volts = 191,000 cal. (from chem. data, using D_{N_2} and D_{O_2})

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