

INTENSITIES IN SINGLET-TRIPLET BANDS OF
DIATOMIC MOLECULES

BY ROBERT SCHLAPP

UNIVERSITY OF WISCONSIN

(Received January 13, 1932)

ABSTRACT

Intensity formulae are found for the rotational structure of bands arising from transitions between a singlet and a triplet state of a diatomic molecule. These intercombinations occur because the wave functions which diagonalize the orbit-spin interaction contain both singlet and triplet terms. In the transition ${}^1\Sigma - {}^3\Sigma$ two cases arise, according as the two states have the same or opposite symmetry as regards reflection of the orbital motions in a plane containing the nuclei, a different set of branches appearing in either case. A comparison is made with measurements of intensities in the atmospheric absorption bands of oxygen; the agreement is satisfactory on the assumption that these bands are due to dipole transitions from the ${}^3\Sigma^-$ ground state to a ${}^1\Sigma^-$ state. Formulae are also found for the transitions ${}^1\Sigma - {}^3\Pi$, ${}^1\Sigma - {}^3\Delta$ when the triplet state comes under either of Hund's cases (a) or (b).

THEORETICAL investigations of intensities in electronic bands have hitherto dealt with transitions between states of the same multiplicity. Certain bands are however known from their structure to be due to "inter-system" combinations between terms of different multiplicities. In this paper only singlet-triplet combinations are considered, since all inter-system bands so far described are of this kind.

The proof of the selection rule for molecular spectra that only terms of like multiplicity combine depends on the possibility of separating the wave function of any state of the stationary molecule into the product of two factors, one depending on the orbital motions, and the other on the electron spins. This separation can be made only when the orbit-spin interaction is negligibly small; the effect of the interaction will be to modify the wave functions in such a way as to permit inter-system transitions of small intensity. In the analogous case of intercombinations between singlet and triplet terms in an atom with two electrons¹ it is necessary to solve this perturbation problem completely before the intensities can be calculated. The molecular problem is simpler in that for our purpose the perturbation problem need not be completely solved, nor indeed would this be possible without definite knowledge of the complete molecular wave functions. We are here concerned with the way in which the intensities depend on the rotation quantum number J for a given electronic transition, and not, as in the atomic case, with the intensities of different electronic transitions.

STATIONARY MOLECULE

Electronic orbital wave functions. The position of an electron with respect to the molecule with nuclei held fixed is specified by Cartesian coordinates

¹ W. V. Houston, Phys. Rev. 33, 297 (1929).

$(\xi\eta\zeta)$ where ζ is along the axis of figure, or by cylindrical coordinates $(\rho\phi\zeta)$, the azimuth ϕ about the ζ -axis being measured from the plane $\eta=0$. In analogy with the usual theory of the helium atom, the wave functions for a molecule with two electrons are, to a first approximation, of the form

$$p(1)e^{i\lambda_1\phi_1}q(2)e^{i\lambda_2\phi_2} \pm p(2)e^{i\lambda_1\phi_2}q(1)e^{i\lambda_2\phi_1}$$

where p , q , are real functions, supposed normalized, which do not involve ϕ_1 and ϕ_2 , and λ_1 , λ_2 , are the components along the axis of figure of the orbital angular momenta I_1 , I_2 of the individual electrons. The sum $\lambda_1+\lambda_2=\Lambda$ is equal to 1, 2, \dots for Π , Δ , \dots states, and the upper sign is appropriate for singlet states, the lower for triplets. If in virtue of the interaction between I_1 and I_2 the individual λ 's are no longer good quantum numbers, the wave function is a linear combination of terms like the above all having the same value of $\lambda_1+\lambda_2=\Lambda$. In these wave functions, which are complex, there is a degeneracy associated with the two possible directions of orbital motion, corresponding to $\pm|\Lambda|$. If $\Lambda=0$ (Σ states), this degeneracy no longer exists. Since the coefficients of the wave equation are all real, the wave functions for Σ states are essentially real, and of the form $F \cos \lambda(\phi_1-\phi_2)$ or $G \sin \lambda(\phi_1-\phi_2)$ where F , G , are real functions of the coordinates of the electrons other than ϕ_1 , ϕ_2 . These two wave functions are respectively even and odd with respect to reflection of the orbital motion in the plane $\eta=0$ (replacement of ϕ by $-\phi$), and represent Σ^+ and Σ^- states.

Spin functions. For a singlet the spin function is, in the usual notation, $(\Phi_{\alpha_1}\Phi_{\beta_2}-\Phi_{\beta_1}\Phi_{\alpha_2})/2^{1/2}$ and for a triplet, $\Phi_{\alpha_1}\Phi_{\alpha_2}$, $(\Phi_{\alpha_1}\Phi_{\beta_2}+\Phi_{\beta_1}\Phi_{\alpha_2})/2^{1/2}$ or $\Phi_{\beta_1}\Phi_{\beta_2}$ according as the projection Σ of the total spin S on the axis of figure is equal to 1, 0, or -1 . The sum $\Lambda+\Sigma$ is denoted by Ω , and is attached as a suffix to the term symbol.

Orbit-spin interaction. The unperturbed system to which these wave functions refer is specified by quantum numbers Λ , Σ and S . The energy H_0 , including the energy of the electrons in the field of the nuclei, their electrostatic interaction, the coupling of orbits and spins separately to the axis of the molecule, and the "exchange" coupling energy of the two spins, is a diagonal matrix. We then take as the small perturbation the orbit-spin interaction $H_1=a_1(I_1 \cdot s_1)+a_2(I_2 \cdot s_2)$, where a_1 , a_2 , are real constants, I_1 the vector with components $(I_1)_\xi=(\hbar/2\pi i)(\eta_1\partial \dots / \partial \zeta_1 - \zeta_1\partial \dots / \partial \eta_1)$ etc. and similarly for I_2 , and s_1 , s_2 are the Pauli spin operators defined as usual.² It is readily verified by the properties of the operators I and s that the matrix H_1 involves terms for which $\Delta\Lambda=0, \pm 1$, and is diagonal in the quantum number Ω . The diagonality in Ω is otherwise obvious since the component of the total angular momentum along the axis of figure is a constant of the perturbed as well as the unperturbed motion.

The perturbed wave functions are therefore linear combinations of the unperturbed wave functions, all the functions in any combination having the same value of Ω , and multiplicities 1 or 3. To begin with we shall consider

² See, for example, J. H. Van Vleck, Phys. Rev. 33, 467 (1929).

the most interesting case ${}^1\Sigma - {}^3\Sigma$ of inter-system combinations; the same method applies to other cases as well. In terms of the old wave functions ψ we have the following new wave functions ψ' for the Σ states:

$$\begin{aligned}\psi'({}^1\Sigma_0) &= a\psi({}^1\Sigma_0) + p\psi({}^3\Pi_0') + q\psi({}^3\Sigma_0) + r\psi({}^3\Pi_0) \\ \psi'({}^3\Sigma_{-1}) &= b\psi({}^3\Sigma_{-1}) + s\psi({}^1\Pi_{-1}) \\ \psi'({}^3\Sigma_0) &= c\psi({}^3\Sigma_0) + t\psi({}^1\Sigma_0) \\ \psi'({}^3\Sigma_1) &= d\psi({}^3\Sigma_1) + u\psi({}^1\Pi_1)\end{aligned}\tag{1}$$

where a, b, c, d , are constants of order unity, and p, q, r, s, t, u are constants much less than unity if, as we shall suppose, the orbit-spin interaction is small. In the wave functions for the triplet states terms in $\psi({}^3\Pi)$ have been omitted, as they cannot contribute to the inter-system intensities ${}^1\Sigma - {}^3\Sigma$. The states denoted ${}^1\Pi_{-1}$ and ${}^3\Pi_0'$ have $\Lambda = -1$.

ROTATING MOLECULE

To obtain the complete wave functions of the rotating molecule, each of the original ψ 's must be multiplied by a function giving the vibrational motion of the nuclei along the line joining them, and by the appropriate symmetrical top function involving the quantum numbers J, Ω, M , in the usual way. As we are concerned with a definite vibrational level of each of the two states in question, the vibrational part of the wave function merely introduces a factor independent of J into the intensities, and may therefore be omitted in what follows. The symmetrical top function will be denoted by $u_{J\Omega M}(\theta, \omega)$. The Eulerian angles θ, ω , specify the orientation of the axes ($\xi\eta\zeta$) with respect to axes fixed in space, θ being the angle between the ζ -axis and a preferential direction in space, taken as the z -axis, and ω giving the azimuth of the ξ -axis about the z -axis, to which it is supposed to remain perpendicular. We do not require the explicit expression of this function; the following property may be verified from the definition given by Van Vleck²

$$u_{J\Omega M}(\pi - \theta, \omega + \pi) = (-1)^J u_{J-\Omega M}(\theta, \omega).\tag{2}$$

Electric moment. We must now form the matrix elements of the components of the electric moment of the molecule, referred to axes fixed in space, and shall work with the z -component, for which $\Delta M = 0$. Denoting the amplitude for a transition from a rotational level J of a state X to a level J' of state Y by $(X - Y)(JJ')$, we have

$$\begin{aligned}({}^1\Sigma_0 - {}^3\Sigma_{-1})(JJ') &= as({}^1\Sigma_0 - {}^1\Pi_{-1})(JJ') + br({}^3\Pi_0 - {}^3\Sigma_{-1})(JJ') \\ ({}^1\Sigma_0 - {}^3\Sigma_0)(JJ') &= at({}^1\Sigma_0 - {}^1\Sigma_0)(JJ') + cq({}^3\Sigma_0 - {}^3\Sigma_0)(JJ') \\ ({}^1\Sigma_0 - {}^3\Sigma_1)(JJ') &= au({}^1\Sigma_0 - {}^1\Pi_1)(JJ') + dp({}^3\Pi_0' - {}^3\Sigma_1)(JJ').\end{aligned}\tag{3}$$

If we remember that $z = \eta \sin \theta + \zeta \cos \theta$, we may write the following explicit expressions for the first terms on the right of these equations

$$\begin{aligned}
 as & \int \psi^*({}^1\Sigma_0)\eta\psi({}^1\Pi_{-1})d\tau \int u_{J_0M}^*u_{J'-1M} \sin^2\theta d\theta d\omega \\
 at & \int \psi^*({}^1\Sigma_0)\xi\psi({}^1\Sigma_0)d\tau \int u_{J_0M}^*u_{J'0M} \sin\theta \cos\theta d\theta d\omega \\
 au & \int \psi^*({}^1\Sigma_0)\eta\psi({}^1\Pi_1)d\tau \int u_{J_0M}^*u_{J'1M} \sin^2\theta d\theta d\omega
 \end{aligned}$$

where the integration $d\tau$ is over the positional coordinates of the two electrons in the stationary molecule, and includes summation over the spin coordinates. The integral over θ and ω is in each case the well-known amplitude factor for the symmetrical top. We denote the quotient of each of the above expressions by the modulus of the corresponding amplitude factor by A , B , C , respectively, so that A , B , C , are constants whose values depend on the internal dynamics of the molecule, and do not concern us, but whose relative phases for a given value of ΔJ are of importance in what follows.

The phases. Consider first the relation between the coefficients s , t , u , defined in equations (1). Since the off-diagonal terms of the energy matrix are much smaller than the diagonal terms, the phases of the elements a , b , \dots , t , u , of the transformation matrix arising in diagonalising H_0+H_1 are the same as those of the corresponding elements of H_0+H_1 . Thus a , b , c , d , are all real. Remembering that with our choice of wave functions $\psi({}^1\Pi_1) = \psi^*({}^1\Pi_{-1})$ and that $\psi({}^3\Sigma_1)$ and $\psi({}^3\Sigma_{-1})$ are real, we readily find that the matrix elements of H_1 between $({}^3\Sigma_1, {}^1\Pi_1)$ and $({}^3\Sigma_{-1}, {}^1\Pi_{-1})$ are complex conjugates, so that $s = u^*$; also that if the triplet state is ${}^3\Sigma^+$, s is real, while if it is ${}^3\Sigma^-$, s is imaginary; t is always imaginary, and vanishes if both states have the same symmetry as regards reflection of the orbits alone in a plane containing the nuclei, i.e., the orbit-spin interaction will combine ${}^3\Sigma_0^+$ with ${}^1\Sigma^-$ but not with ${}^1\Sigma^+$.

If we denote the three integrals over the internal coordinates τ by l , m , n , respectively, we have $l = n^*$, and l is real or imaginary according as the singlet state is ${}^1\Sigma^-$ or ${}^1\Sigma^+$; m is always real.

In virtue of the integration over the coordinates θ , ω , and the property (2) of the symmetrical top function, A and C will differ by a factor $(-1)^{J+J'}$; the sign of B remains undetermined. Summing up we now have

$$A:B:C = sl:\pm tm:(-)^{J+J'}un = sl:\pm tm:(-)^{\Delta J}s^*l^*.$$

We therefore distinguish two cases:

$$\begin{aligned}
 \text{(i)} & \quad {}^1\Sigma^+ - {}^3\Sigma^- \text{ or } {}^1\Sigma^- - {}^3\Sigma^+: A = (-)^{\Delta J}C, B \neq 0 \\
 \text{(ii)} & \quad {}^1\Sigma^+ - {}^3\Sigma^+ \text{ or } {}^1\Sigma^- - {}^3\Sigma^-: A = (-)^{\Delta J+1}C, B = 0
 \end{aligned} \tag{4}$$

where A , B , C , are all real. A similar argument applied to the second terms on the right of equations (3) leads to the same result. Since the two transitions in any line of (3) have the same values of $\Delta\Omega$, ΔJ , ΔM , they depend on J in the same way, so that the form of the result (4) still holds when both

transitions are taken into account. In this section on phases we have made use of a model of the molecule which is somewhat specialised in that it has only two valence electrons. It is however reasonable to suppose that the phase relations are much more general than the model which was used to determine them.

The amplitudes. We now have the following scheme for the amplitudes of the three transitions ${}^1\Sigma_0 - {}^3\Sigma_{-1}$, ${}^1\Sigma_0 - {}^3\Sigma_0$, ${}^1\Sigma_0 - {}^3\Sigma_1$ for $\Delta M = 0$. The factors depending on J and M are taken from a paper by Kronig,³ and are written so that J refers to the ${}^3\Sigma$ state.

$\Delta\Omega =$	-1	0	1	
$\Delta J = -1$	$A[JQ(J+1)]^{1/2}$	$B[(J+1)Q(J+1)]^{1/2}$	$C[JQ(J+1)]^{1/2}$	(5)
0	$AM/[J(J+1)]^{1/2}$	0	$CM/[J(J+1)]^{1/2}$	
1	$A[(J+1)Q(J)]^{1/2}$	$B[JQ(J)]^{1/2}$	$C[(J+1)Q(J)]^{1/2}$	

where $Q(J) = (J^2 - M^2)/J(2J-1)(2J+1)$. In this table, which really represents two distinct cases (i) and (ii), the constants A , B , C , satisfy the relations (4).

ROTATIONAL UNCOUPLING OF THE SPIN

In the rotating molecule, the ${}^3\Sigma$ state comes under Hund's case (b), in which the coupling between the spin and the axis of figure is negligible compared with that between the spin and the rotation of the molecule. The amplitudes given in the preceding table are not the actual amplitudes, but amplitudes for transitions between the ${}^1\Sigma$ state and a hypothetical ${}^3\Sigma$ state belonging to case (a), in which the spin is imagined as being firmly coupled to the axis of figure, so that the suffixes $-1, 0, 1$, in the ${}^3\Sigma$ state have a meaning as quantum numbers. To pass from these amplitudes to the actual amplitudes in which the ${}^3\Sigma$ state comes under case (b) we must consider the influence of the rotation in uncoupling the spin from the axis of figure.

The method of doing this has been given in a convenient form by Van Vleck,² who showed that the effect depends on a Hamiltonian function H , where

$$H(\Sigma; \Sigma \pm 1) = 2\beta[J(J+1) - \Omega(\Omega \pm 1)]^{1/2}s_\eta(\Sigma; \Sigma \pm 1)$$

$$H(\Sigma; \Sigma) = f(\Sigma) + \beta[J(J+1) + S(S+1) - \Omega^2 - \Sigma^2].$$

In these expressions β is the usual constant $h^2/8\pi^2I$, and s_η is the η component of the Pauli operator for the total electron spin. The term $f(\Sigma)$ is the coupling energy between the total spin S and the axis of figure of the molecule, and is ordinarily proportional to $\Lambda\Sigma$. Here however we are interested in the case $\Lambda=0$, $S=1$; for this case Kramers⁴ has shown that the interaction of the spins of the two electrons is equivalent to a coupling energy proportional to $(3 \cos^2\chi - 1)$ between the spin and the axis of figure, χ being the angle between them. The matrix elements of this coupling energy are thus of the

³ R. de L. Kronig, *Zeits. f. Physik* **45**, 458 (1927).

⁴ H. A. Kramers, *Zeits. f. Physik* **53**, 422 (1929).

form $\alpha(2s_\xi^2 - s_\xi^2 - s_\eta^2)$ where α is a constant which may be either positive or negative.

We now set up the secular determinant, noting that with our choice of ψ 's the elements of s_η are imaginary. Strictly speaking we should calculate the matrix elements with respect to the wave functions ψ' of the stationary molecule, which take into account the orbit-spin interaction; but since the latter is small, we may without great error use the unperturbed functions ψ . The secular determinant is

$$\begin{vmatrix} J(J+1) + \lambda - w & -i[2J(J+1)]^{1/2} & 0 \\ i[2J(J+1)]^{1/2} & J(J+1) + 2 - 2\lambda - w & -i[2J(J+1)]^{1/2} \\ 0 & i[2J(J+1)]^{1/2} & J(J+1) + \lambda - w \end{vmatrix}$$

where $\lambda = \alpha/\beta$, and is therefore large or small according as the state is nearly case (a) or case (b); and $w = W/\beta$. The secular equation may be solved accurately, the roots being

$$w = J(J+1) + \lambda, \quad J(J+1) + 1 - \lambda/2 \pm [(2J+1)^2 + 9\lambda^2/4 - 3\lambda]^{1/2}. \quad (6)$$

If we neglect λ altogether, the roots are $J(J-1)$, $J(J+1)$, $(J+1)(J+2)$. These give the rotational levels of the triplet belonging to a given value of J in case (b). Since in case (b) the energy is given mainly by $w = K(K+1)$ where K is the total angular momentum of the molecule exclusive of spin, we see that the three levels are distinguished by having $K = J-1, J, J+1$, respectively (T_1, T_2, T_3 terms in Mulliken's notation). If λ is so small that its square is negligible, we obtain for the levels the formulae which were obtained by Kramers. His unperturbed system consisted of a free rotator and a free spin vector, with the coupling between them as the perturbation; only those elements of the coupling energy were taken into account which are diagonal in K . This is a good approximation so long as the splitting of the levels caused by this perturbation is small compared with the rotational intervals, which is not always the case in practice. The exact formula (6) is not subject to this restriction; the terms in $\lambda^2, \lambda^3 \dots$ may be looked on as giving the effect of the off-diagonal terms of the coupling which were neglected by Kramers.

In the neighborhood of case (a) $\lambda \gg 1$, and the roots of the secular equation are approximately $\lambda, \lambda, -2\lambda$; the root -2λ refers to the state ${}^3\Sigma_0$. Since the roots of the secular equation do not cross when the parameter λ changes from large negative to large positive values, we see that the (a) state ${}^3\Sigma_0$ passes into the (b) state $K = J-1$ or $K = J+1$ according as the coupling constant α is positive or negative. The correlation of the states ${}^3\Sigma_1, {}^3\Sigma_{-1}$, which have identical energies, with the two remaining (b) states cannot be determined by this argument. But since case (a) states are purely hypothetical when $\Lambda = 0$, the final intensity formulae must be independent of the correlation adopted between them and the actual (b) states. It is found that in oxygen the constant α is positive; we shall adopt the correlation ${}^3\Sigma_{-1} \sim {}^3\Sigma_J, {}^3\Sigma_0 \sim {}^3\Sigma_{J-1}, {}^3\Sigma_1 \sim {}^3\Sigma_{J+1}$, where we use the notation ${}^3\Sigma_{J-1}, {}^3\Sigma_J, {}^3\Sigma_{J+1}$ for the (b) states of ${}^3\Sigma$ usually denoted T_1, T_2, T_3 .

For complete uncoupling of the spin ($\lambda=0$) the transformation matrix arising from the secular problem is

$$S = \begin{pmatrix} 1/2^{1/2} & 0 & 1/2^{1/2} \\ -[(J+1)/2(2J+1)]^{1/2} & i[J/(2J+1)]^{1/2} & [(J+1)/2(2J+1)]^{1/2} \\ [J/2(2J+1)]^{1/2} & i[(J+1)/(2J+1)]^{1/2} & -[J/2(2J+1)]^{1/2} \end{pmatrix}.$$

The columns refer to the (a) states ${}^3\Sigma_{-1}$, ${}^3\Sigma_0$, ${}^3\Sigma_1$ respectively, and the rows to the three (b) states ${}^3\Sigma_J$, ${}^3\Sigma_{J-1}$, ${}^3\Sigma_{J+1}$, in that order, with which we have correlated them. Each row may be multiplied by an arbitrary complex constant, which however does not affect the intensities. Here J refers to the ${}^3\Sigma$ state.

To pass from the amplitudes in the hypothetical transitions ${}^1\Sigma(a) - {}^3\Sigma(a)$ to the actual amplitudes ${}^1\Sigma(a) - {}^3\Sigma(b)$ it is necessary, as shown by Hill and Van Vleck,⁵ to post-multiply the (a) amplitudes of (5) by S^* , so that for example the z -amplitude in the transition ${}^1\Sigma - {}^3\Sigma_J$ is given by the inner product of the appropriate row of the scheme (5) into the first row of $\tilde{\zeta}^*$. This shows that the result is independent of the correlation; the quantum number of the hypothetical (a) state merely plays the part of an index of summation.

The following scheme gives the designations of the nine possible branches; the letters P , Q , R , are the usual symbols corresponding to $\Delta J=1, 0, -1$, and the upper left-hand affix gives the value of ΔK according to the same scheme, so that for example ${}^{RR}R$ means $\Delta J=-1, \Delta K=-2$.

$\Delta(K-J)$	${}^1\Sigma - {}^3\Sigma_{J-1}$ -1	${}^1\Sigma - {}^3\Sigma_J$ 0	${}^1\Sigma - {}^3\Sigma_{J+1}$ 1
$\Delta J = -1$	${}^{RR}R$	${}^{RR}R$	${}^{QR}R$
0	${}^{RQ}Q$	${}^{RQ}Q$	${}^{PQ}Q$
1	${}^{QP}P$	${}^{QP}P$	${}^{PP}P$

Instead of writing down the amplitudes, we shall content ourselves with giving the total intensities, which are obtained from the amplitudes for $\Delta M=0$ by taking three times the square of the modulus, and summing for all values of M from $-J$ to J . If we use the relations (4) between A , B , C , we find that in cases (i) and (ii) complementary sets of branches appear, whose intensities, arranged according to the preceding scheme, are as follows.

Case (i): Singlet and triplet states have opposite symmetry:

$$\begin{array}{ccc} [2A^2 + B^2]J(J+1)/(2J+1) & 0 & [2A^2J^2 + B^2(J+1)^2]/(2J+1) \\ 0 & 2A^2(2J+1) & 0 \\ [2A^2(J+1)^2 + B^2J^2]/(2J+1) & 0 & [2A^2 + B^2]J(J+1)/(2J+1). \end{array}$$

Case (ii): Singlet and triplet states have the same symmetry:

$$\begin{array}{ccc} 0 & 2A^2J & 0 \\ 2A^2(J+1) & 0 & 2A^2J \\ 0 & 2A^2(J+1) & 0. \end{array}$$

⁵ E. L. Hill and J. H. Van Vleck, Phys. Rev. **32**, 250 (1928).

The appearance of complementary sets of branches in the two cases (i) and (ii) is in agreement with the selection rule that only states of opposite symmetry as regards reflection of nuclei and electrons in the origin can combine with each other. If as usual we call the two types of symmetry with respect to this reflection "positive" and "negative", the three component levels of a ${}^3\Sigma$ state belonging to a given value of K , and having $J = K + 1, K, K - 1$, all have the same symmetry, and are alternately positive and negative for successive values of K . Two possible cases arise, according as the states ${}^1\Sigma, {}^3\Sigma$ have (i) opposite, or (ii) the same symmetry, with regard to reflection in the origin, for a given value of K . These two cases are exactly equivalent to the two cases (i) and (ii) above, in which we considered symmetry as regards reflection of the orbits in a plane through the nuclei, since a Σ^+ state may alternatively be defined as one which is positive on reflection in the centre for even J , and a Σ^- state as one which is negative for even J . The nine possible branches fall into two sets, ${}^P P, {}^P Q, {}^R Q, {}^R R$, having ΔK odd, and ${}^{P P P}, {}^Q P, {}^Q Q, {}^Q R, {}^{R R R}$, having ΔK even, and it is readily seen that the rule excluding transitions between states of like symmetry will exclude the first set or the second set in cases (i) and (ii) respectively.

COMPARISON WITH EXPERIMENT

There are no experimental data for the case in which the singlet and triplet states have opposite symmetry. According to one interpretation,⁶ the atmospheric absorption bands of oxygen arise in transitions between a ${}^1\Sigma^-$ state and the ${}^3\Sigma^-$ ground state of the molecule; four branches are observed, which are classed as ${}^P P, {}^P Q, {}^R Q, {}^R R$. Reliable measurements of intensities are exceedingly difficult to make, but recently Childs and Mecke⁷ have made a determination of intensities in the A bands of the absorption spectrum of atmospheric oxygen at room temperatures. The following table gives a comparison between the experimental results and those calculated above. The notation used by Childs and Mecke for the branches is different from that which has been adopted here; in the table both notations are given. We may observe in passing that there is no theoretical justification for the correlation of the triplet states which we have called ${}^3\Sigma_{J-1}, {}^3\Sigma_J, {}^3\Sigma_{J+1}$ with ${}^3\Sigma_{-1}, {}^3\Sigma_0, {}^3\Sigma_1$ respectively, which is the correlation adopted by Childs and Mecke. We have adhered to a more rational correlation, but the matter is not of importance, as we have shown above that the final result does not depend on the correlation. In the formulae of Childs and Mecke J refers to the singlet state; for the sake of comparison the calculated inten-

⁶ R. S. Mulliken, Phys. Rev. **32**, 880 (1928). Mulliken's interpretation that the bands are ${}^1\Sigma_u^- - {}^3\Sigma_g^-$ is the usually accepted one. There are difficulties in accounting for the existence of the ${}^1\Sigma_u^-$ term in the oxygen molecule, and an alternative suggestion, also due to Mulliken, (Reviews of Modern Physics, Jan. 1931, on p. 96) is that the bands are quadrupole transitions ${}^1\Sigma_g^+ - {}^3\Sigma_g^-$. Inter-system quadrupole intensities would of course be very weak indeed; the fact that we obtain good agreement between experiment and theory if we adopt Mulliken's first interpretation is evidence in its favour. See also, Rev. Mod. Phys. **4**, 1 (1932).

⁷ W. H. J. Childs and R. Mecke, Zeits. f. Physik **68**, 344 (1931).

sities have been written in terms of this J instead of in terms of the J of the triplet state, as was done above.

Branch		Int. obs.	Int. calc.
${}^P P$	P_2	$(J+2)/2$	$(J+2)/2$
${}^P Q$	P_3	$(J+\frac{1}{2})/2$	$J/2$
${}^R Q$	R_1	$(J+\frac{1}{2})/2$	$(J+1)/2$
${}^R R$	R_2	$(J-1)/2$	$(J-1)/2$

The fact that in each branch only alternate lines are present is of course accounted for by the identity of the two nuclei and the absence of nuclear spin.

The agreement for the branches ${}^P P$ and ${}^R R$ is perfect; for ${}^P Q$ and ${}^R Q$ there is a discrepancy. Although the experiments just quoted are the most reliable that have so far been made, the actually observed intensities from which Childs and Mecke deduce the law of variation with J as given in the third column of the table show such considerable fluctuations that it is difficult to be certain about their interpretation.

In either of cases (i) and (ii) it is easily shown that the sum of the intensities of all lines having a given level J of the ${}^1\Sigma$ state in common is proportional to $2J+1$; also the sum of the intensities of all the lines having a given value of J in the ${}^3\Sigma$ states in common is proportional to $2J+1$; this value of J will in general occur in all three ${}^3\Sigma$ states, and the rule just given holds for the sum of the intensities from all levels of the triplet having the same J .

INTENSITIES FOR ${}^1\Sigma - {}^3\Pi$, ${}^1\Sigma - {}^3\Delta$

When the triplet state is a Π or a Δ state, it may come under case (a) or case (b), or it may be intermediate between (a) and (b). We consider only the extreme cases. Consider first the three transitions ${}^1\Sigma - {}^3\Pi_0$, ${}^1\Sigma - {}^3\Pi_1$, ${}^1\Sigma - {}^3\Pi_2$, where the triplet state is case (a). The amplitude of the first transition is a linear combination of the amplitudes ${}^1\Sigma - {}^1\Sigma$ and ${}^3\Pi_0 - {}^3\Pi_0$, the amplitude of the second is a linear combination of the amplitudes ${}^1\Sigma - {}^1\Pi_1$ and ${}^3\Sigma_0 - {}^3\Pi_1$, while the amplitude of the third transition vanishes. It may easily be shown, by consideration of the wave functions, that the amplitudes ${}^1\Sigma - {}^3\Pi_0$ and ${}^1\Sigma - {}^3\Pi_1$ differ in phase by a factor i . The total intensities are given by the following table. D and E denote constants.

Branch	P	Q	R
${}^1\Sigma - {}^3\Pi_0$	$2D^2J$	0	$2D^2(J+1)$
${}^1\Sigma - {}^3\Pi_1$	$E^2(J+1)$	$E^2(2J+1)$	E^2J

To pass to the intensities when the ${}^3\Pi$ state comes under case (b) it is necessary to calculate the uncoupling matrix corresponding to the matrix S used above, and apply it to the amplitudes from which the intensities just written down were obtained. As before, nine branches are obtained, whose designations are given by the scheme (7), and whose intensities, arranged according to that scheme, are

$$\begin{array}{ccc}
 D-E]^2(J+1)(J-1)/(2J+1) & [D(J+1)-E]^2/(J+1) & [D(J+1)+EJ]^2(J+2)/(2J+1)(J+1) \\
 E^2(J+1)(J-1)/J & E^2(2J+1)/J(J+1) & E^2J(J+2)/(J+1) \\
 [DJ-E(J+1)]^2(J-1)/J(2J+1) & [DJ-E]^2/J & [D+E]^2J(J+2)/(2J+1).
 \end{array}$$

If the triplet state is $^3\Delta$, case (a), the only component that can combine with $^1\Sigma$ is $^3\Delta_1$. The amplitude is then a linear combination of the amplitudes $^1\Sigma - ^1\Pi_1$ and $^3\Pi_0 - ^3\Delta_1$, and the total intensity is, apart from a constant factor.

Branch	<i>P</i>	<i>Q</i>	<i>R</i>
$^1\Sigma - ^3\Delta_1$	$J+1$	$2J+1$	J

The intensities of the nine branches arising when the state is case (b) are

$$\begin{array}{ccc}
 (J+2)(J+3)/(2J+1) & (J-2)(J+3)/(J+1) & J(J-1)(J-2)/(J+1)(2J+1) \\
 (J+2)(J+3)/J & (J-2)(J+3)(2J+1)/J(J+1) & (J-1)(J-2)/(J+1) \\
 (J+1)(J+2)(J+3)/J(2J+1) & (J-2)(J+3)/J & (J-1)(J-2)/(2J+1).
 \end{array}$$

In all the formulae of this section *J* refers to the triplet state. To obtain the formulae in terms of *J'* referring to the singlet state, it is necessary to replace *J* by *J'+1*, *J'*, *J'-1*, in expressions relating to *P*, *Q*, and *R* branches respectively. In every case it is readily shown that for a given *J* or *J'* the sum of all the intensities is proportional to $2J+1$ or $2J'+1$.

It is a pleasure to acknowledge the continued helpful interest of Professor J. H. Van Vleck in this work, and to thank Professor Mulliken for the opportunity of discussion.