

Theory of Continuous Absorption of Oxygen at 1450A

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The continuous absorption of O₂ has lately been measured by Ladenburg, Van Voorhis and Boyce. Their suggested explanation in the term diagram of the molecule is compared to the corresponding matrix elements.

PART I. THEORY OF CONTINUOUS ABSORPTION IN DIATOMIC MOLECULES

CONTINUOUS absorption and emission in diatomic molecules have been explained as transitions between electronic states with discrete vibrational energy and electronic states with continuous energy.

Condon¹ gave in his paper a qualitative way of obtaining the relative intensities of the observed continua. This has been applied to the continuous emission of H₂ by Winans and Stueckelberg² and by Finkelburg and Weizel.³ Other applications have been made by Kuhn.⁴

The present paper gives a quantitative explanation of the continuous absorption of O₂ as measured by Ladenburg, Van Voorhis and Boyce.⁵ The probability (number of transitions per second) of a transition from the discrete state k to the energy continuum W is:

$$\Gamma_{kW} = (\pi^2/h) |H_{kW}|^2 (dQ_W/dW).$$

H_{kW} is the matrix element of the perturbing energy H , and dQ_W/dW is the number of states per region dW . In our case we have $H = \mathbf{M}\mathbf{E}$ where \mathbf{M} is the electric moment of the system, and $\mathbf{E} = \mathbf{E}_0 \cos 2\pi\nu t$ the electric field strength of the incoming light wave. One obtains $|H_{kW}|^2 = |M_{kW}|^2 E_0^2/3$. The factor $\frac{1}{3}$ is due to the averaging over the angle between \mathbf{E}_0 and \mathbf{M} . Let N_k be the number of molecules in the state k per cm³, and let n be the number of incident light quanta per cm² and sec. The number of quanta absorbed in the thin layer Δl per sec. is

$$\Delta l dN_k/dt = \Delta n = - \sum_k \Gamma_{kW} N_k \Delta l.$$

Between n and E_0^2 we have the relation: $cE_0^2/8\pi = nh\nu = I_\nu$. This leads to the following expression for the absorption coefficient:

$$\alpha_\nu = - \frac{\Delta n}{n \Delta l} = \frac{8\pi^3}{3} \sum_k \frac{N_k}{h} |M_{kW}|^2 \frac{\nu}{c} \frac{dQ}{d\nu}; I_{\nu t} = I_{\nu 0} e^{-\alpha_\nu t}. \quad (1)$$

¹ E. U. Condon, *Phys. Rev.* **32**, 858 (1928).

² J. G. Winans and E. C. G. Stueckelberg, *Proc. Nat. Acad. Amer.* **14**, 867 (1928).

³ W. Finkelburg and W. Weizel, *Zeits. f. Physik* **68**, 577 (1931).

⁴ H. Kuhn, *Zeits. f. Physik* **63**, 558 (1930).

⁵ R. Ladenburg, C. C. Van Voorhis and J. C. Boyce, *Phys. Rev.* **40**, 1018 (1932); referred to as L.V.a.B.

The electric moment $\mathbf{M}(\epsilon, r\theta\phi)$ depends on the coordinates ϵ of all the electrons and on the usual coordinates $r\theta\phi$ of the two heavy nuclei. We assume, that the wave function $\Psi_k(\epsilon, r\theta\phi)$ can be decomposed into

$$\psi_k(\epsilon, r\theta\phi) = \phi_n(\epsilon, r) \Theta_{JM}(\theta\phi) \psi_{nv}(r).$$

The matrix element $\mathbf{M}(n''J''M''v'', n'J'M'v')$ can be written, after integrating over $\epsilon, \theta\phi$,⁶ (if $J \gg 1$ and $\Lambda' = \Lambda'' = 0$, and if there is no external magnetic field) as:

$$|M(n''J''v'', n'J'v')| = |M_{k'W'}| = (2J)^{1/2} \int dr \cdot M_{n''n'}(r) \psi_{n''v''}(r) \psi_{n'v'}(r). \quad (2)$$

$M_{n''n'}(r) = M(r)$ is the electric moment associated with an electron jump from state $n' \rightarrow n''$, if the nuclei are held fixed at the distance r . We assume for the vibrational states v'' the states of a harmonic oscillator i.e.:

$$\psi_{n''v''}(r) = e^{(-1/2)(r-r_0'')^2/a''^2} \times \text{Polynomial in } (r - r_0'') \quad (3)$$

$$\psi_{n''v''=0}(r) = \psi_0 = a^{-1/2} \pi^{-1/4} e^{(-1/2)(r-r_0'')^2/a''^2}, \quad (3b)$$

where a'' (in cm) is defined by the molecular constants ω_0'' and μ :

$$a''^2 = a^2 = (h^2/8\pi^2\mu)(1/hc\omega_0''/2);$$

$$1/\mu = 1/M_I + 1/M_{II} \quad W'' = hc\omega_0''(v'' + \frac{1}{2})$$

and where r_0'' is the equilibrium separation. The functions (3a) and (3b) are different from zero only in the immediate neighborhood of r_0'' . We expand:

$$M(r) = M(r_0'') + (r - r_0'')M'(r_0'') + \dots \quad (4)$$

(2) will be of a similar form:

$$M_{k'W'} = g[M(r_0'') + \beta \cdot M'(r_0'') + \dots]. \quad (5)$$

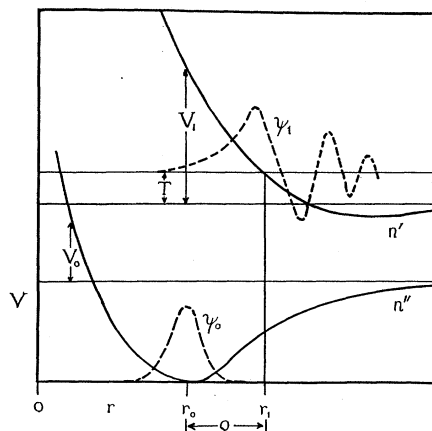


Fig. 1. Potential energy functions $V(r)$ and nuclear wave functions: $\psi_1(r)$ for a non-quantized level of the electronic state n' , $\psi_0(r)$ for the lowest vibrational level of the electronic state n'' .

⁶ W. Weizel, Bandenspectren Hb.d. Exp. Phys. Ergänzungsband I, p. 164.

We are left with the determination of the wave function $\psi_{n',W'}$ representing an oscillation between a finite $r=r_1$ and infinity ($r=R, \lim R=\infty$) (see Fig. 1). r_1 is the separation at which the potential energy V_1 equals the kinetic energy at infinity T . We make use of the method by Kramers⁷ in order to obtain an expression for $\psi_{n',W'}=\psi_1$. His solution is, if $p^2=8\pi^2\mu(T-V_1)/h^2$; and if $\gamma=(8\pi^2\mu)/h^2 \cdot \partial/\partial r \cdot V_1(r)$; $\rho=r_1-r_0''$; $\xi=r-r_1$; $p_\infty^2=8\pi^2\mu T/h^2$:

$$\xi \gg 0; T - V_1 \gg 0: \psi_1 = \psi_{1>} = R^{-1/2} \left(\frac{2p_\infty}{p} \right)^{1/2} \cos \left[\int_0^\xi p d\xi - \frac{\pi}{4} \right]$$

$$\xi \cong 0; T - V_1 \cong 0: \psi_1 = \psi_{10} = R^{-1/2} \left(\frac{2p_\infty}{\gamma^{1/3}} \right)^{1/2} \omega(\gamma^{1/3}\xi) \quad (6)$$

$$\xi \ll 0; T - V_1 \ll 0: \psi_1 = \psi_{1<} = R^{-1/2} \text{ neg. real. exp.}$$

Condon² has shown in a qualitative way, that the part where $T - V_1 \cong 0$, i.e., the region near r_1 , is the most important in evaluating (2). We assume therefore that the part of the integrand in the neighborhood of r_1 only (i.e., the function ψ_{10}) is of importance. This is certainly true, if the slope of the potential energy curve γ of the state n' is constant over the range where ψ_0 is different from zero, and if $\gamma a^3 \ll 1$.

(2) becomes:

$$M_{k',W'} \cong g M(r_0) \cong M(r_0) \left\{ \frac{4}{\pi^{1/2}} \frac{J p_\infty}{\gamma^{1/3} a R} \right\}^{1/2} \int_{-\infty}^{+\infty} d\xi e^{-\xi^2/2a^2} \omega(\gamma^{1/3}\xi).$$

The function $\omega(z)$ is tabulated by Kramers⁷ and can be expressed by a complex integral (Airy's Integral):⁸

$$\omega(z) = \frac{-i}{2\pi^{1/2}} \int_{(P)} dt e^{z t + t^3/3} \quad (\text{for the path } P \text{ see Kramers}).^7$$

Then one has for g .

$$g = \left[\frac{4}{\pi^{1/2}} \frac{J p_\infty}{R \gamma^{1/3} \cdot a} \right]^{1/2} \frac{-i}{2\pi^{1/2}} \int_{(P)} dt$$

$$\int_{-\infty}^{+\infty} d\xi e^{-I(\xi + \rho - a^2 \gamma^{1/3} t)^2/2a^2} e^{(t^3/3) + (1/2)a^2 \gamma^{2/3} t^2 - \gamma^{1/3} \rho \cdot t}.$$

If the substitutions $\xi' = \xi + \rho - a^2 \gamma^{1/3} t$; $\tau = t + b$; $b = \frac{1}{2} \gamma^{2/3} a^2$; and $x = \gamma^{1/3} \rho$ are made, the integration over $d\xi'$ can be carried out:

$$g = \left[\frac{8\pi^{1/2} J p_\infty a}{R \gamma^{1/3}} \right]^{1/2} e^{b x + (2/3)b^3} \omega(- (x + b)) = \left[\frac{4\pi^{1/2} J p_\infty}{R \gamma a} \right]^{1/2} f^{1/2}. \quad (8)$$

We abbreviate

$$f = 4b\omega^2(- (x + b)) e^{2b + (4/3)b^3}. \quad (9a)$$

⁷ A. H. Kramers, Zeits. f. Physik 828 (1926).

⁸ G. N. Watson, Theory of Functions, p. 188, Cambridge, 1922.

If the argument of $\omega(z)$ takes large negative values ($-z > 2$), a good approximation is

$$2\omega(z) = (-z)^{-1/4} e^{-(2/3)(-z)^{3/2}}$$

we make a further substitution: $y = x/b^2 = (\rho/a)(4/\gamma a^3)$ and have for $-(x+c) \gg 2$:

$$\begin{aligned} f &= (1+y)^{-1/2} \exp \left[-\frac{4b^3}{3} \left\{ (1+y)^{3/2} - (1+(3/2)y) \right\} \right] \\ &= \left(1 + 4\frac{\rho}{a} \frac{1}{\gamma a^3} \right)^{-1/2} e^{-(\rho^2/a^2) - \dots} \end{aligned} \quad (9b)$$

If $\gamma a^3 \gg 1$, this is practically the same result as one obtains if one "reflects" the function ψ_0^2 on the potential energy curve of the repulsive state $\nu/c = (\nu/c)(\rho)$.

If the argument of the function ω is positive, i.e., if $(x+b^2)$ is negative the expression for M_0 oscillates. This was also predicted from the qualitative picture of Condon.² The conditions for oscillations are

$$\begin{aligned} -(x+c^2) &= -\gamma(\frac{1}{4}\gamma a^3(a+\rho)) \gg 0 \quad (\text{order of } 1) \\ -\rho/a &\gg \frac{1}{4}\gamma a^3 + 1/(\gamma a^3)^{1/3}. \end{aligned}$$

The next step is to justify the application of ψ_{10} in (7) in the whole region ξ between $-\infty$ and $+\infty$.

The function $M(r)$ depends on r . The final result involves an average value of $M(r)$, say $M(r_i)$. If r_i coincides with r_1 , we can conclude, that the region around $r=r_1$ is the most important one. Taking the expansion (4) and (5) this means $\beta = r_1 - r_0 = \rho$.

In the integral:

$$g\beta M'(r_0) = M'(r_0) \int_{-\infty}^{+\infty} d\xi (\rho + \xi) \psi_0(r) \psi_1(r) \quad (10)$$

we make the same substitutions and notice, that

$$\int_{-\infty}^{+\infty} dt \gamma^{1/3} t e^{(t^3/3) + (1/2)\gamma^{2/3} a^2 t^2 - \gamma^{1/3} t \rho} = -\frac{\partial}{\partial \rho} \int_{-\infty}^{+\infty} dt e^{(t^3/3) + \dots}$$

This gives:

$$\beta = -(a^2/4)(1/f)(\partial/\partial \rho)f. \quad (10a)$$

As long as $y < 1$, we have roughly:

$$\beta = \rho + a[1/(\gamma a^3)^{1/3}] \cong (r_1 - r_0), \text{ if } \gamma a^3 > 1.$$

The application of ψ_{10} is therefore justified. The parts of the integrand due to $\psi_{1<}$ and $\psi_{1>}$ are negligible to the same extent as the far away parts of ψ_{10} , which, even if taken into account, do not change appreciably the final result, as long as

$$\gamma a^3 \gg 1 \text{ or } a^3(\partial/\partial r)V_1 \gg h^2/(8\pi^2\mu). \quad (11)$$

The evaluation of matrix elements for which $v'' \neq 0$ can be carried out in the same way as (10) and (10a).

The number of energy levels dQ/dp_∞ in the unstable part of state n' per region dp_∞ goes to infinity as the radius R becomes infinite: $dQ = (R/\pi)dp_\infty$. Going from p to $h\nu$, we have for the number of levels per $d\nu$

$$dQ/d\nu = 4\pi\mu R/hp_\infty. \quad (12)$$

If $\omega_0'' \gg kT/hc$, practically all the molecules are in the level $v'' = 0$. The expression for the absorption coefficient is, making use of (1), (7), (8) and (12):

$$\alpha_\nu = \frac{128\pi^{9/8}}{3} \frac{\mu}{h^2\gamma a} \sum_J \left(\frac{\nu}{c}\right) M^2(r_1) f J N_J.$$

We have to average over the different rotational levels J . (ν/c) , M^2 and f can be considered as independent of J : $\sum_J J \cdot N_J \cong (3\pi^{1/2}/2) N (kT'/hc \cdot B_0)^{1/2}$ (see Weizel⁶ p. 167).

$$\alpha_\nu = 64\pi^5 \cdot \frac{N\mu(kT/hc \cdot B_0)^{1/2}}{h^2 \cdot \gamma a} \left(\frac{\nu}{c}\right) M^2(r_1) f \cdot \text{cm}^{-1}. \quad (13)$$

PART II. THE CONTINUOUS ABSORPTION OF OXYGEN

The continuous absorption of oxygen, extending from 1750A to 1300A, has been measured by L.V.a.B.⁵ They explain this absorption as a transition from the normal $^3\Sigma$ state of the molecules to the upper $^3\Sigma$ state. The Frank-Condon principle applied to the potential energy curves, calculated by Morse⁹ and Stueckelberg,¹⁰ gives the right order of magnitude for ν/c . We have $\omega_0'' \gg kT/hc$ and $\Lambda' = \Lambda'' = 0$ for $\Sigma \rightarrow \Sigma$ transitions. Therefore a comparison between the experimental curve $\alpha_\nu = \alpha_\nu(\nu/c)$ by L.V.a.B.⁵ and the theoretical expression (13) can be carried out in the following way. We plot

$$\text{const.} - \log [\alpha_\nu/(\nu/c)] = - \log f = (4b^3/3)[(1+y)^{3/2} - (1+(3/2)y)] \\ + \frac{1}{2} \log [1+y]$$

as a function of y (Fig. 2). To do this we had to assume a value for $b = b_0$. As a is a known quantity ($\omega_0'' = 1566 \text{ cm}^{-1}$; $a = 5.16 \times 10^{-10} \text{ cm}$) this fixes the value of $\gamma = \gamma_0$.

The comparison between $-\log f$ and the experimental curve of $-\log (\alpha_\nu/(\nu/c))$ gives ν/c as a function of y . This relation is also plotted in Fig. 2. Instead of marking the individual points, an area was drawn. According to the theory $\nu/c = (\nu/c)(y)$ ought to be a straight line, if M and γ are constants over the region. This seems to be true within the limits of error. We obtain a value for $d(\nu/c)/dy$. The definition of y and γ leads to the relation

⁹ P. M. Morse, Phys. Rev. **34**, 57 (1929).

¹⁰ E. C. G. Stueckelberg, Phys. Rev. **34**, 65 (1929).

$$\gamma^2 = [32\pi^2 \cdot \mu c / h a^4] [d(\nu/c) / dy].$$

This newly determined value of $\gamma = \gamma_1$, gives a new value for $b = b_1$. The procedure is repeated until $\gamma_m = \gamma_{m-1}$. This is the case in Fig. 2. The probable

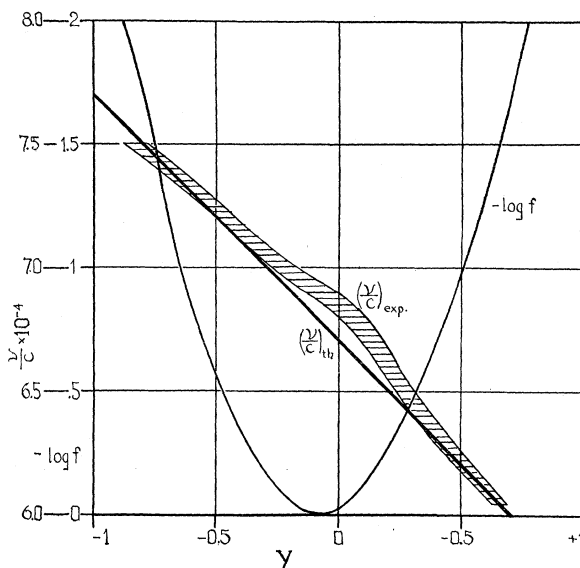


Fig. 2. $-\log f = -\log (\alpha_\nu / (\nu/c))$ and wave number (ν/c) as functions of the parameter $y = 4\rho/\gamma a^4$. The experimental points (L.V. and B.) are plotted as a broad stripe. The black line has been chosen to determine curve A in Fig. 3.

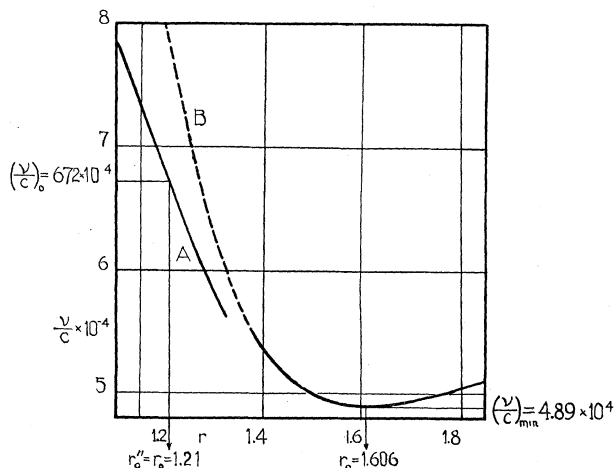


Fig. 3. Potential energy curves for the upper $^3\Sigma$ -state of the O_2 molecule. The ordinates are the energy in wave numbers (ν/c) , measured from the lowest vibrational level of the normal $^3\Sigma$ -state. $r_0'' = r_0$ is the equilibrium separation of the normal $^3\Sigma$ -state. (r in 10^{-8} cm $^{-1}$.)

error in γ is about 2 percent. The value of ν/c for $y = \rho = 0$ determines the height of the potential energy curve over the equilibrium separation r_0'' .

The value of γ determines the inclination of the potential energy curve at this point.

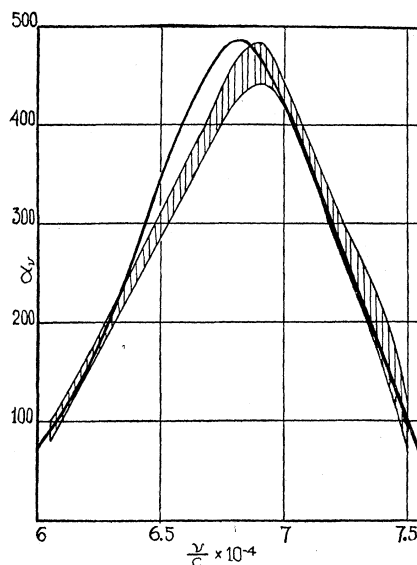


Fig. 4. Absorption coefficient of O_2 as a function of (ν/c) . The broad stripe represents the experimental result of L.V. and B., while the black line shows the theoretical absorption coefficient α_ν based upon the potential energy curve A in Fig. 3.

The results are:

$$\begin{aligned} (\nu/c)_{r=r_0} &= (6.72 \pm 0.05) \times 10^4 \text{ cm}^{-1} \\ \gamma &= (0.51 \pm 0.01) \times 10^{29} \text{ cm}^{-3} \\ (d(\nu/c)/dr)_{r=r_0} &= (10.8 \pm 0.2)(10^4 \text{ cm}^{-1}/10^{-8} \text{ cm}). \end{aligned}$$

Fig. 3 is a comparison between the so defined curve A and the curve calculated by Morse⁹ and Stueckelberg,¹⁰ B . One sees that the extrapolation of their calculation (dotted line B in Fig. 3) is too steep. However the curve A seems to point in the right direction. Fig. 4 compares the theoretical absorption coefficient (based upon A) with the experimental values of L.V.a.B. Like in Fig. 2, an area is plotted instead of marking their individual points.

Eq. (13) permits a determination of $M(r_0)$ under the assumption of room temperature ($T=290^\circ\text{K}$) and with $B_0=1.44 \text{ cm}^{-1}$:⁶

$$M(r_0) = (4.77 \times 10^{-10} g^{1/2} \text{ cm}^{3/2} \text{ sec.}^{-1/2}) \times (0.65 \times 10^{-8} \text{ cm}).$$

This is a reasonable result.