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Variation with Temperature of the Continuous Absorption Spectrum of Diatomic Molecules: Part II. Theoretical

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A method of calculating the matrix components, corresponding to the continuous absorption of light by diatomic molecules in various vibrational and rotational levels of the lower state, is described and applied to the calculation of the absorption of Cl_2 gas at various temperatures. The theory shows that the absorption from a single vibrational level is practically independent of temperature, and that the temperature effect is due to the changing distribution of the absorbing molecules among the various levels. Assuming the Morse function to be approximately correct for the potential energy of the lower state, the theory enables one to calculate the form of the upper potential energy curve. The matrix component of the electric moment corresponding to the absorption from the lower state has been calculated for Cl_2 and found to correspond to the displacement of one electronic charge through 0.016A.

I. THE FUNDAMENTAL EQUATION FOR THE ABSORPTION COEFFICIENT

IN chlorine[1] the transition which gives rise to the continuum at $\lambda=3300$A is from the normal ${}^1\Sigma_+$ state to a 0^+ state. At the highest temperature investigated (1038°K) practically none of the 0^+ states are excited. The molecules of the gas are distributed initially among the vibrational and rotational states of ${}^1\Sigma_+$. The absorption coefficient

$$k_\nu=\frac{\epsilon_\nu\cdot\ln 10}{6.06\times 10^{20}}=-\frac{1}{N}\frac{d\ln I}{dl}, \qquad (1)$$

where I is the intensity of the incident light, (ϵ has been defined in Part I, the subscript ν merely designating it for light of a particular frequency) N is the number of molecules per cm^3 and l in cm is the distance traversed by the light. k_ν is given by the equation

$$k_\nu N=\sum_{\alpha''}\sum_{\alpha'} P_{\alpha''\alpha'}N_{000}e^{-E_{\alpha''}/kT}. \qquad (2)$$

Here, α'', α' are short for the respective sets of quantum numbers $(v''J''M'')$, $(v'J'M')$, N_{000} is the number of molecules per cm^3 in the state of lowest energy ($v''=0$, $J''=0$, $M''=0$), $E_{\alpha''}$ is the energy in ergs of the state α'' measured from the state (0, 0, 0), (i.e., $E_{000}=0$), T is the absolute temperature, $k=1.372\times 10^{-16}$ ergs/°K and

$$P_{\alpha''\alpha'}=(8\pi^3\nu/3hc)\,|D_{\alpha''\alpha'}|^2 \qquad (3)$$

is the absorption coefficient per molecule,[2] referring to an incident beam of 1 photon crossing unit area per second per unit frequency range. The matrix component in Eq. (3) is defined by the equation

$$D_{\alpha''\alpha'}=\int \varphi''_{\alpha''}\cdot D\cdot \varphi'_{\alpha'}d\tau, \qquad (4)$$

where $\varphi''_{\alpha''}$, $\varphi'_{\alpha'}$ are the eigenfunctions of ${}^1\Sigma_+$ and 0^+ respectively, and D is the electric moment (a function of all the coordinates). We assume with Born and Oppenheimer[3] that each of these eigenfunctions may be represented as a product of an electronic, a rotational, and a vibrational eigenfunction, and also that in the integration over the electronic coordinates the nuclear separation r is to be regarded as an (approximately) constant parameter. Hence Eq. (4) may be written

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[1] See Part I, of this title, Phys. Rev. **44**, 188 (1933).

[2] Dirac, *Principles of Quantum Mechanics*, p. 168, Eq. (24) (1930). (See also paragraph 61, Eq. (59) and paragraph 71, p. 232.

[3] M. Born and R. Oppenheimer, Ann. d. Physik **84**, 474 (1927).

$$
\begin{aligned}
D_{\alpha''\alpha'} &= \int P''_{J''M''}(\phi,\theta)F''_{v''J''}(r)\left[\int \varphi_{n''}(\chi)D\varphi_{n'}(\chi)d\chi\right]P'_{J'M'}(\phi,\theta)F'_{E'J'}(r)d\tau \\
&= \int F''_{v''J''}P''_{J''M''}D_{n''n'}P'_{J'M'}F'_{E'J'}d\tau,
\end{aligned}
\tag{5}
$$

where F represents the vibrational eigenfunctions multiplied by r, P_{JM} the rotational eigenfunctions (Tesseral harmonics), $d\tau$ represents the appropriate differential of the nuclear coordinates r, θ, ϕ, and E' is the energy which goes with v'. The integral $D_{n''n'}$ over the electronic variables χ strictly speaking is a function of r, but we shall assume it to be constant over the small range of r for which the eigenfunction $F''_{v''J''}(r)$ has appreciable values.

Integrating Eq. (5) over θ and ϕ and then over r we obtain

$$
D_{\alpha''\alpha'} = D_{n''n'}L_{J''J'}^{M''M'}\int_0^R F''_{v''J''}F'_{E'J'}dr = D_{n''n'}L_{J''J'}^{M''M'}\cdot F_{v''E'J''J'} \tag{6}
$$

where R is the bounding nuclear separation (Lim $R=\infty$), determined by the size of the containing vessel.

The rotational matrix components $L_{J''J'}^{M''M'}$ have been calculated by Hönl and London[4] and are zero for Cl_2 unless $J'-J''=\pm1$, $M'-M''=\pm1$ or 0.

They obey the equation

$$
\sum_{JM} L_{J''J'}^{M''M'^2} = 2J''+1, \tag{7}
$$

where the summation includes all possible transitions from the state J''. This relationship will be used later on in carrying out the summations in Eq. (2). Before this can be done, however, we must first evaluate the eigenfunctions $F_{v''J''}$ and $F_{E'J'}$ and calculate the matrix component $F_{v''E'J''J'}$ which occurs in Eq. (6).

II. Evaluation of $F''_{v''J''}(r)$

We shall write, for short, $F''=F''_{v''J''}(r)$. The Schroedinger equation is

$$
\partial^2F''/\partial r^2+\kappa^2(E''-V''-J''(J''+1)/\kappa^2r^2)F''=0, \tag{8}
$$

where $\kappa^2=8\pi^2\mu_0/h^2$, where μ_0 is the reduced mass. For $J''=0$ the potential energy $V''(\rho)$ (where $\rho=r-r_0$) was taken to be of the form $-(\gamma/\rho)+(\beta/\rho^2)$ and the constants r_0, γ and β were chosen so as to give the best agreement with the Morse curve (lower curve in Fig. 1) in the region near the minimum of $V''(\rho)$. Writing $\kappa^2E''_{v''}=-a^2_{v''}$, and $\kappa^2\beta=m(m-1)$, the quantum condition becomes $\kappa^2\gamma/2a_{v''}-m=v''$, where $v''=0, 1, 2, \cdots$. Setting $\xi=2a_{v''}\rho$ and $2m-1=\alpha$, the normalized eigenfunctions of Eq. (8) are given by[5]

$$
\begin{aligned}
F''_{v''} &= [v''!/(2m+2v'')]^{\frac{1}{2}}[\Gamma(2m+v'')]^{-\frac{3}{2}}e^{-\xi/2}\xi^m L^{\alpha}_{v''+\alpha}(\xi) \\
\text{where}\quad L^{\alpha}_{v''+\alpha}(\xi) &= e^{i\pi(\alpha+v'')}\frac{\Gamma(\alpha+v''+1)}{v''!}\left[\xi^{v''}-\frac{(\alpha+v'')v''}{1!}\xi^{v''-1}\right. \\
&\qquad\left.+\frac{(\alpha+v'')(\alpha+v''-1)v''(v''-1)}{2!}\xi^{v''-2}+\cdots\right].
\end{aligned}
\tag{9}
$$

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[4] W. Weizel, *Bandenspektren*, Handb. d. Exp. Phys., p. 167 ff. (1931).

[5] Schroedinger, Ann. d. Physik **80**, 483 (1926).

The four lowest eigenfunctions ($v''=0$, 1, 2, 3) are

$$\begin{aligned}
&\text{(a)}\quad F_0''(r)=\frac{(2a_0)^{m+\frac{1}{2}}}{\{\Gamma(2m+1)\}^{\frac{1}{2}}}\rho^m e^{-a_0\rho}\\
&\text{(b)}\quad F_1''(r)=\frac{(2a_1)^{m+\frac{1}{2}}\cdot 2m}{\{(2m+2)\Gamma(2m+1)\}^{\frac{1}{2}}}\rho^m e^{-a_1\rho}\left[1-\frac{a_1\rho}{m}\right]\\
&\text{(c)}\quad F_2''(r)=\frac{(2a_2)^{m+\frac{1}{2}}2m(2m+1)}{\{2(2m+4)\Gamma(2m+2)\}^{\frac{1}{2}}}\rho^m e^{-a_2\rho}\left[1-\frac{4a_2\rho}{2m}+\frac{4(a_2\rho)^2}{2m(2m+1)}\right] \qquad (10)\\
&\text{(d)}\quad F_3''(r)=\frac{(2a_3)^{m+\frac{1}{2}}\cdot 2m(2m+1)(2m+2)}{\{3!(2m+6)\Gamma(2m+3)\}^{\frac{1}{2}}}\rho^m e^{-a_3\rho}\left[1-\frac{6a_3\rho}{2m}+\frac{12(a_3\rho)^2}{2m(2m+1)}-\frac{8(a_3\rho)^3}{2m(2m+1)(2m+2)}\right].
\end{aligned}$$

The data are all for $J''=0$. The effect of J'' will be discussed in paragraph 5. The expression (9) is normalized for integration with respect to ξ instead of r, so (10) differs from (9) by a factor $(2a_{v''})^{\frac{1}{2}}$. In addition the factor $e^{-i\pi\alpha}$ has been dropped from (10) since α was taken to be an even integer in our calculations.

III. EVALUATION OF $F'_{v'J'}(r)$ FOR $J'=0$

The Schroedinger equation is

$$\frac{\partial^2 F'}{\partial r^2}+\kappa^2\left(E'-V'-\frac{J'(J'+1)}{\kappa^2 r^2}\right)F'=0. \qquad (11)$$

We are concerned here with the potential energy $V'(r)$ in the neighborhood of $r=2$Å since it is only in this region that the eigenfunctions F'' have appreciable values. As an empirical formula for $V'(r)$ which leads to a convenient solution when substituted in (11) we have chosen[6]

$$V'(r)=V_\infty'+[(\omega^2-\tfrac{1}{4})/\kappa^2\rho^2], \qquad (12)$$

where $\rho=r-r_0$ as in paragraph 2 and V_∞' and ω are constants to be determined later by comparing the calculated and observed absorption coefficients. This expression cannot be used for $\rho<0$, that is $r<r_0$. This, however, is of no practical importance, as the eigenfunction will already be very small (the approximate one actually zero) at this point. We may extend all our integrals from $\rho=0$ to $\rho=R$ instead of from $r=0$ to $r=R$.

Taking again the case of zero rotation ($J'=0$) the normalized integral of Eq. (11) with $V'(r)$ as given by Eq. (12) is

$$F_{v'}'(r)=(\pi b'/R)^{\frac{1}{2}}\rho^{\frac{1}{2}}J_\omega(b\rho), \qquad (13)$$

where $b=\kappa(E'-V_\infty')^{\frac{1}{2}}$ and $J_\omega(b\rho)$ is the Bessel function of order ω and argument $b\rho=b(r-r_0)$. The normalizing factor is $(\pi b'/R)^{\frac{1}{2}}$ where

$$b'=\kappa(E'-E_D')^{\frac{1}{2}} \qquad (14)$$

and R, it will be remembered, is the bounding nuclear separation. The energy of the 0^+ molecule when dissociated into atoms at rest is E_D'. This is not equal to V_∞' since Eq. (12) only holds for a limited range of r, and is untrue when $r=\infty$. Were $E_D'=V_\infty'$, then b would naturally occur instead of b' in Eq. (13) and the ratio of the amplitude of the oscillations of Eq. (13) at a point in the important range of r (where $V'=V_a'$, say) to the amplitude at infinite r would be $(E_\infty'-V_\infty')^{\frac{1}{4}}(E'-V_a')^{-\frac{1}{4}}$. In the actual case the ratio of amplitudes is $(E'-E_D')^{\frac{1}{4}}\times(E'-V_a')^{-\frac{1}{4}}$. So we must multiply Eq. (13) (if b instead of b' were in it) by

$$(E'-E_D')^{\frac{1}{4}}(E'-V_a')^{-\frac{1}{4}}/(E'-V_\infty')^{\frac{1}{4}}(E'-V_a')^{-\frac{1}{4}}$$

to give us Eq. (13) as it stands.

IV. EVALUATION OF THE VIBRATIONAL MATRIX COMPONENT $F_{v''E'J''J'}$

Taking $J''=0$, $J'=1$ for which the effect of rotation is certainly negligible, we have, combining Eqs. (6), (10a), and (13), and writing $m+3/2=\mu$

$$F_{0E'01}=A_0\int_0^R\rho^{\mu-1}e^{-a_0\rho}J_\omega(b\rho)d\rho \qquad (15)$$

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[6] C. Zener, Phys. Rev. **37**, 556 (1931).

where

$$A_0=(\pi b'/R)^{\frac{1}{2}}(2a_0)^{m+\frac{1}{2}}/\{\Gamma(2m+1)\}^{\frac{1}{2}}. \tag{16}$$

Writing $I_0/a_0^{\mu}=F_{0E'01}/A_0$ we have for the integral in Eq. (15)*

$$I_0/a_0^{\mu}=\frac{(\frac{1}{2})^{\omega}}{a_0^{\mu}}\frac{\Gamma(\mu+\omega)}{\Gamma(\omega+1)}x_0^{\omega/2}(1+x_0)^{-\mu+\frac{1}{2}}{}_2F_1\left(\frac{\omega-\mu+1}{2},\frac{\omega-\mu}{2}+1;\omega+1;-x_0\right), \tag{17}$$

where

$$x_0=b^2/a_0^2=\kappa^2(E'-V_{\infty}')/a_0^2 \tag{18}$$

and ${}_2F_1$ is the hypergeometric function of parameters and variable indicated.

In a similar manner, using Eqs. (10b, c and d) we obtain the matrix components $F_{1E'01}$, $F_{2E'01}$, $F_{3E'01}$. Before evaluating these, however, we shall discuss the effect of rotation, and carry out the summations indicated in Eq. (2).

V. THE DEPENDENCE OF THE VIBRATIONAL MATRIX COMPONENTS $F_{v''E'J''J'}$ ON THE ROTATIONAL QUANTUM NUMBER J''

We return to the Schroedinger Eqs. (8) and (11). To each of the potential energies $V''(r)$ and $V'(r)$ we have to add the term $[J(J+1)]/\kappa^2r^2$. The average value of J'' at 1000°K is about 50 and $2.1>r>1.9$A is the region where the three lowest eigenfunctions $F''_{v''}(r)$ have values large enough to contribute noticeably to the matrix component. Apart from a slight distortion (around ± 50 cm^{-1} at the limits of the important range of r for $J=50$), each potential energy curve is therefore raised by the same amount (about 1000 cm^{-1} when J'' goes from 0 to 50) since $J'=J''\pm 1\cong J''$.

The eigenvalues of the lower state are $E''_{v''J''}-E''_{v''0}=[J''(J''+1)]/\kappa^2r_0^2$ while in the continuum the eigenvalues are independent of J'. We are concerned with the value of the matrix component $F_{v''E'J''J'}$ for a given value of $h\nu=E'_{J'}-E''_{J''}$. Since the two potential energy curves are raised by practically the same amount, the value of $F_{v''E'J''J'}$ is affected only by the slight distortion of the curves and we shall make a very small error if we take it to be independent of J.

The chief effect of this distortion is to shift the minimum of the potential curve very slightly to the right, so that it is under a slightly lower part of the V' curve. For $J=50$ the minimum is shifted by about 4×10^{-3}A and the value of V' is only about 200 cm^{-1} lower at that point than it is at the minimum for $J=0$. It is readily seen that the effect on the final curves of Fig. 4 is entirely negligible.

VI. SUMMATION OVER α', α'' AND FINAL FORMULA FOR k_ν

Since α' is in the region of continuous eigenvalues we have a large number $Z_\nu\Delta\nu$ of transitions $\alpha''\rightarrow\alpha'$ of practically equal probability $P_{\alpha''\alpha'}$ in any small region $\Delta\nu$. In our case Z_ν can readily be shown to have the value

$$Z_\nu=h\kappa^2R/2b'\pi. \tag{19}$$

Since $P_{\alpha''\alpha'}$ in Eq. (3) is defined for a single transition per unit frequency range, the summation over α' is equivalent to multiplication by Z_ν. Hence, combining Eqs. (2), (3), (6), (7) and (19) we have

$$k_\nu N=\sum_{v''J''}(8\pi^3\nu/3hc)D^2_{n''n'}(2J''+1)N_{000}F^2_{v''E'J''J'}e^{-E_{v''J''}/kT}\cdot h\kappa^2R/2b'\pi, \tag{20}$$

where the vibrational matrix component, $F_{v''E'J''J'}$ was shown in Part V to be practically independent of J'', when E' is chosen so that $E'-E''=h\nu$. Each of these matrix components contains the square of the normalizing factor $(\pi b'/R)^2$. By writing

$$(\pi b'/R)\mathfrak{F}^2_{v''E'}=F^2_{v''E'J''J'} \tag{21}$$

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* See Watson, *Bessel Functions*, p. 385.

Eq. (20) becomes

$$\frac{3c}{4\pi^3\nu\kappa^2 D^2_{n''n'}}k_\nu N=\sum_{v''J''}\mathfrak{F}^2_{v''E'}(2J''+1)N_{000}e^{-E_{v''J''}/kT}=\sum_{v''}\mathfrak{F}^2_{v''E'}N_{v''},\tag{22}$$

where $N_{v''}$ is the number of molecules in the state v''. Writing $(4\pi^3\nu\kappa^2D^2_{n''n'}/6hc)\mathfrak{F}^2_{v''E'}=k_{v''}$ we obtain an equation equivalent to the Eq. (1) used in Part I to calculate the values of $\epsilon_{v''}$ from the experimental values.

VII. Determination of ω and V_∞' by Comparison with Experiment

The calculation of the hypergeometric function ${}_2F_1$ in (17) is somewhat laborious. For this reason the approximate expression

$${}_2F_1\cong[1-[(\omega-\mu+2)/2(\omega+1)]x_0]^{-(1-\mu+\omega)/2}\tag{23}$$

was substituted in Eq. (17), and used to obtain provisional values of ω and V_∞'. To do this we calculated the approximate half widths of the function (17) for various values of ω and interpolated graphically to find the value of ω which gave the half width in agreement with experiment. This gave $\omega\cong150$. Substituting this value in the exact Eq. (17) and evaluating ${}_2F_1$ by actual summation of the series we obtained a half width differing slightly from the correct value. From the amount of this difference we were now able to estimate the value of ω which, substituted in (17), would give the correct half width. In this way we found the value $\omega=162$, which was used in the final calculations. Substituting now in Eq. (18) for x_0 the value which corresponds to the maximum of (17) and for E_0' the experimental value of the energy at the absorption maximum of ϵ_0 we can solve (18) for V_∞'. This gives $V_\infty'=3617$ cm^{-1}.

VIII. Calculation of the Matrix Components for the Vibrational States $v''=1, 2, 3$

In place of Eq. (15) we have now, from (6), (9) and (13)

$$F_{v''E'01}=\bar{A}_{v''}\int_0^R\rho^{\mu-1}e^{-a\rho}L^{\alpha}_{v''+\alpha}(2a\rho)J_\omega(b\rho)d\rho\tag{24}$$

where $\bar{A}_{v''}$ is a constant depending on μ, ω and $a(=a_{v''})$. By writing

$$I_p/a^{\mu+p}=\int_0^R\rho^{\mu-1+p}e^{-a\rho}J_\omega(b\rho)d\rho,\tag{25}$$

Eq. (24) becomes (omitting the J quantum numbers)

$$F_{v''E'}=\sum_{p=0}^{p=v''}C_pI_p/a^{\mu+p},\tag{26}$$

where the C_p are again constants depending on a, μ and ω. The matrix component is therefore a linear aggregate of expressions of the form (17) with $\mu+p$ in place of μ.

We note that

$$(\partial^p/\partial a^p)(I_0/a^\mu)=(-1)^pI_p/a^{\mu+p}\tag{27}$$

and since $x=b^2/a^2$

$$(\partial/\partial a)=-(2x/a)(\partial/\partial x).\tag{28}$$

With the aid of (27) and (28) we can express $F_{v''E'}$ in terms of I_0/a^μ and its differential coefficients with respect to x. Much labor was saved in the numerical calculations by noting that the logarithm of ${}_2F_1$ in (17) is approximately linear in x, and could therefore be expressed with amply sufficient accuracy by the interpolation formula

$$\log{}_2F_1+10=6.78302-12.797\eta-9.711\eta^2-13.02\eta^3,\tag{29}$$

where $\eta=x-0.3$. The error introduced by the use of (29) is well within the accuracy of the experimental determinations of the absorption coefficients.

Performing the necessary algebra we obtain from (26), (27), (28) and (29) the following formulas for the matrix components.

$$\begin{aligned}
&\text{(a)}\quad v''=0,\quad F_{0E}=B_0,\\
&\text{(b)}\quad v''=1,\quad F_{1E}=B_1Q,\\
&\text{(c)}\quad v''=2,\quad F_{2E}=B_2[2\mu-15-4Q+Q^2+16x^2(dP/dx)]=B_2S,\\
&\text{(d)}\quad v''=3,\quad F_{3E}=B_3[3S(2\mu-1)+(2\mu-3)(2\mu-2)(2\mu-1)-8U],
\end{aligned}\tag{30}$$

where

$$\begin{aligned}
&\text{(a)}'\quad B_{v''}=\left(\frac{\pi b'}{R}\right)^{\frac{1}{2}}\frac{2^{\mu-\omega-1}\Gamma(\mu+\omega)}{a_{v''}\Gamma(\omega+1)[\Gamma(2\mu-3+v'')v''!(2\mu-3+2v'')]^{\frac{1}{2}}}\,x^{\omega/2}(1+x)^{-\mu+\frac{1}{2}}\cdot{}_2F_1,\\
&\text{(b)}'\quad P=\omega/2x-[(\mu-\tfrac{1}{2})/(1+x)]+[d\ln F/dx]=d\ln I_0/dx,\\
&\text{(c)}'\quad Q=-3-4xP,\\
&\text{(d)}'\quad R'=(-Q+2\mu+1)/2,\\
&\text{(e)}'\quad U=R'^3+3R'^2-3(\mu^2+\mu/2+9/2)R'+2(\mu+2)+3(\mu+\tfrac{1}{2})(\mu-\tfrac{1}{2})(\mu-1)\\
&\qquad\qquad +12R'(R'+1)x^2(dP/dx)+8x^3(d^2P/dx^2).
\end{aligned}\tag{30$'$}$$

IX. COMPARISON OF THEORY WITH EXPERIMENT

In Eq. (22) there are three constants which may be fixed arbitrarily, *viz.*, $D_{n''n'}$, ω (the order of the Bessel function), and V_∞'. The unknown electric moment, $D_{n''n'}$ appears in all the results as a constant factor. The position of the upper potential curve with respect to the lower and hence the energies of the transitions, are determined by V_∞'. The slope and curvature of the upper potential energy curve, and the width of the curve representing ϵ_0 depend on the value of ω. As explained in paragraph 7, V_∞' was fixed by making the maxima, and ω by making the widths, of the theoretical and experimental ϵ_0 curves coincide. The value of $D_{n''n'}$ was determined by making the actual values of the ordinates of the theoretical and experimental curves coincide at the maximum of ϵ_0. This done, the rest of the calculations proceeded with no further assumptions. Our values of the various constants were

$$D_{n''n'}=(4.77\times10^{-10})\times(0.016\times10^{-8})\text{ e.s.u. cm.}$$

$$\left.\begin{aligned}\beta&=74{,}574.6\\ \gamma&=154{,}292\end{aligned}\right\}\text{in the units to give the potential energy curve in cm}^{-1}\text{ and A.}$$

$$\omega=162,\ \mu=281,\ m=279.5,\ V_\infty'=3617\text{ cm}^{-1}.$$

$$r_0=1.009\text{A},\ a_0=2.881\times10^{10}\text{ cm}^{-1}.$$

$$\left.\begin{aligned}E_0''&=-79{,}517\text{ cm}^{-1}\\ E_1''&=-78{,}951\text{ cm}^{-1}\\ E_2''&=-78{,}391\text{ cm}^{-1}\\ E_3''&=-77{,}837\text{ cm}^{-1}\end{aligned}\right\}\text{given by the formula } E''_{v''}=-(\kappa^2\gamma^2/4m^2)[v''/m+1]^{-2}.$$

We used Birge's[7] values for h, c, etc. The value of $D_{n''n'}$ corresponds to the displacement of one electronic charge through a distance of 0.016A, which seems to be a reasonable result.

The heavy broken curve in Fig. 1, lying just above the upper Morse curve, is the upper

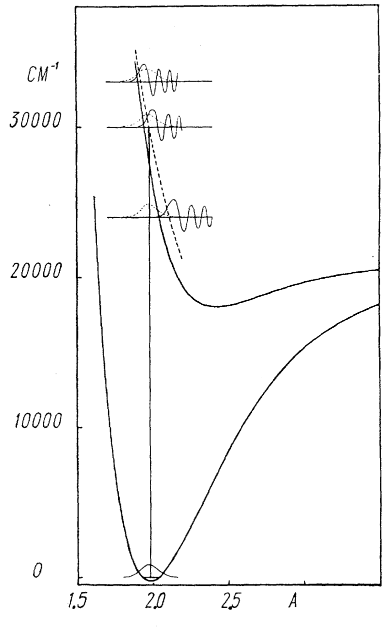

FIG. 1. The heavy continuous curves are the Morse curves for the Cl_2 molecule. The heavy broken curve is our upper potential energy function. The light oscillating curves are the corresponding eigenfunctions and the light dotted curves represent the eigenfunction for $v''=0$.

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[7] R. T. Birge, Phys. Rev. Sup. 1, 1 (1929).

potential curve which was determined by our values of ω and V_∞'. The oscillating curves are three of the corresponding proper functions, $F'_{E'}(r)$, and at each energy we have repeated $F_0''(r)$ (shown dotted). The amount of overlapping of F' and F'' gives one a pictorial representation of the amount of absorption from the level $v''=0$ at different parts of the spectrum. At 24,000 cm^{-1} the overlap is small and ϵ_0 has only 1/100 of its maximum value. At 30,000 cm^{-1}, where the overlap is considerable, ϵ_0 is almost a maximum. At 33,000 cm^{-1} the overlapping is greater still but there is also considerable cancellation because of the negative part of F'. At this point, ϵ_0 has $\frac{1}{2}$ of its maximum value.

The values of the squares of the matrix components for the transitions from the levels $v''=0$, 1, 2 and 3 are drawn in Fig. 2, the vertical scale being arbitrary. In Fig. 3, we have compared the theoretical and experimental values of ϵ_0 and ϵ_1. The check is excellent for ϵ_0 and less good for ϵ_1 but it must be remembered that the experimental values of ϵ_1 were very rough.

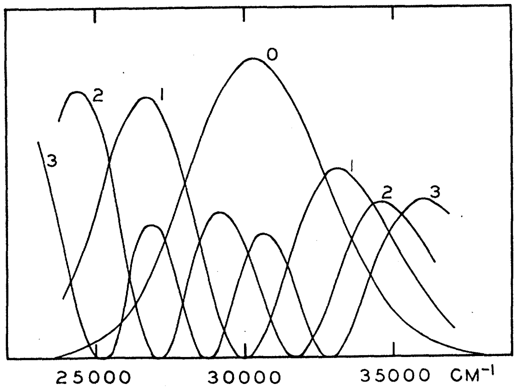

FIG. 2. The squares of the matrix components for transition from the levels $v''=0$, 1, 2 and 3.

A better comparison of the theory with the experimental data is given in Fig. 4. The curves are the theoretical values of ϵ at our extreme temperatures, 291 and 1038°K, calculated by means of Eq. (22), by using the theoretical values of the absorption from the first four vibrational levels of the normal state of the molecule. The points are the experimental values taken from Table I of Part I. The check at 291°K is excellent.

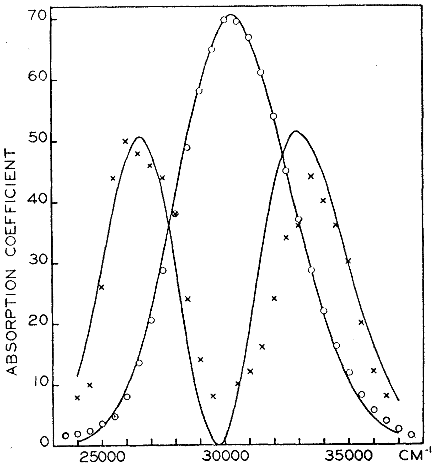

FIG. 3. A comparison of the experimental (points) and theoretical (curves) values of ϵ_0 and ϵ_1. The circles are the experimental values of ϵ_0, and the crosses those of ϵ_1, taken from Table II of Part I.

In discussing the check at 1038°K, it should be borne in mind that only the first four vibrational levels were used, leaving five percent of the molecules unaccounted for. One would therefore expect that the theoretical curve would be a few percent too low.

In a recent paper Stueckelberg[8] has calculated the continuous absorption curve of O_2, by a method which is in principle the same as ours. He uses the Hermitic eigenfunctions (simple

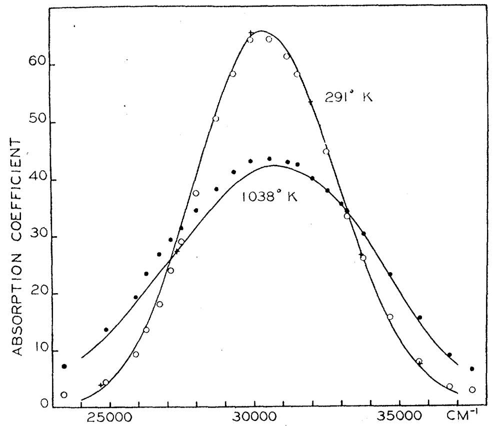

FIG. 4. A comparison of the experimental and theoretical values of the absorption coefficient of Cl_2 at the extreme experimental temperatures. The curves are theoretical; the circles, our experimental result from Table I of Part I, and the crosses are the results of Halban and Siedentopf at room temperature.

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[8] E. C. G. Stueckelberg, Phys. Rev. **42**, 522 (1932).

harmonic oscillator) for the lower state and the Kramers approximations for the eigenfunctions of the upper state, which involves the approximation that the potential energy curve for the upper state is linear over the important range of r. There is an error in his calculation of the rotational effect: His Eq. (13) on page 522 should not contain the temperature factor. The author informs us that he is publishing a correction.

X. Validity of the Franck-Condon Principle

Our determination of the upper potential energy curve enables one to see how closely the classical Franck-Condon principle is obeyed. The heavy vertical line in Fig. 1 represents the most probable transition, according to this principle, from the level $v''=0$. The point at which it cuts the upper potential curve should give the energy of the maximum of ϵ_0. It cuts the Morse curve at 27,500 cm^{-1}, and our potential curve at 30,000 cm^{-1}, the actual maximum of ϵ_0 being at 30,300 cm^{-1}. Assuming our potential function to be the correct one, it is seen that the Franck-Condon principle is in error by only 300 cm^{-1}, which is a surprising result when one considers the broad maxima of the upper and lower proper functions and the nature of the integration.

XI. An Alternative Form of $V''(r)$

In the preceding calculations we have assumed the validity of the Morse formula for the lower potential energy V''. This assumption is certainly a good approximation to the truth in the region of our calculations. It seemed desirable, however, to investigate the effect of a slight change in the form of the lower potential energy curve. For this purpose we assumed the eigenfunction to be of the form

$$\psi_0''=\rho^m e^{-a^2\rho^2}. \qquad (31)$$

It is then easy to find the form of V'' which substituted in the Schroedinger equation will give Eq. (31) as a solution. We find

$$V''=\beta/\rho^2+\gamma\rho^2 \qquad (32)$$

with $\kappa^2\beta=m(m-1)$ and $\kappa^2\gamma=4a^4$ so that the Schroedinger equation is

$$d^2\psi/d\rho^2+\kappa^2(E''-\beta/\rho^2-\gamma\rho^2)\psi=0. \qquad (33)$$

The potential energy curve (32) is more symmetrical than the Morse curve.

The eigenvalues of (33) are given by

$$\kappa^2E''_{v''}=2a^2(2m+1+2v''), \qquad (34)$$

$E''_{v''}$ being referred to a different zero from that of the previous case.

It is interesting to note that the energies are equally spaced like those of the simple harmonic oscillator.

The eigenfunctions are given by

$$\psi''_{v''}=\rho^m e^{-a^2\rho^2}\Lambda_{v''}(\rho^2), \qquad (35)$$

where $\Lambda_{v''}(\rho^2)$ is a polynomial of degree v'' in $\rho^2=(r-r_0)^2$.

We have not troubled to find the general form of $\psi''_{v''}$, but have calculated the absorption coefficient for $v''=0$.

The matrix component

$$F_{0E}=\int \rho^{m+\frac{1}{2}}e^{-a^2\rho^2}J_\omega(b\rho)d\rho \qquad (36)$$

can also be expressed in terms of a hypergeometric function (Watson, p. 393) which, however, does not converge rapidly enough to make the calculation feasible in the case of chlorine. We therefore evaluated the integral (36), by a method (summation of ordinates) equivalent to graphical integration. We shall omit the details of the calculation and merely mention that the experimental results for the absorption from $v''=0$ are given equally well by the new formula for $V''(\rho)$. The only effect of the change is to raise the curve for $V'(\rho)$ in Fig. 1 by about 600 cm^{-1} relative to the minimum of $V''(\rho)$.

The Franck-Condon principle thus gives a value lying midway between the values obtained from the two formulas for $V''(\rho)$.