

MAGNETIC DIPOLE AND ELECTRIC QUADRUPOLE LINE STRENGTHS FOR THE ATMOSPHERIC OXYGEN ($b^1\Sigma_g^+ - X^3\Sigma_g^-$) SYSTEM*

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Expressions are developed for the magnetic dipole line strengths of rotational transitions in the A-band (0-0 band) of the atmospheric oxygen ($b^1\Sigma_g^+ - X^3\Sigma_g^-$) system. The line strengths so derived incorporate effects of spin-uncoupling and orbit-rotation interaction besides, of course, spin-orbit perturbation and are absolute in the sense that the dominant transition moment and intensity parameter which enter the formulae are explicitly expressed in terms of the mutual perturbations characterizing the b and X states. Since S-branch transitions (necessarily) of electric quadrupole character, have also been detected in the A-band (Brault [11]), we have included a general discussion of branch line strengths for the electric quadrupole intercombination transition $^1\Sigma^+ - ^3\Sigma^-$.

1. Introduction

The ground electron configuration $\dots(\sigma_g 2p)^2(\pi_u 2p)^4(\pi_g 2p)^2$ of O_2 gives rise to the normal state $X^3\Sigma_g^-$ and the two (metastable) 'singlet oxygen' states $a^1\Delta_g$ and $b^1\Sigma_g^+$, in the ascending order of their energies. Since all these states carry the same vibronic parity label ('g' in this case), transitions among them are rigorously forbidden by the electric dipole selection rules but do occur through the much weaker, magnetic dipole (M1) and/or electric quadrupole (E2) mechanisms [1-3]. In particular, the intercombination transition $b^1\Sigma_g^+ - X^3\Sigma_g^-$ giving rise to the well-known atmospheric oxygen bands [4] is predominantly of M1 character and owes its occurrence to spin-orbit mixing between the $b^1\Sigma_g^+$ and $X^3\Sigma_{g0}^-$ states. Incidentally, this mixing also results in a second order contribution to the spin-splitting parameter λ of $X^3\Sigma_g^-$. Thanks to accurate ab initio calculations [5,6], the $b : X$ perturbation is well characterized. The $b - X$ transition thus affords a happy instance wherein one is in a position to make reliable prediction of absolute intensities of some of the bands.

On the experimental side, the observation of the $b - X$ transition in the solar (absorption) spectrum and in nightglow and auroral (emission) spectra [2], prompted Miller, Boese and Giver to measure systematically the absorption intensities of lines in the 0-0, 1-0 and 2-0 bands [7-9]. While seeking a fit of the

* Dedicated to Professor István Kovács on his eightieth birthday

measured intensities of lines in the A -band (0-0 band) to theory, Miller et al [7] noticed that for $N'' > 11$, the observed intensities of ${}^P P$ and ${}^P Q$ lines tended to be systematically larger than the values computed on the basis of the rigorous Hönl-London factors published by Watson [10]. This suggested that it might prove useful to include the effect of rotational perturbations in the line strength theory for the $b^1\Sigma_g^+ - X^3\Sigma_g^-$ transition and explore possible generalizations. This forms the major theme of the present paper. In the wake of detection by Brault [11], of a few pure E2 lines belonging to the ${}^T S$ branch in the A -band, we have thought it worthwhile to present a derivation of the line strength formulae for a general intercombination E2 transition of the kind ${}^1\Sigma^+ - {}^3\Sigma^-$.

With great reverence and admiration we dedicate the present work to Professor István Kovács as a token tribute. His masterly elucidation of multiplet structure and line intensity in the theory of the rotating diatomic molecule has been a constant source of inspiration for subsequent researchers in the field.

2. Theory

2.1. Perturbed rotational eigenfunctions

In the absence of perturbations, the M1 operator cannot connect states differing in their spin multiplicities. The present discussion is limited to treating the interaction between the b and X states. Further generalizations will be explored in due course. In the non-rotating molecule, the electronic states $b^1\Sigma_g^+$ and $X^3\Sigma_g^-$ ($\Omega = 0$) are already mixed by spin-orbit perturbation ($H_{s.o}$). Accordingly we may write

$$|b^1\Sigma_g^+ \rangle_0 = \cos\theta |b^1\Sigma_g^+ \rangle + \sin\theta |X^3\Sigma_{g0}^- \rangle, \quad (1a)$$

$$|X^3\Sigma_{g0}^- \rangle_0 = \cos\theta |X^3\Sigma_{g0}^- \rangle - \sin\theta |b^1\Sigma_g^+ \rangle. \quad (1b)$$

In the above equations the left hand side kets carry the subscript 0 in anticipation of the fact that these are to form the zeroth order basis functions for the subsequent calculations. Also, we have chosen to express the mixing coefficients in terms of trigonometric functions and θ is defined by

$$\sin 2\theta = 2 \langle b^1\Sigma_g^+ | H_{s.o} | X^3\Sigma_{g0}^- \rangle / \Delta T(b, X), \quad (2)$$

where $\Delta T(b, X) = T_b - T_X$ is the term value difference between the b and X (strictly the $\Omega = 0$ component) states. In the absence of rotation, the states $b^1\Sigma_g^+$ and $X^3\Sigma_g^-$ ($\Omega = \pm 1$) cannot mix since $H_{s.o}$ can cause only 'homogeneous' ($\Delta\Omega = 0$) perturbations [12]. To calculate the branch intensities for the $b - X$ transition, we actually need the rovibronic wave functions which are eigenfunctions of the rovibronic Hamiltonian [13]

$$H = H_{ev} + (2\lambda/3)(3S_z^2 - S^2) + B(\mathbf{J} - \mathbf{S})^2 + \gamma(\mathbf{J} - \mathbf{S}) \cdot \mathbf{S} \quad (3a)$$

$$= H_0 - (B - \gamma/2)(J_+ S_- + J_- S_+). \quad (3b)$$

The vibronic part H_{ev} in (3a) includes the spin-orbit term H_{so} . All the 'diagonal' terms in (3a) are lumped in the part H_0 of (3b). Whenever necessary centrifugal corrections [13] may be added to (3a) or (3b). As outlined in [13], in effecting the diagonalization of (3) it is useful to work with the following rotation-electronic basis functions having well-defined rovibronic inversion parities [14-16].

$$|b^1\Sigma_g^+ JMe \rangle_0 = [\cos\theta|b^1\Sigma_g^+ \rangle + \sin\theta|X^3\Sigma_{g0}^- \rangle]|0JM \rangle, \quad (4a)$$

$$|X^3\Sigma_{g1}^- JMe \rangle = 2^{-1/2}[|X^3\Sigma_{g1}^- JM \rangle + |X^3\Sigma_{g-1}^- JM \rangle], \quad (4b)$$

$$|X^3\Sigma_{g1}^- JMf \rangle = 2^{-1/2}[|X^3\Sigma_{g1}^- JM \rangle - |X^3\Sigma_{g-1}^- JM \rangle], \quad (4c)$$

$$|X^3\Sigma_0^- JMe \rangle_0 = [\cos\theta|X^3\Sigma_{g0}^- \rangle - \sin\theta|b^1\Sigma_g^+ \rangle]|0JM \rangle. \quad (4d)$$

In what follows, we shall suppress the M label, for the sake of brevity. Note the functions (4a) to (4d), supplemented by the appropriate vibrational parts, are eigen-solutions of H_0 . The spin-uncoupling part $-(B - \gamma/2)(J_+S_- + J_-S_+)$ in (3b) has matrix elements connecting (4a) and (4b) caused by the presence of $|X^3\Sigma_{g0}^- J_e \rangle$ in (4a) as a contaminant. To allow for this (in the first order), we 'transform' to the (first order) 'perturbed' basis functions (written with subscript p)

$$|b^1\Sigma_g^+ J_e \rangle_p = |b^1\Sigma_g^+ J_e \rangle_0 - \varepsilon\sqrt{J(J+1)}\sin\theta|X^3\Sigma_{g1}^- J_e \rangle, \quad (5a)$$

$$|X^3\Sigma_{g1}^- J_e \rangle_p = |X^3\Sigma_{g1}^- J_e \rangle_0 + \varepsilon\sqrt{J(J+1)}\sin\theta|b^1\Sigma_g^+ J_e \rangle_0, \quad (5b)$$

with

$$\varepsilon = 2(B_X - \gamma/2)/\Delta T(b, X). \quad (6)$$

The rovibronic eigenfunction of the state b and the intermediate coupling eigenfunctions corresponding to the three rotational term series of X are now given by

$$|b^1\Sigma_g^+ J'e, v' \rangle_p = |b^1\Sigma_g^+ J'e \rangle_p |bv' \rangle, \quad (7)$$

$$|X, F_1(J)e, v'' \rangle = [s_J|X^3\Sigma_{g1}^- J_e \rangle_p + c_J|X^3\Sigma_{g0}^- J_e \rangle_0]|Xv'' \rangle, \quad (8a)$$

$$|X, F_2(J)f, v'' \rangle = |X^3\Sigma_{g1}^- Jf \rangle |Xv'' \rangle, \quad (8b)$$

$$|X, F_3(J)e, v'' \rangle = [c_J|X^3\Sigma_{g1}^- J_e \rangle_p - s_J|X^3\Sigma_{g0}^- J_e \rangle_0]|Xv'' \rangle. \quad (8c)$$

The coefficients s_J and c_J are defined in [13], in terms of the spectroscopic parameters of the X state.

2.2. Magnetic dipole line strengths

The general ideas underlying the calculation of electric dipole line strengths as expounded by Kovács [12], Hougen [14] and Whiting and Nicholls [17] may be

readily adapted to the magnetic dipole case. The $M1$ operator is given by [18], $\mathbf{M} = \mu_B(\mathbf{L} + 2\mathbf{S})$ and the line strength by

$$S(fJ', iJ) = 3 \sum_M | \langle fJ'M | M_Z | iJM \rangle |^2, \quad (9)$$

involving the matrix elements of anyone space-fixed component, say $M_Z = \mu_B(L_Z + 2S_Z)$, between the initial and final states. μ_B is, of course, the Bohr magneton. The use of Hund's case (a) basis functions requires that we first express M_Z in terms of the molecule-fixed components M_r and the direction cosines α_{Rr} as [17]

$$M_Z = M_x \alpha_{Zx} + 2^{-1/2}(M_x + iM_y) \cdot 2^{-1/2}(\alpha_{Zx} - i\alpha_{Zy}) + 2^{-1/2}(M_x - iM_y) \cdot 2^{-1/2}(\alpha_{Zx} + i\alpha_{Zy}). \quad (10)$$

In the context of the $b - X$ transition we may achieve further simplification by exploiting the fact that the perturbed eigenfunctions (7) and (8) are linear combinations of the perturbed basis functions (4c), (4d), (5a) and (5b). This suggests that we first arrive at the effective 'perturbed' amplitudes $\mathcal{A}(bO^+e - X\Omega e/f, J)$ corresponding to each subtransition $|b^1\Sigma_g^+ J'e, v' \rangle_p \rightarrow |X^3\Sigma_{g\Omega}^- J_e/f, v'' \rangle_p$. Here \mathcal{A} stands for a generic branch symbol like P , Q or R . Since \mathbf{M} is an axial vector operator (inversion parity +), we have the obvious selection rules $\Delta J = 0, \pm 1$ with no change of inversion parity. For the $b - X$ system, this implies that the $\Delta J = 0$ (Q -branch) transitions should correspond to the combination $e - e$ while those having $\Delta J = \pm 1$ (R or P -branch) should go with $e - f$. Additionally, in the b and X states of O_2 , only 'positive' rotational levels can occur [1]. Since the operator \mathbf{M} is made up of \mathbf{L} and \mathbf{S} , even the vibronic part of the matrix elements of the molecule-fixed components of \mathbf{M} in (10) can be explicitly evaluated except for the vibrational overlap factor. The procedure described in [17] leads to the following perturbed subamplitudes (neglecting terms in ε^2)

$$Q(b0^+e - X0^+e, J) = -(K\varepsilon \cos \theta)[J(J+1)(2J+1)]^{1/2}, \quad (11a)$$

$$Q(b0^+e - X1e, J) = K(2J+1)^{1/2}(1-\varepsilon), \quad (11b)$$

$$P(b0^+e - X1f, J) = -K(J+1)^{1/2}[1+\varepsilon(J-1)], \quad (11c)$$

$$R(b0^+e - X1f, J) = KJ^{1/2}[1-\varepsilon(J+2)]. \quad (11d)$$

Here

$$K = 2\mu_B(\sin \theta) \langle bv' | Xv'' \rangle. \quad (12)$$

Note that $\sin \theta$ or $\cos \theta$ is already fixed by (2) and ε by (6). Note also that K includes the vibrational overlap factor. From the relations (11b)–(11d) in conjunction with (12) we observe, with Klotz et al [6], that the $b - X$ transition is essentially made up of the 'spin-flips' $X^3\Sigma_{g0}^- - X^3\Sigma_{g\pm 1}^-$.

The large spin-orbit matrix element of 175.6 cm^{-1} between the X and b states [6] and their relative proximity are factors which dictate that the $b : X$ interaction

Table I
 Perturbed amplitudes for the magnetic dipole subtransitions
 $b^1\Sigma_{g0}^+ J'e - X^3\Sigma_{g\Omega}^- J(e \text{ or } f)$

Transition [†]	Amplitude [‡]
$R(b0^+e - X1f, J)$	$KJ^{1/2}[1 - \eta - \zeta(J + 2)]$
$P(b0^+e - X1f, J)$	$-K(J + 1)^{1/2}[1 - \eta + \zeta(J - 1)]$
$Q(b0^+e - X1e, J)$	$K(2J + 1)^{1/2}(1 - \eta - \zeta)$
$Q(b0^+e - X0^+e, J)$	$-K\chi[J(J + 1)(2J + 1)]^{1/2}$

[†] For the notation see text.

[‡] $K = 2\mu_B(\sin \theta) < bv' | Xv'' >$ with $\mu_B = eh/4\pi mc$ (Bohr magneton)

$$\eta = 8^{-1/2}[\alpha_1 \cot \theta < b^1\Sigma_g^+ | L_- |^1\Pi_g > + a_1 < X^3\Sigma_g^- | L_- |^3\Pi_g > + a_0'^* < ^3\Pi_g | L_+ | X^3\Sigma_g^- >]$$

$$\zeta = [2(B_x - \gamma/2)/\Delta T(b, X)] + \delta(^1\Pi', ^1\Pi) \cdot 2^{-1/2} \alpha_1 c_1'^* \cot \theta$$

with $\delta(^1\Pi', ^1\Pi) = 1$ when $^1\Pi' \equiv ^1\Pi$ and = 0 otherwise.

$$\chi = (\cos \theta) \{ 2(B_x - \gamma/2)/\Delta T(b, X) + 2^{-1} [c_1'^* < ^1\Pi_g' | L_+ | b^1\Sigma_g^+ > - c_1 < X^3\Sigma_g^- | L_- | ^3\Pi_g > + d_1 < b^1\Sigma_g^+ | L_- | ^1\Pi_g' > - d_1'^* < ^3\Pi_g | L_+ | X^3\Sigma_g^- >] \}$$

Table II
 Intermediate coupling magnetic dipole line strengths for the atmospheric oxygen
 $(b^1\Sigma_g^+ - X^3\Sigma_g^-)$ system

Branch	Line strength [†]
$^R R_2(J)$	$K^2 J [1 - \eta - \zeta(J + 2)]^2$
$^P P_2(J)$	$K^2 (J + 1) [1 - \eta + \zeta(J - 1)]^2$
$^R Q_1(J)$	$K^2 (2J + 1) [(1 - \eta - \zeta)s_J - \chi c_J \sqrt{J(J + 1)}]^2$
$^P Q_3(J)$	$K^2 (2J + 1) [(1 - \eta - \zeta)c_J + \chi s_J \sqrt{J(J + 1)}]^2$

[†] K, η, ζ and χ are defined in the footnote to Table I

should dominate the perturbation process. In a more rigorous approach, spin-orbit and orbit-rotation perturbations caused by farther-lying states may have to be incorporated in the intensity theory. The necessary generalization along these lines is treated in the Appendix. The perturbed subamplitudes including these additional interacting states are given in Table I. The generalized intermediate coupling line strengths for the four branches $^P P, ^P Q, ^R R$ and $^R Q$ that finally result, are given in Table II.

2.3. Electric quadrupole line strengths for $^1\Sigma^+ - ^3\Sigma^-$ transitions

In the introductory Section we had drawn attention to the identification by Brault [11], of $^T S$ branch transitions in the A-band. These transitions have $\Delta J = 2$ and necessarily originate in the E2 mechanism. An elegant discussion of E2 transi-

tions as applied to diatomic molecules has been given by Chiu [19]. Balasubramanian et al [20] extended Chiu's results for singlet transitions to the case of multiplet transitions and obtained the E2 line strength formula

$$S(fJ', iJ) = [2(2J+1)/3] \sum_{\Omega\Omega'\lambda} a_{i\Omega} a_{f\Omega'}^* \langle n'\Lambda'S'\Sigma', v' | \tilde{Q}_{2\lambda} | n\Lambda\Sigma, v \rangle \times C(J2J'; \Omega\lambda\Omega')^2. \quad (13)$$

In the above relation, unprimed quantum numbers refer to the lower state and the initial and final vibronic state functions are supposedly expressed as linear combinations of Hund's case (a) basis functions with linear coefficients $a_{i\Omega}$. The operator $\tilde{Q}_{2\lambda}$ ($\lambda = -2, -1, 0, 1, 2$) is a molecule-fixed spherical component of the E2 operator and C is a Clebsch-Gordon coefficient. As $\tilde{Q}_{2\lambda}$ is a purely orbital operator, its matrix elements between Hund's case (a) substates vanish unless $S' = S$ and $\Sigma' = \Sigma$. Thus, as before, we need to invoke perturbations in dealing with the intercombination E2 transition $^1\Sigma^+ - ^3\Sigma^-$. A slight (homogeneous) contamination of the $^3\Sigma_0^-$ component by a $^1\Sigma^+$ state (not necessarily the upper state, here under discussion) and the $^3\Sigma_{\pm 1}^-$ by a $^1\Pi$ state (both through spin-orbit perturbation) is all that we need to make the (vibronic) matrix elements

$$Q_{20} = \langle ^1\Sigma^+, v' | \tilde{Q}_{20} | ^3\Sigma_0^-, v \rangle, \quad (14a)$$

$$Q_{2\mp 1} = \langle ^1\Sigma^+, v' | \tilde{Q}_{2\mp 1} | ^3\Sigma_{\pm 1}^-, v \rangle \quad (14b)$$

non-vanishing. These are indeed the transition moments needed in the present intensity problem. It is clear that in dealing with intercombination E2 transitions, it may be instructive to replace the matrix element in (13) by $\langle n'\Omega', v' | \tilde{Q}_{2\lambda} | n\Omega, v \rangle$ appropriate for Hund's case (c) vibronic states. The use of case (c) notation at once makes it obvious that for the $^1\Sigma^+ - ^3\Sigma^-$ line strength problem, in the absence of orbit-rotation perturbations, no transition moments other than the ones defined by (14a) and (14b) will be needed.

We now demonstrate that the moments Q_{20} and $Q_{2\mp 1}$ are real and that $Q_{2-1} = Q_{21}$. First of all, we observe that the phases of the quadrupole operator components $\tilde{Q}_{2\lambda}$ may be so chosen that they transform exactly like the spherical harmonics $Y_{2\lambda}$ (referred to the molecular frame) under the (molecule-fixed) reflection operation σ_{xz} and of time reversal \mathcal{J} . For the vibronic functions we adopt the standard phase choice suggested by Hougen [14].

Thus we have

$$\sigma_{xz} \tilde{Q}_{2\lambda} = (-)^\lambda \tilde{Q}_{2-\lambda}, \quad (15a)$$

$$\mathcal{J} \tilde{Q}_{2\lambda} = (-)^\lambda \tilde{Q}_{2-\lambda}, \quad (15b)$$

$$\sigma_{xz} |\Sigma^\pm\rangle = \pm |\Sigma^\pm\rangle, \quad (16a)$$

$$\sigma_{xz} |S\Sigma\rangle = (-)^{S-\Sigma} |S-\Sigma\rangle, \quad (16b)$$

$$\mathcal{J} |\Sigma^\pm\rangle = + |\Sigma^\pm\rangle, \quad (16c)$$

$$\mathcal{J} |S\Sigma\rangle = (-)^\Sigma |S-\Sigma\rangle \quad (\text{integral } S \text{ and } \Sigma). \quad (16d)$$

Table III
Intermediate coupling electric quadrupole line strengths for
 $^1\Sigma^+ - ^3\Sigma^-$ transition

Branch	Line strength [†]
$^T S_1(J)$	$[(J+2)/(2J+3)] \{ Q_{2-1} s_J (4J/3)^{1/2} + Q_{20} c_J (J+1)^{1/2} \}^2$
$^R S_3(J)$	$[(J+2)/(2J+3)] \{ Q_{2-1} c_J (4J/3)^{1/2} - Q_{20} s_J (J+1)^{1/2} \}^2$
$^R R_2(J)$	$2Q_{2-1}^2 (J+2)/3$
$^R Q_1(J)$	$[2(2J+1)/(2J-1)(2J+3)] \{ Q_{2-1} s_J - Q_{20} c_J [J(J+1)/3]^{1/2} \}^2$
$^P Q_3(J)$	$[2(2J+1)/(2J-1)(2J+3)] \{ Q_{2-1} c_J + Q_{20} s_J [J(J+1)/3]^{1/2} \}^2$
$^P P_2(J)$	$2Q_{2-1}^2 (J-1)/3$
$^P O_1(J)$	$[(J-1)/(2J-1)] \{ Q_{2-1} s_J [4(J+1)/3]^{1/2} - Q_{20} c_J J^{1/2} \}^2$
$^N O_3(J)$	$[(J-1)/(2J-1)] \{ Q_{2-1} c_J [4(J+1)/3]^{1/2} + Q_{20} s_J J^{1/2} \}^2$

[†] $Q_{2-1} = \langle b^1 \Sigma_g^+ | \tilde{Q}_{2-1} | X^3 \Sigma_{g1}^- \rangle$, $Q_{20} = \langle b^1 \Sigma_g^+ | \tilde{Q}_{20} | X^3 \Sigma_{g0}^- \rangle$

A general transition moment relevant to the present problem is given by

$$Q_{2\lambda} = \langle ^1\Sigma^+, v' | \tilde{Q}_{2\lambda} | ^3\Sigma_{\Omega=-\lambda}^-, v \rangle .$$

Applying σ_{xz} to both sides, we obtain

$$\sigma_{xz} Q_{2\lambda} = Q_{2\lambda} = (-)^\lambda \cdot (-)^{1+1+\lambda} \langle ^1\Sigma^+, v' | \tilde{Q}_{2-\lambda} | ^3\Sigma_{\lambda}^-, v \rangle = +Q_{2-\lambda} .$$

Application of \mathcal{J} to both sides in the above equation, gives

$$\mathcal{J} Q_{2\lambda} = Q_{2\lambda}^* = (-)^{-\lambda} \cdot (-)^\lambda \langle ^1\Sigma^+, v' | \tilde{Q}_{2\lambda} | ^3\Sigma_{-\lambda}^-, v \rangle = Q_{2\lambda} .$$

Thus we have proved that $Q_{2\lambda}$ is real and that $Q_{2\lambda} = Q_{2-\lambda}$ for $\lambda = 1$. Consequently, for a $^1\Sigma^+ - ^3\Sigma^-$ transition, the quadrupole line strengths are governed by the two real transition moments Q_{20} and $Q_{21} = Q_{2-1}$. We may mention that the same results will hold for a $^1\Sigma^- - ^3\Sigma^+$ transition (with the reflection parities of the Σ states reversed). On the other hand, had we considered the transition $^1\Sigma^+ - ^3\Sigma^+$ (between Σ states of same parity), the moment Q_{20} would have vanished due to symmetry and one would have had to include only the moment $|Q_{2-1}| = |Q_{21}|$ in the intensity theory.

It now remains to formally complete the line strength derivation. Application of the E2 selection rules $\Delta J = 0, \pm 2$ ($e - e$) and $\Delta J = \pm 1$ ($e - f$) to the $^1\Sigma^+ - ^3\Sigma^-$ transition leads to 8 rotational branches. The intermediate coupling eigenfunctions of the three rotational term series $F_i(J)$ (with $i = 1, 2, 3$) of $^3\Sigma^-$ are given by relations analogous to (8a)–(8c). Explicit formulae for the Clebsch–Gordon coefficients have been tabulated by Condon and Shortley [18]. Use of these in conjunction with the transition moments (14a) and (14b) finally leads to the desired

expressions which are listed in Table III. For ready recognition, the lower state term series index has been added to the branch symbol as a subscript. When the ratio λ/B (of the spin-splitting parameter to the rotational constant) in the $^3\Sigma^-$ state is small, the state will switch to Hund's case (b) rather rapidly. The case (b) limits for the line strengths may be realized by the substitution, $c_J = [J/(2J + 1)]^{1/2}$, $s_J = [(J + 1)/(2J + 1)]^{1/2}$ in the expressions in Table III.

3. Discussion

Let us now apply the magnetic dipole line strengths derived in Section 2.2 to the A -band ($0-0$ band) of the $O_2 b-X$ system. In order to make quantitative comparison with experimental results, we need the values of the parameters contained in the expressions in Table II. The parameters η , ζ and χ are relatively insignificant and may be ignored, initially. The value of the principal moment K given by relation (12) is arrived at as follows. First of all, the use in (2) of the spin-orbit matrix element $\langle b|H_{so}|X \rangle = 175.6 \text{ cm}^{-1}$ from [6] and $\nu_0 = 13121 \text{ cm}^{-1}$ (A -band origin) from [2], gives $\sin \theta = 1.3384 \times 10^{-2}$. The vibrational overlap factor calculated analytically using harmonic oscillator functions [21], is $\langle bv' = 0|Xv'' = 0 \rangle = 0.9666$ so that K becomes $(2.5873 \times 10^{-2})\mu_B$. We use this to compute the net spontaneous emission transition rate from the level $b^1\Sigma_g^+(v' = 0, J')$ to all possible J'' levels of $X^3\Sigma_g^-(v'' = 0)$. Accordingly [1],

$$A(bv' = 0, J') = \frac{64\pi^4}{3h(2J' + 1)} \sum_{J''} [\nu(J', J'')]^3 S(J', J''), \quad (17)$$

where S is the line strength factor and ν is the line wave number. If we replace ν by ν_0 (ignoring the small line to line variation) and use the sum rule $\sum_{J''} S(J', J'') = 2K^2(2J' + 1)$, which trivially follows from the formulae in Table II, we get

$$A(bv' = 0, J' \rightarrow Xv'' = 0) \approx A_0^0 = \frac{64\pi^4}{3h} \nu_0^3 (2K^2) = 0.0816 \text{ s}^{-1}.$$

This is strikingly close to the experimental value $A_0^0 = 0.077 \pm 0.003 \text{ s}^{-1}$ deduced by Miller et al from their painstaking (absorption) measurements on the A -band [7]. This agreement between theory and experiment should leave no doubt that the $b-X$ intercombination ($M1$) transition is indeed dominated by 'spin-flips' and that contributions from more remote perturbers are far less significant. A previous calculation by Klotz et al [6] did not take into account the vibrational overlap factor (necessarily less than unity) and thus gave the larger value $A_0^0 = 0.087 \text{ s}^{-1}$.

Miller et al [7] have drawn attention to the fact that for $N'' > 11$, the measured intensities of lines belonging to the $^P P$ and $^P Q$ branches were generally larger than their computed values, despite the use of Watson's rigorous Hönl-London ($H-L$) factors [10] in the computation. This discrepancy cannot be due to non-inclusion

Table IV
 Hönl-London (H-L) factors and absorption intensities
 (in $\text{cm}^{-1}/\text{km atm}$ at 293 K) for rotational transitions in the A-band
 of the $b^1\Sigma_g^+ - X^3\Sigma_g^-$ transition of O_2

N''	H-L factor		Intensity			H-L factor		Intensity		
	calc ^a	calc ^b	calc ^a	calc ^b	obs ^c	calc ^a	calc ^b	calc ^a	calc ^b	obs ^c
	<i>P</i> <i>P</i>					<i>P</i> <i>Q</i>				
1	2.00	2.00	6.89	6.89	6.5					
3	4.00	4.01	12.84	12.86	13.1	2.69	2.69	8.73	8.74	8.9
5	6.00	6.01	16.96	17.00	16.8	4.69	4.70	13.39	13.42	13.0
7	8.00	8.02	18.82	18.88	18.4	6.69	6.71	15.89	15.93	15.3
9	10.00	10.04	18.50	18.57	18.3	8.69	8.72	16.23	16.29	15.9
11	12.00	12.06	16.50	16.58	16.3	10.69	10.74	14.84	14.91	14.4
13	14.00	14.08	13.53	13.61	13.8	12.69	12.76	12.44	12.51	12.4
15	16.00	16.11	10.27	10.34	10.8	14.69	14.78	9.55	9.61	9.6
17	18.00	18.13	7.25	7.30	7.7	16.69	16.81	6.81	6.86	7.2
19	20.00	20.17	4.78	4.82	5.0	18.69	18.84	4.52	4.56	4.9
21	22.00	22.20	2.94	2.97	3.4	20.69	20.88	2.80	2.82	3.2
23	24.00	24.24	1.70	1.72	2.2	22.69	22.91	1.63	1.65	2.1
25	26.00	26.29	0.92	0.93	—	24.69	24.96	0.89	0.90	—
27	28.00	28.33	0.47	0.48	0.4	26.69	27.00	0.45	0.46	0.4
29	30.00	30.38	0.23	0.23	0.2	28.69	29.04	0.22	0.22	0.2
31	32.00	32.44	0.10	0.10	0.1	30.69	31.10	0.10	0.10	0.1
	<i>R</i> <i>R</i>					<i>R</i> <i>Q</i>				
1	1.00	0.99	3.44	3.41	3.5	2.31	2.31	8.02	8.01	8.2
3	3.00	2.99	9.63	9.61	9.5	4.31	4.30	13.97	13.94	13.4
5	5.00	4.99	14.13	14.09	13.8	6.31	6.29	18.02	17.97	17.1
7	7.00	6.98	16.46	16.40	16.1	8.31	8.28	19.74	19.66	18.6
9	9.00	8.96	16.65	16.58	16.1	10.31	10.26	19.26	19.17	18.6
11	11.00	10.94	15.13	15.05	14.6	12.31	12.24	17.11	17.01	16.5
13	13.00	12.92	12.56	12.48	12.0					

^a From Ref. [7] based on the line strengths of Watson [10]
^b Based on the present line strength expressions given in Table II
^c From Ref. [7]

of centrifugal corrections to the c_J and s_J coefficients, since the H-L factors for P *P* and R *R* do not even involve these coefficients. The H-L factors derived here (that is, the line strength formulae listed in Table II, without the K^2 factor), which incorporate rotation-induced corrections, seem to provide at least a partial explanation. Referring to the footnotes in Table I, if we ignore the effects of remote perturbers, we would have $\eta = 0$, $\zeta = \chi = 2(B_X - \gamma/2)/\Delta T(b, X) = 2.2 \times 10^{-4}$. Since this parameter is positive, it contributes to a J -dependent multiplicative correction, larger than unity, to the H-L factors of P *P* and P *Q*. It may be recalled that these corrections originate in the spin-uncoupling process which tends to mix the $|b^1\Sigma_g^+ J e >_0$ and $|X^3\Sigma_{g1}^- J e >$ via $|X^3\Sigma_{g0}^- J e >_0$, [see relations (4a), (5a) and (5b)]. In Table IV,

the H-L factors of Watson [10] (corrected for centrifugal effects on the c_J , s_J coefficients) and the present H-L factors are compared. (The former were multiplied by the factor 2 to make them conform to our normalization). The resulting intensities are also compared in the Table. The intensities of ${}^P P$ and ${}^P Q$, computed using the present H-L factors do change in the right direction although the improvement may seem marginal. In the generalized version of the theory presented in the Appendix, the condition $\zeta = \chi$ will have to be relaxed, (see footnotes to Table I). Therefore, one might be tempted to seek better agreement between experiment and theory by treating these as two independent, adjustable parameters. However, in the case of the $b-X$ system such an approach would be hard to justify, given the fact that practically the whole of the transition intensity is determined by the $b : X$ interaction. Perhaps a more justifiable step in the computation is the inclusion of the systematic change in the energy denominator $\Delta T(b, X)$ due to rotation of the molecule. One recalls that strictly, $\Delta T(b, X)$ which enters the main transition moment K through $\sin \theta$, [see relations (12) and (2)] should represent $\Delta T(bv = 0, J; X0^+, v = 0, J)$. This change should amount to a slow decrease in ΔT and a corresponding increase in the intensities of all the branches. But given the level of the experimental uncertainties [7], these refinements, perhaps, are merely ornamental. We may also remark that admittedly, a more rigorous approach to the $b - X$, M1 line strengths is to start with a direct numerical diagonalization of the 3×3 matrix, say in the 'unperturbed' basis $|b^1\Sigma_g^+ J_e v' \rangle$, $|X^3\Sigma_{g0}^- J_e v \rangle$ and $|X^3\Sigma_{g1}^- J_e v \rangle$. We have largely obviated the need for this by rigorously incorporating the dominant spin-orbit part of the perturbation right at the start and using the spin-orbit-perturbed zeroth order basis so obtained for the subsequent stage. This hybrid procedure has the advantage that treating effects of a farther-lying perturbers (as outlined in the Appendix), is more readily accomplished.

As for the application of the electric quadrupole line strengths derived in Section 2.3, we have nothing much to offer. The difficulties are twofold. On the experimental side, the available intensity data are too scanty; only 8 lines of the ${}^T S$ branch have been measured [11]. On the theoretical side, no reliable ab initio values for the two transition moments Q_{20} and Q_{2-1} (defined in Table III) are available. Brault's measurements [11] show that quadrupolar contribution to the A -band intensity is smaller by the factor 10^{-5} compared to the M1 contribution. An earlier attempt made by Klotz et al [6] to estimate the quadrupolar contribution to the A -band intensity is incomplete as it ignored the moment Q_{2-1} . In principle it must be possible to determine the two moments from the experimental data. Transitions with $\Delta J = \pm 2$ should offer the best prospect as their intensities cannot have magnetic dipole admixtures. Any determination based on scanty data relating to a single branch like the ${}^T S$ as available for the A -band, is bound to prove unreliable because of the correlated manner in which the two moments enter the line strength formulae (see Table III).

Before closing, we state the sum rules obeyed by the quadrupolar line strengths. Direct summation of the appropriate expressions in Table III gives the line strength sum $\frac{2}{3}(2J+1)(Q_{2-1}^2 + Q_{20}^2)$ for all transitions sharing fixed $J'' = J$ of the $F_1(J)$ and $F_3(J)$ term series. For the two branches ${}^P P_2(J)$ and ${}^R R_2(J)$ terminating on $F_2(J)$,

we obtain the sum $\frac{2}{3}(2J + 1)Q_{2-1}^2$. One may construct similar sums for transitions involving fixed J' .

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Appendix

We outline how the M1 transition line strengths derived in Sections 2.1 and 2.2 may be generalized to include more remote perturbers. The starting zeroth order basis functions are relations (4a)–(4d) of Section 2.1. In addition to H_{so} , we need the orbit–rotation perturbation (or ‘ L -uncoupling’) term which has the form [12], $H_{or} = -B(L_+J_- + L_-J_+)$. As before, Hougen’s [14] standard phase convention [relations (16a)–(16d) of Section 2.3] supplemented by $\sigma_{xz}|\Lambda \rangle = (-)^{\Lambda} |-\Lambda \rangle$, $J|\Lambda \rangle = (-)^{\Lambda} |-\Lambda \rangle$ for non- Σ electronic states, is adopted. The perturbed basis functions, to first order, are given by

$$|b^1\Sigma_g^+ J_e \rangle_p = |b^1\Sigma^+ J_e \rangle_0 - 2^{1/2}a' \sin \theta |^3\Pi_0 J_e \rangle - x^{1/2}[\varepsilon \sin \theta |X^3\Sigma_1^- J_e \rangle - 2^{1/2}c' \cos \theta |^1\Pi' J_e \rangle - 2^{1/2}d' \sin \theta |^3\Pi_1 J_e \rangle], \tag{A1}$$

$$|X^3\Sigma_{g1}^- J_f^e \rangle_p = |X^3\Sigma_1^- J_f^e \rangle - a_1 |^3\Pi_1 J_f^e \rangle - \alpha_1 |^1\Pi_1 J_f^e \rangle + x^{1/2}[\delta(e, f) \cdot \varepsilon \sin \theta |b^1\Sigma^+ J_e \rangle_0 \pm c_0(f) |^3\Pi_0 J_f^e \rangle] + (x - 2)^{1/2}c_2 |^3\Pi_2 J_f^e \rangle, \tag{A2}$$

$$|X^3\Sigma_{g0}^- J_e \rangle_p = |X^3\Sigma_0^- J_e \rangle_0 - 2^{1/2}a_0 \cos \theta |^3\Pi_0 J_e \rangle + (2x)^{1/2}[c_1 \cos \theta |^3\Pi_1 J_e \rangle - d_1 \sin \theta |^1\Pi' J_e \rangle]. \tag{A3}$$

Here $x = J(J + 1)$ and $\delta(e, f)$ in (A2) stands for $\delta(e, e) = 1$, $\delta(e, f) = 0$. The additional spin–orbit mixing coefficients are denoted by a , α , etc. and the orbit–rotation perturbation coefficients by c , d , etc. Primed quantities refer to the upper state. Typically we have $a' = \langle ^3\Pi_0 | H_{so} | b^1\Sigma^+ \rangle / \Delta T(^3\Pi_0, b^1\Sigma^+)$, $c' = \langle ^1\Pi' | BL_+ | b^1\Sigma^+ \rangle / \Delta T(b^1\Sigma^+, ^1\Pi')$, etc. Note that the different Ω -substates of $^3\Pi$, including the 0^\pm components of $^3\Pi_0$, are treated as independent states. It is to be understood that all the perturbing states have ‘ g ’ vibronic symmetry although we have chosen to suppress this index in (A1)–(A3), on the right hand side. If more perturbing states are involved, appropriate sums over these states will have

to be used. The parameter ϵ appearing in (A1) and (A2) has been defined already [Eq. (6)]. These perturbed basis functions now take the place of the corresponding functions on the right of relations (7) and (8a)–(8c) of Section 2.1.

To gain clarity in the subsequent calculation, we first work out the perturbed subtransition amplitudes $\mathcal{A}(b0^+e - X\Omega J e \text{ or } f)$. The standard procedure described in [17] yields the subamplitudes listed in Table I (only terms up to the order warranted by the limit of accuracy of the perturbed wave functions have been retained). One interesting feature to note is that the part $\mu_B L$ of the M1 operator also contributes to the transition moment. In the previous calculation (Section 2.2) only the $\mu_B(2S)$ part was of consequence. We might draw attention to the fact that the phase convention adopted here leads to the somewhat peculiar result that all the singlet–singlet and singlet–triplet perturbation matrix elements are real while the triplet–triplet matrix elements are pure imaginary. Nevertheless, the same phase choice ensures that all the transition moments come out real. Referring to Table I, we see that the generalized amplitudes contain in all four intensity parameters, namely, K , η , ζ and χ , instead of the two (K and $\zeta = \chi$) that arose in the limited treatment presented in Section 2. The parameter η represents a ‘remote perturber spin–orbit’ correction to the vibronic moment K . Likewise ζ and χ (or rather, $K\zeta$ and $K\chi$), are both in the nature of rovibronic moments containing orbit–rotation corrections due to the distant perturbers. Notice that in ζ this correction term is non-zero only if the $b^1\Sigma_g^+(Je)$ and $X^3\Sigma_{g\pm 1}^-$ are perturbed by one and the same $^1\Pi(Je)$ state. In the case of the A -band, the very favourable vibrational overlap factor $\langle bv' = 0 | Xv'' = 0 \rangle = 0.97$ and, of course, the promixity of the b and X states strongly suggest that the equality $\zeta = \chi$ should hold to a good approximation. For the $1 - 0(B^-)$ and $2 - 0(\gamma^-)$ bands, however, this equality may be expected to break down progressively.

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