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Absorption intensities of rovibronic transitions in the A-band of $^{16}O_2$: Analysis and calculation of magnetic dipole and electric quadrupole contributions

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ABSTRACT

The recently measured magnetic dipole (M1) absorption intensities of rovibronic transitions in the A-band ($b^1\Sigma_g^+ - X^3\Sigma_g^-$, 0–0 band) of $^{16}O_2$ are theoretically analyzed employing a model in which the $b^1\Sigma_g^+ : X^3\Sigma_g^-$ mutual perturbations are treated to a sufficient degree of accuracy. Effects of rotational perturbations became manifest in the data analysis and rovibronic correction parameters are needed to reconcile theory and experiment. At a subtle level there is evidence of Herman–Wallis (HW) type effect arising from vibration–rotation interaction in the b and X states. The functional form for the HW correction factor is arrived at from first principles. The final calculations reproduce the measured intensities to fraction of a percent, well within the measurement accuracy. The present analysis leads to the value $\langle M1 \rangle_{0,0} = 0.02679(4)\,\mu_B$ for the M1 transition moment, and the spontaneous emission rate (Einstein-A coefficient) $\Gamma_{0,0} = 0.0874\,s^{-1}$. For the sake of completeness, the electric quadrupole (E2) contribution to the observed intensities is also quantitatively assessed.

1. Introduction

The advent of cavity-enhanced laser absorption spectroscopy has brought several ultra-weak molecular transitions within the ambit of laboratory investigations. The identification of electric quadrupole lines in the $b^1\Sigma_g^+ - X^3\Sigma_g^-$, 0–0 band (the so called A-band) in O_2 by Long et al. [1] and in the O_2 $a^1\Delta_g - X^3\Sigma_g^-$, 0–0 band by Gordon et al. [2] in laboratory experiments provide fine examples of the power of this technique. To this one must add the recent ultra-sensitive measurements of high N (J) M1 transitions in the PP and PQ branches in the A-band reported by Havey et al.

[3] in the extended N-range $33 \leq N \leq 51$, complementing the previous measurements of Robichaud et al. [4] for $N \leq 33$. In a more recent work, Long et al. [5] measured several RR and RQ transitions involving $1 \leq N \leq 41$.

In a previous communication from our laboratory, Balasubramanian and Narayanan [6], had addressed the problem of magnetic dipole (M1) and electric quadrupole (E2) branch linestrengths in the O_2 A-band. In the wake of laboratory measurements of E2 transitions in the A-band and the theoretical analysis reported by Long et al. [1], we recently revisited our linestrength derivation and demonstrated [7] that the E2 linestrength formulas derived in [6] adequately described the experimental intensities. The theoretical part of Long et al.'s work [1] contains a brief discussion of the M1 transition intensities as well. By applying their theoretical results to the M1 line intensity measurements in the O_2 A-band reported by Robichaud et al. [4], Long et al. [1] arrived at the value $M1 = 0.06868\,\mu_B$

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for the transition moment, which is far too large compared to the *ab initio* value 0.026 μ_B computed by Minaev et al. [8] and others [6]. This rather large discrepancy suggested that we attempt a fit of the same $M1$ intensity data [4], to the equations derived in [6]. This resulted in the value $M1 = 0.0268\ \mu_B$ bringing it much closer to the *ab initio* value. As the fitting progressed we were struck by the exceptional quality of the experimental data given in [4]. This became even more apparent when we realized that the intensities of the RR and RQ lines predicted on the basis of this limited analysis—limited to the PP, PQ lines with $N \le 33$ [4], closely reproduced the measured values [5]. Since the measurements reported in [3–5] were all carried out using the frequency-stabilized cavity ring-down spectrometer (FS-CRDS) located at NIST, we expected the data from all these measurements to be of the same high quality. This suggested that we enlarge the scope of our initial travail and attempt a comprehensive analysis and calculation of the line intensities given in Refs. [3–5], based on the theoretical framework developed in [6]. It may be recalled that the $M1$ transitions involve $\Delta J = 0, \pm 1$ with $+ \leftrightarrow +$, $- \leftrightarrow -$ for the rovibronic parity and therefore, are also allowed by the much weaker E2 mechanism. Since the measured intensities carry this independent, additive contribution from E2, we thought it would be of interest to know the extent of this contribution in quantitative terms. Details of these calculations are discussed in this paper.

2. Theoretical background, fitting procedure and calculations

2.1. M1 intensities

In this paper we shall be concerned mainly with the intensity measurements of Robichaud et al. [4] (for PP and PQ with $3 \le N \le 33$), Havey et al. [3] (for PP and PQ with $33 \le N \le 51$), and of Long et al. [5] (for RR and RQ with $1 \le N \le 41$). In [5] Long et al. have critically examined all the previous A-band line intensity measurements in relation to the data reported in [3–5]. This in-depth and professionally thorough inter-comparison exercise includes fitting of the various data sets to the standard intensity model described by the relation [5]

$$S_m = \frac{C_b S_b g \tilde{\nu}_m L_m e^{-E''hc/k_B T_{ref}}(1 - e^{-\tilde{\nu}_m c/k_B T_{ref}})}{Q(T_{ref})\tilde{\nu}_b}. \tag{1}$$

The symbols occurring in this expression are explained in [5]. An interesting feature that emerged from all these fittings is the fact that the use of Watson's [9] rotational intensity factors L_m in Eq. (1) led to systematic residuals, quadratic in N, in the obs.–cal. differences despite the fact that Watson's formulas for L_m are based on a full intermediate coupling treatment. To place matters in prospective, in relation to the NIST FS-CRDS data [3–5], Eq. (1) undercalculates the PP and PQ transition intensities to the extent of 3.6% at $N = 43$, while in the case of the RR and RQ branches, at $N = 39$, there occurs a overcalculation to a smaller extent amounting to 1.0%. These departures are much too large compared to the (relative) standard experimental errors which are typically $< 0.3\%$ for the better-measured lines. These N-dependent residuals could be allowed for by incorporating a quadratic

Herman–Wallis (HW) type multiplicative factor $(1+a_1 m +a_2 m^2)^2$ in Eq. (1). In this way Long et al. [5] could successfully fit the combined NIST FS-CRDS data [3–5] to the standard intensity model with the choice $a_1 = -2.6580 \times 10^{-4}$ and $a_2 = 3.622 \times 10^{-6}$, for the HW coefficients determined from the fit. We shall presently show that the major part of the coefficients a_1 and a_2 attributed to the HW effects arises naturally in the theoretical framework developed in [6].

Ref. [6] presents a derivation of generalized linestrength expressions for the four branches $P(N)P(J=N)$, $P(N)Q(J=N-1)$, $R(N)R(J=N)$ and $R(N)Q(J=N+1)$ of the A-band allowed by the $M1$ selection rules. In that work [6], these branches were equivalently designated as $^PP_2$, $^PQ_3$, $^RR_2$, and $^RQ_1$, respectively. These formulas contain the dominant transition moment K, which hereinafter, we denote by $\langle M1 \rangle$ and besides, certain rovibronic interaction correction terms ζ, χ, η. When effects due to remote perturbers are ignored and only the vibronic and rovibronic perturbations between $b^1\Sigma_g^+$ and $X^3\Sigma_{g\Omega}^-$ are considered, the expressions for the rotational intensity factors or Hönl–London factors L_m reduce to

Branch	L_m (= Rotational linestrength/$\langle M1 \rangle_{0,0}^2$)
$P(N)P(J=N)$ $R(N)R(J=N)$	$\|m-1\|\{f(m)(1-\varepsilon-\varepsilon m)\}^2$ (2)
$P(N)Q(J=N-1)$	$\|2m+1\|\{f(m)[(1-\varepsilon)c_J + \varepsilon s_J\sqrt{m(m+1)}]\}^2$ (3)
$R(N)Q(J=N+1)$	$\|2m+1\|\{f(m)[(1-\varepsilon)s_J - \varepsilon c_J\sqrt{m(m+1)}]\}^2$ (4)

In the above relations $m = -N$ for the PP and PQ transitions, $m = N+1$ for the RR and RQ transitions. $\langle M1 \rangle_{0,0}$ is the N-independent transition moment. The use of m rather than J in Eqs. (2)–(4) represents a slight departure from the usage in [6]. It makes the linestrength expressions appear more symmetrical between the P and R branches and, more importantly, in this form it more readily relates to the discussion in [5]. In intermediate coupling, the coefficients c_J and s_J are best expressed in terms of J and so are subscripted with J. These coefficients are defined in [2,9] in terms of the $^3\Sigma$ state parameters.

In respect of Eqs. (2)–(4) certain comments are in order. First we note that with the substitution $\varepsilon = 0$, $f(m) = 1$, the above expressions for L_m reduce to those of Watson [9] except for a uniform numerical factor of 2 arising from a difference in the normalization convention for the linestrength sum adopted in [6]. It is shown in [6] that the parameter $\varepsilon = (2B_{0x} - \gamma_{0x})/\Delta T(b,X)$ in which B_{0x} and γ_{0x} are, respectively, the rotational and spin-rotation constants in the $X^3\Sigma_g^-(v=0)$ vibronic state and $\Delta T(b,X) = T(b^1\Sigma_g^+ v=0) - T(X^3\Sigma_g^- v=0) = 13122.0056\ \text{cm}^{-1} = \tilde{\nu}_b$, the A-band origin [6]. Use of the X-state molecular parameters reported in [1] gives $\varepsilon = 2.1977 \times 10^{-4}$. Since ε is already quite small, the N-dependence of the energy denominator in the definition of ε has been ignored. The prefactor $f(m)$ in the braces calls for some explanation. From the *ab initio* theoretical calculations of Minaev et al. [8], Koltz et al. [10] and others [6] it is known that the A-band derives most of its intensities from spin-flip (microwave) transitions,

transmitted *via* the spin-orbit (SO) mixing of the $b^1\Sigma_g^+$ and $X^3\Sigma_{g0}^-$ states. It is shown in [6] that the transition moment $\langle M1 \rangle$ is given by

$$\langle M1 \rangle = 2\mu_B \langle b^1\Sigma_g^+ | H_{SO} | X^3\Sigma_g^- \rangle / \Delta T(b,X). \tag{5}$$

Strictly, the energy denominator is J-dependent and for the A-band one should use $\Delta T = T(b^1\Sigma_g^+ v = 0, J') - T(X^3\Sigma_{g0}^- v = 0, J'' = J')$ on the right hand side of Eq. (5) and correspondingly denote the transition moment as $\langle M1(bv = 0J'e; Xv = 0J'' = J'e) \rangle$. The need to let $J'' = J'$ arises from the fact that the perturbation process should conform to the J-rule $\Delta J = 0$, with no change of rovibronic parity [11]. In the $b^1\Sigma_g^+$ state there is no distinction between N and J and the rotational energy is given by $B_{0b}J'(J' + 1) = B_{0b}N'(N' + 1)$. On the other hand in the $X^3\Sigma_g^-$ state, for a given N there arise three J-levels, $N+1$, N, $N-1$ of which $J = N+1$ and $N-1$, respectively, go with the $F_1(J)$ and $F_3(J)$ term series of e-parity while $J = N$ goes with the $F_2(J)$ manifold of f-parity [11]. Nevertheless, the rotational term energies are effectively described by $B_{0x}N(N + 1)$, (except for a first few N levels for which the $f(m)$ correction is unimportant). As a result the energy denominator in Eq. (5) should be replaced by

$$\tilde{\nu}_b + (B_{0b} - B_{0x})m(m + 1) = \tilde{\nu}_b \left[1 + \frac{B_{0b} - B_{0x}}{\tilde{\nu}_b} m(m + 1) \right].$$

In the above discussion centrifugal correction terms (D) have been ignored. After the use of the known values of B_{0x}, B_{0b}, and $\tilde{\nu}_b$ from [1], Eq. (5) reduces to

$$\langle M1(bv = 0J'; Xv = 0J') \rangle = 2\mu_B \frac{\langle b^1\Sigma_g^+ v = 00 | H_{SO} | X^3\Sigma_{g0}^- v = 00 \rangle}{\tilde{\nu}_B} f(m)$$

$$= \langle M1 \rangle_{0,0} f(m)$$

where $f(m) = [1 - 3.538 \times 10^{-6} m(m+1)]^{-1}$. Note that $\langle M1 \rangle_{0,0}$ above still contains the vibrational overlap factor. Since $f(m)$ and the terms in ε both arise from the b-X interaction, we have chosen to club them together in Eqs. (2)–(4). The need to include the factor $f(m)$ in accurate calculations was indicated in the discussion part of [6].

The two correction factors placed in braces in Eqs. (2)–(4), together, could capture a major part of the residuals. The small residual remnants that still persisted could be reconciled by invoking the Herman–Wallis (HW) effect. We now digress briefly to discuss the HW effect and seek a formal derivation to arrive at the form of the corresponding factor which we denote by $f_{HW}(m)$. In the non-rotating diatomic molecule, the vibrational wavefunctions $|v\rangle$ are decided by the (adiabatic) potential function $U(r)$ in a given electronic state. In the presence of rotation, characterized by the quantum number N, the nuclear motion takes place in the effective potential [11]

$$U_N(r) = U(r) + B(r)N(N + 1). \tag{6}$$

here r is the internuclear separation and $B(r) = h/8\pi^2 c\mu r^2$. For the $X^3\Sigma_g^-$ state, Eq. (6) should be supplemented by the spin-uncoupling term but we wish to keep the discussion simple. The vibrational wavefunctions are now modified and should carry the additional label N. Accordingly, we denote them by $|v, N\rangle$. When the change in r due to

centrifugal stretching is small, the $B(r)$ term can be treated as a perturbation. As a result we write

$$|v, N\rangle = |v, 0\rangle + N(N + 1) \sum_{n \neq v} a_{1n} |n, 0\rangle, \tag{7}$$

to first order. Typically

$$a_{1n} = \frac{\langle n, 0 | B(r) | v, 0 \rangle}{G(v) - G(n)}, \tag{8}$$

where $G(n)$ is the vibrational term energy (in cm^{-1}) of the nth vibrational level [11].

We refer again to Eq. (5) and notice that the b-X spin-orbit matrix element as well as the energy denominator are, strictly, functions of r so that $\langle M1 \rangle$ on the left should be replaced by the rotationally perturbed transition moment. Accordingly, we write (specifically for the A-band)

$$\langle M1 (b\,v = 0\,N'; X\,v = 0\,N'' = N) \rangle = 2\mu_B \langle b\,v = 0, N' | \alpha(r) | v = 0, N \rangle, \tag{9}$$

in which

$$\alpha(r) = \frac{\langle b^1\Sigma_g^+(r) | H_{SO} | X^3\Sigma_{g0}^-(r) \rangle}{\Delta T(b, X(r))} \tag{10}$$

is the spin-orbit mixing coefficient. Using the rotation-dependent vibrational wavefunction from Eq. (7) in Eq. (9) we get

$$\langle M1(b\,v = 0\,N'; X\,v = 0\,N) \rangle$$
$$= 2\mu_B \Big\{ \langle b\,v = 0, 0 | \alpha(r) | X\,v = 0, 0 \rangle + N'(N' + 1)$$
$$\times \sum_{n \neq 0} a'_{1n} \langle b\,n, 0 | \alpha(r) | X\,v = 0, 0 \rangle + N(N + 1)$$
$$\times \sum_{n \neq 0} a''_{1n} \langle b\,v = 0, 0 | \alpha(r) | X\,n, 0 \rangle \Big\},$$

which can be more conveniently written as

$$2\mu_B \langle bv = 0, 0 | \alpha(r) | Xv = 0, 0 \rangle \{1 + N'(N' + 1)b'_1 + N(N + 1)b''_1\},$$

in which b'_1 and b''_1 are new constants, expressible in terms of a'_{1n}, a''_{1n}, and certain matrix elements of $\alpha(r)$. For the R-branch transitions we have $N' = N+1$ while for the P-branch $N' = N-1$, so that collectively, one may write

$$\langle M1(b0\,N'; X0, N) \rangle = 2\mu_B \langle bv = 0, 0 | \alpha(r) | v = 0, 0 \rangle$$
$$\times \{1 + (b'_1 - b''_1)m + (b'_1 + b''_1)m^2\}$$
$$= 2\mu_B \langle bv = 0, 0 | \alpha(r) | v = 0, 0 \rangle (1 + \xi_1 m + \xi_2 m^2).$$

here ξ_1 and ξ_2 are the linear and quadratic HW coefficients, and the *intensity* correction factor from the HW effect should take the form $(1 + \xi_1 m + \xi_2 m^2)^2$.

In the work of Long et al. [5] a similar form for the HW factor was chosen by appealing to the work of Watson [12] on the quadratic HW factors in the fundamental bands of linear molecules. Of course, in [5] the authors do point out that to carry over the results of Watson [12] to an electronic transition would need some justification aside of the fact that it proves useful as an empirical hypothesis. Our approach here from first principles is more straightforward. In principle, from the known potential curves of the b- and X-states combined with a knowledge of $\alpha(r)$ from *ab initio* theory, one should be able to evaluate ξ_1 and ξ_2. Since $\alpha(r)$ in Eq. (10) includes the r-dependence of the energy denominator the HW factor derived here should inherently contain the factor $f(m)$ occurring in Eqs. (2)–(4). On the

other hand, the theoretical work of Minaev et al. [8] shows that the r-dependence of $\alpha(r)$ arises mainly from the change in the energy denominator. It is for this reason that in Eqs. (2)–(4) we have resorted to the artifact of factoring out $f(m)$ from the total HW factor as an approximate procedure, as it leads to better physical insight. We concede that this factoring can be done only approximately but for reconciling extremely small residuals it is good enough.

We now turn to the fitting of the experimental intensities given in [3–5] using the standard model, Eq. (1). For convenience we worked with the equivalent expression (supplemented by the HW correction factor)

$$S_m(M1) = (C\langle M1\rangle_{0,0}^2)\tilde{\nu}_m \exp(-c_2 E''_J/T)[1-\exp(-c_2\tilde{\nu}_m/T)]L_m f_{HW}^2(m),$$

(11)

where $c_2 = hc/k$ is the second radiation constant and the prefactor $C\langle M1\rangle_{0,0}^2$ as well as the HW coefficients are to be determined from the fit. The calculations were performed for $T=296$ K. The transition wavenumbers $\tilde{\nu}_m$ and the lower state energies were taken from [5]. The Hönl–London factors L_m were calculated using Eqs. (2)–(4). A preliminary fit without the f_{HW} term left small but systematic residuals in the obs.–cal. intensity differences, amounting to 0.51% undercalculation in the PP and PQ lines at $N=43$ and 0.27% overcalculation in the RR and RQ lines at $N=39$. It was at that stage we thought of including

f_{HW} in the fit. The final fit (wherein data points deviating by larger than 1% were rejected) gave $C\langle M1\rangle_{0,0}^2 = 1.1910(37) \times 10^{-28}$ cm^2/molecule and $f_{HW}(m)=1-4.712$ $(\pm 2.00) \times 10^{-5} m + 2.9(\pm 1.5) \times 10^{-7} m^2$. The error limits in the HW coefficients are relatively large because these parameters are needed to capture remnants of the residuals just at the limit of the measurement errors [3–5]. The $M1$ transition intensities resulting from the final calculations along with the observed intensities are given in Tables 1–4. The values of the present L_m (Eqs. (2)–(4)) are also given in the tables. For ready comparison we have included the calculated intensities reported in [5].

2.2. E2 intensities

Transitions obeying $\Delta J = 0, \pm 1$ are also allowed for the E2 mechanism. Reference [6] lists the E2 linestrength expressions, applicable to the A-band. In [7], we have proved by direct calculation, the equivalence of our theoretical approach to the analysis of the E2 transition intensities to that of Long et al. [1]. The measured intensities of $\Delta J = \pm 2$ (S- and O-branch) transitions reported in [1] were first fitted to the expression

$$S_{JJ'}(E2) = (CQ_{20}^2)\tilde{\nu}^3 \exp(-c_2 E''_J/T)[1-\exp(-c_2\tilde{\nu}/T)]S_x(E2:J'.J'')/Q_{20}^2.$$

(12)

Table 1
Calculated $M1$ and E2 intensities of $P(N)P(J)$ transitions in the O_2 A-band.

Transition	m	$\tilde{\nu}_m$ (cm^{-1})[a]	E_J'' (cm^{-1})[a]	L_m present work	$S_m(M1)$ (cm^{-1})/(molecule cm^{-2})			$S_{JJ'}$ (E2) Calc. (cm^{-1}/molecule cm^{-2}) Present work[c]
					Cal.			
					Ref [5]	Present work	Obs.[b]	
$P(1)P(1)$	-1	13118.044661	3.96108	2.0000	3.066E-24	3.066E-24	–	0
$P(3)P(3)$	-3	13112.015868	18.33718	4.0037	5.721E-24	5.721E-24	5.738(8)E-24	40.7E-30
$P(5)P(5)$	-5	13105.616870	44.21171	6.0114	7.573E-24	7.572E-24	7.557(9)E-24	71.7E-30
$P(7)P(7)$	-7	13098.848243	81.58050	8.0235	8.426E-24	8.425E-24	8.423(10)E-24	89.5E-30
$P(9)P(9)$	-9	13091.710358	130.43750	10.0403	8.312E-24	8.312E-24	8.262(8)E-24	94.0E-30
$P(11)P(11)$	-11	13084.203384	190.77481	12.0622	7.445E-24	7.445E-24	7.437(7)E-24	87.5E-30
$P(13)P(13)$	-13	13076.327282	262.58268	14.0895	6.131E-24	6.131E-24	6.113(5)E-24	73.9E-30
$P(15)P(15)$	-15	13068.081811	345.84949	16.1226	4.679E-24	4.679E-24	–	57.4E-30
$P(17)P(17)$	-17	13059.466520	440.56179	18.1617	3.324E-24	3.325E-24	–	41.3E-30
$P(19)P(19)$	-19	13050.480752	546.70424	20.2074	2.207E-24	2.207E-24	2.213(15)E-24	27.7E-30
$P(21)P(21)$	-21	13041.123637	664.25967	22.2599	1.372E-24	1.372E-24	1.376(3)E-24	17.3E-30
$P(23)P(23)$	-23	13031.394096	793.20908	24.3196	8.005E-25	8.007E-25	8.010(12)E-25	10.2E-30
$P(25)P(25)$	-25	13021.290834	933.53157	26.3869	4.388E-25	4.390E-25	4.389(11)E-25	5.60E-30
$P(27)P(27)$	-27	13010.812342	1085.20445	28.4621	2.263E-25	2.264E-25	2.268(7)E-25	2.89E-30
$P(29)P(29)$	-29	12999.956891	1248.20315	30.5456	1.099E-25	1.100E-25	1.103(4)E-25	1.41E-30
$P(31)P(31)$	-31	12988.722531	1422.50128	32.6378	5.029E-26	5.033E-26	5.017(12)E-26	0.645E-30
$P(33)P(33)$	-33	12977.107088	1608.07059	34.7390	2.170E-26	2.172E-26	2.168(5)E-26	0.278E-30
$P(35)P(35)$	-35	12965.108162	1804.88101	36.8496	8.838E-27	8.847E-27	8.866(38)E-27	
$P(37)P(37)$	-37	12952.723123	2012.90065	38.9701	3.397E-27	3.401E-27	3.407(20)E-27	
$P(39)P(39)$	-39	12939.949105	2232.09578	41.1008	1.234E-27	1.235E-27	1.224(7)E-27	
$P(41)P(41)$	-41	12926.783009	2462.43083	43.2420	4.233E-28	4.239E-28	4.154(50)E-28	
$P(43)P(43)$	-43	12913.221492	2703.86842	45.3943	1.373E-28	1.375E-28	1.375(46)E-28	
$P(45)P(45)$	-45	12899.260968	2956.36938	47.5579	4.211E-29	4.219E-29	4.12(15)E-29	
$P(47)P(47)$	-47	12884.897600	3219.89269	49.7333	1.222E-29	1.225E-29	1.31(11)E-29	
$P(49)P(49)$	-49	12870.127299	3494.39554	51.9210	3.356E-30	3.364E-30	3.72(50)E-30	
$P(51)P(51)$	-51	12854.945718	3779.83330	54.1212	8.726E-31	8.748E-31	1.1(3)E-30	

The observed intensities are also listed under $S_m(M1)$.
  [a] From Ref. [5].
  [b] From Refs. [3,4].
  [c] Calculated only up to $N=33$ (see text).

Table 2
Calculated M1 and E2 intensities of $P(N)Q(J)$ transitions in the O_2 A-band.

Transition	m	$\tilde{\nu}_m$ (cm^{-1})[a]	E_J'' (cm^{-1})[a]	L_m present work	$S_m(M1)$ (cm^{-1})/(molecule cm^{-2})			$S_{JJ''}$ (E2) Calc. (cm^{-1}/molecule cm^{-2})
					Cal.			Present work[c]
					Ref [5]	Present work	Obs.[b]	
$P(3)Q(2)$	-3	13114.100185	16.25286	2.6932	3.888E-24	3.888E-24	3.901(8)E-24	1.530E-30
$P(5)Q(4)$	-5	13107.628463	42.20012	4.6968	5.974E-24	5.975E-24	5.974(9)E-24	0.011E-30
$P(7)Q(6)$	-7	13100.821748	79.60699	6.7065	7.110E-24	7.111E-24	7.089(9)E-24	0.563E-30
$P(9)Q(8)$	-9	13093.655833	128.49202	8.7213	7.287E-24	7.289E-24	7.256(8)E-24	1.19E-30
$P(11)Q(10)$	-11	13086.125129	188.85306	10.7411	6.690E-24	6.692E-24	6.667(7)E-24	1.54E-30
$P(13)Q(12)$	-13	13078.227537	260.68242	12.7664	5.605E-24	5.608E-24	5.608(5)E-24	1.58E-30
$P(15)Q(14)$	-15	13069.961892	343.96941	14.7975	4.332E-24	4.334E-24	4.338(4)E-24	1.40E-30
$P(17)Q(16)$	-17	13061.327268	438.70104	16.8346	3.108E-24	3.110E-24	–	1.10E-30
$P(19)Q(18)$	-19	13052.322739	544.86225	18.8782	2.079E-24	2.081E-24	2.082(12)E-24	0.790E-30
$P(21)Q(20)$	-21	13042.947271	662.43604	20.9286	1.301E-24	1.302E-24	1.304(3)E-24	0.522E-30
$P(23)Q(22)$	-23	13033.199679	791.40349	22.9862	7.629E-25	7.636E-25	7.635(23)E-25	0.319E-30
$P(25)Q(24)$	-25	13023.078597	931.74381	25.0513	4.200E-25	4.205E-25	4.208(10)E-25	0.182E-30
$P(27)Q(26)$	-27	13012.582464	1083.43433	27.1243	2.174E-25	2.177E-25	2.180(5)E-25	0.112E-30
$P(29)Q(28)$	-29	13001.709517	1246.45053	29.2055	1.059E-25	1.061E-25	1.063(4)E-25	0.048E-30
$P(31)Q(30)$	-31	12990.457779	1420.76603	31.2954	4.860E-26	4.868E-26	4.852(15)E-26	0.023E-30
$P(33)Q(32)$	-33	12978.825055	1606.35262	33.3943	2.102E-26	2.106E-26	2.103(5)E-26	
$P(35)Q(34)$	-35	12966.808930	1803.18025	35.5026	8.579E-27	8.595E-27	8.607(29)E-27	
$P(37)Q(36)$	-37	12954.406761	2011.21702	37.6207	3.304E-27	3.311E-27	3.304(21)E-27	
$P(39)Q(38)$	-39	12941.615675	2230.42921	39.7490	1.202E-27	1.204E-27	1.208(11)E-27	
$P(41)Q(40)$	-41	12928.432561	2460.78127	41.8878	4.130E-28	4.140E-28	4.147(60)E-28	
$P(43)Q(42)$	-43	12914.854071	2702.23585	44.0375	1.341E-28	1.345E-28	1.337(42)E-28	
$P(45)Q(44)$	-45	12900.876614	2954.75373	46.1986	4.119E-29	4.131E-29	4.236(76)E-29	
$P(47)Q(46)$	-47	12886.496349	3218.29394	48.3715	1.197E-29	1.200E-29	1.203(66)E-29	
$P(49)Q(48)$	-49	12871.709183	3492.81365	50.5565	3.290E-30	3.301E-30	3.00(39)E-30	
$P(51)Q(50)$	-51	12856.510765	3778.26826	52.7541	8.562E-31	8.593E-31	1.09(23)E-30	

The observed intensities are also listed under $S_m(M1)$.
  [a] From Ref. [5].
  [b] From Refs. [3,4].
  [c] Calculated only up to $N=31$ (see text).

Table 3
Calculated M1 and E2 intensities of $R(N)R(J)$ transitions in the O_2 A-band.

Transition	m	$\tilde{\nu}_m$ (cm^{-1})[a]	E_J'' (cm^{-1})[a]	L_m present work	$S_m(M1)$ (cm^{-1})/(molecule cm^{-2})			$S_{JJ''}$ (E2) Calc. (cm^{-1}/molecule cm^{-2})
					Cal.			Present work[b]
					Ref [5]	Present work	Obs.[a]	
$R(1)R(1)$	2	13126.391964	3.96108	0.9987	1.531E-24	1.531E-24	1.530(6)E-24	65.7E-30
$R(3)R(3)$	4	13131.491402	18.33718	2.9938	4.282E-24	4.281E-24	4.28(1)E-24	102.2E-30
$R(5)R(5)$	6	13136.217029	44.21171	4.9861	6.289E-24	6.289E-24	6.30(2)E-24	126.3E-30
$R(7)R(7)$	8	13140.567357	81.58050	6.9759	7.338E-24	7.338E-24	7.35(2)E-24	135.6E-30
$R(9)R(9)$	10	13144.540696	130.43750	8.9635	7.437E-24	7.437E-24	7.44(2)E-24	130.8E-30
$R(11)R(11)$	12	13148.135152	190.77481	10.9493	6.776E-24	6.776E-24	6.79(2)E-24	115.4E-30
$R(13)R(13)$	14	13151.348626	262.58268	12.9336	5.646E-24	5.646E-24	5.64(2)E-24	94.0E-30
$R(15)R(15)$	16	13154.178813	345.84949	14.9168	4.344E-24	4.345E-24	4.34(1)E-24	71.1E-30
$R(17)R(17)$	18	13156.623203	440.56179	16.8992	3.105E-24	3.106E-24	3.09(1)E-24	50.2E-30
$R(19)R(19)$	20	13158.679074	546.70424	18.8811	2.071E-24	2.072E-24	2.079(7)E-24	33.1E-30
$R(21)R(21)$	22	13160.343498	664.25967	20.8629	1.292E-24	1.293E-24	1.292(5)E-24	20.5E-30
$R(23)R(23)$	24	13161.613332	793.20908	22.8448	7.559E-25	7.563E-25	7.59(2)E-25	11.9E-30
$R(25)R(25)$	26	13162.485220	933.53157	24.8274	4.153E-25	4.155E-25	–	6.50E-30
$R(27)R(27)$	28	13162.955591	1085.20445	26.8108	2.145E-25	2.147E-25	–	3.34E-30
$R(29)R(29)$	30	13163.020655	1248.20315	28.7954	1.043E-25	1.044E-25	–	1.62E-30
$R(31)R(31)$	32	13162.676399	1422.50128	30.7816	4.777E-26	4.782E-26	–	0.738E-30
$R(33)R(33)$	34	13161.918589	1608.07059	32.7696	2.063E-26	2.065E-26	2.049(9)E-26	0.316E-30
$R(35)R(35)$	36	13160.742763	1804.88101	34.7600	8.404E-27	8.415E-27	8.3(2)E-27	
$R(37)R(37)$	38	13159.144227	2012.90065	36.7529	3.232E-27	3.236E-27	3.24(2)E-27	
$R(39)R(39)$	40	13157.118058	2232.09578	38.7487	1.174E-27	1.175E-27	1.17(2)E-27	
$R(41)R(41)$	42	13154.659092	2462.43083	40.7478	4.026E-28	4.033E-28	3.96(15)E-28	

The observed intensities are also listed under $S_m(M1)$.
  [a] From Ref. [5].
  [b] Calculated only up to $N=33$ (see text).

Table 4
Calculated $M1$ and E2 intensities of $R(N)Q(J)$ transitions in the O_2 A-band.

Transition	m	$\tilde{\nu}_m$ (cm^{-1})[a]	E_J'' (cm^{-1})[a]	L_m present work	$S_m(M1)$ (cm^{-1})/(molecule cm^{-2})			$S_{J'J''}$ (E2) Calc. (cm^{-1}/molecule cm^{-2}) Present work[b]
					Cal.			
					Ref [5]	Present work	Obs.[a]	
$R(1)Q(2)$	2	13128.268754	2.08429	2.3048	3.566E-24	3.567E-24	3.57(1)E-24	19.92E-30
$R(3)Q(4)$	4	13133.440971	16.38761	4.3005	6.209E-24	6.210E-24	6.22(2)E-24	16.06E-30
$R(5)Q(6)$	6	13138.204770	42.22397	6.2917	8.013E-24	8.014E-24	8.03(3)E-24	14.66E-30
$R(7)Q(8)$	8	13142.583244	79.56461	8.2800	8.797E-24	8.797E-24	8.80(3)E-24	13.15E-30
$R(9)Q(10)$	10	13146.580459	128.39773	10.2661	8.603E-24	8.604E-24	8.61(3)E-24	11.25E-30
$R(11)Q(12)$	12	13150.196583	188.71338	12.2504	7.658E-24	7.659E-24	7.65(3)E-24	9.10E-30
$R(13)Q(14)$	14	13153.430440	260.50087	14.2332	6.277E-24	6.278E-24	6.25(2)E-24	6.95E-30
$R(15)Q(16)$	16	13156.280200	343.74811	16.2149	4.772E-24	4.772E-24	4.76(1)E-24	5.00E-30
$R(17)Q(18)$	18	13158.743620	438.44137	18.1958	3.379E-24	3.380E-24	3.38(1)E-24	3.38E-30
$R(19)Q(20)$	20	13160.818147	544.56517	20.1763	2.237E-24	2.237E-24	2.249(7)E-24	2.16E-30
$R(21)Q(22)$	22	13162.500954	662.10222	22.1566	1.387E-24	1.388E-24	–	1.30E-30
$R(23)Q(24)$	24	13163.788973	791.03344	24.1372	8.075E-25	8.078E-25	8.12(2)E-25	7.38E-31
$R(25)Q(26)$	26	13164.678897	931.33790	26.1184	4.417E-25	4.419E-25	4.43(1)E-25	3.95E-31
$R(27)Q(28)$	28	13165.167191	1082.99285	28.1004	2.274E-25	2.275E-25	-	1.99E-31
$R(29)Q(30)$	30	13165.250091	1245.97372	30.0837	1.102E-25	1.103E-25	-	9.50E-32
$R(31)Q(32)$	32	13164.923607	1420.25407	32.0686	5.035E-26	5.038E-26	5.04(2)E-26	4.27E-32
$R(33)Q(34)$	34	13164.183518	1605.80566	34.0555	2.169E-26	2.170E-26	2.177(16)E-26	
$R(35)Q(36)$	36	13163.025375	1802.59840	36.0446	8.818E-27	8.825E-27	–	
$R(37)Q(38)$	38	13161.444496	2010.60039	38.0363	3.384E-27	3.387E-27	3.34(8)E-27	
$R(39)Q(40)$	40	13159.435962	2229.77787	40.0309	1.227E-27	1.228E-27	1.224(10)E-27	
$R(41)Q(42)$	42	13156.994619	2460.09530	42.0289	4.204E-28	4.208E-28	4.16(9)E-28	

The observed intensities are also listed under $S_m(M1)$.
[a] From Ref. [5].
[b] Calculated only up to $N=31$ (see text).

The factor $S_x(E2 : J',J'')/Q_{20}^2$ may be identified with the Hönl–London factor $L_{J'J''}(E2)$. It may be noted that transitions with $\Delta J = \pm 2$ cannot carry any $M1$ admixture. As discussed in [7], optimal fit gave $CQ_{20}^2 = 2.708 \times 10^{-42}$ cm^4/molecule, and $Q_{2-1}/Q_{20} = -2.3382$ for the ratio of the two transition moments. Use of the appropriate E2 branch linestrength expressions from [6], in Eq. (12) yielded the E2 intensity values for the PP, PQ, RR and RQ transitions given in the last column of Tables 1–4. We have limited the calculations to $N \leq 33$ because (i) the intensities for higher N-values decrease rapidly and (ii) at higher N-values the HW effect may become important to correct for which we have no experimental data backup.

3. Discussion

Although many intensity measurements in the O_2 A-band have been reported over the last decade [13–16], we have chosen to base the present $M1$ intensity calculation on the NIST FS-CRDS measurements reported in [3–5] both because of the extensive nature of the data set and its high quality. We have limited our $M1$ calculations to the N range for which experimental data were available. Extending these to higher N-values is straightforward but would involve extrapolation beyond the range of validity of the empirically determined HW parameters. Now a brief remark about the use of the improved linestrength expressions, given by Eqs. (2)–(4), in the present analysis and subsequent calculations. These are extensions of the formulas originally due to Watson [9]. Both the rovibronic terms involving ε and the prefactor $f(m)$ in Eqs. (2)–(4) arise naturally in the theoretical

model adopted in [6]. They contain no unknowns and are fully determinable in terms of the molecular parameters of the b and X states. The formulas are rigorously valid for intermediate coupling, much like in the treatment of Watson [9]. These two terms placed in braces in Eqs. (2)-(4), together capture a major part of the residuals. As could be gauged from a comparison of the observed versus calculated intensities listed in Tables 1–4, the present calculations in most cases reproduce the observed intensities to within fraction of a percent, mostly less than 0.3% which represents the typical standard error in the measurements [3–5]. Also gratifying is the fact that our calculated values agree remarkably closely with the calculations in [5]. The mean absolute error in respect of the data points included in the fit is 0.22% whereas their algebraic mean is 0.02%. We are concerned, though, that the two strong transitions $P(9)P(9)$ and $P(9)Q(8)$ are overcalculated, well outside their error margins, although in percentage terms, the obs.–cal. differences are still at the limit of 0.5%. The same trend is observed in the calculations in [5].

Since the present $M1$ intensity calculation and that computed in [5] agree to a remarkable degree, one must be able to relate the two theoretical treatments. In order to unravel this connection we start with the HW correction factor or rather its square root

$$[F_{HW}(m)]^{1/2} = 1 - 2.658(88) \times 10^{-4}m + 3.36(44) \times 10^{-6} m^2,$$
(13)

determined in [5]. Let us compare this with the product $f(m)(1-\varepsilon-\varepsilon m) = [1-2.1977 \times 10^{-4} \quad (m+1)]/[1-3.538 \times 10^{-6}m(m+1)]$ which to a good approximation reduces to

$1 - 2.1627 \times 10^{-4}m + 3.538 \times 10^{-6}m^2$ (neglecting m^3 and higher terms). The fair agreement between the coefficients of m and m^2 in the two expressions, both in magnitude and algebraic sign, is not fortuitous and goes to prove that the major part of the HW coefficients (a_1 and a_2) determined in [5] really originates in the b–X perturbations, be it of the spin-uncoupling type [6] or of the spin-orbit type with the energy denominator changing (actually decreasing) with N. It may be recalled that the value of ε and of the coefficient of $m(m+1)$ in $f(m)$ are fixed by the theory developed in [6] and are *not* adjustable parameters. If we now combine the $f_{HW}(m) = 1 - 4.712(\pm 2.00) \times 10^{-5}m + 2.9(\pm 1.5) \times 10^{-7}m^2$ with the above (reduced) quadratic product we obtain

$$f(m)(1 - \varepsilon - \varepsilon m)f_{HW}(m) = 1 - 2.634(\pm 0.200) \times 10^{-4}m$$
$$+ 3.826(\pm 0.15) \times 10^{-6}m^2. \quad (14)$$

The near agreement between the corresponding coefficients in Eqs. (13) and (14) explains the equivalence of the present and Long et al.'s [5] approaches from the practical standpoint. Those theoretically inclined may find our approach more convincing because a large part of the obs.–cal. residuals gets accounted for naturally within the framework of the theory.

Given the enormous interest in the A-band, perhaps, a more rigorous approach to the $M1$ branch intensities is warranted. Firstly, the b–X perturbations will have to be treated more fully going beyond the first-order calculations attempted in [6]. Next the small orbital contribution to the rovibronic moment should be quantitatively assessed and included. Thirdly, reliable values for the HW coefficients ξ_1, ξ_2, ... should be computed from the known potential energy curves of the b and X states and the r-dependence of the transition moment. These aspects will be explored in a future endeavor.

From the basic relation connecting the integrated absorption coefficient and Einstein's $B_{2 \leftarrow 1}$ coefficient for induced absorption [11], it is possible to deduce

$$C\langle M1 \rangle_{0,0}^2 = \frac{8\pi^3}{3hc} \frac{1}{Q(T)} \langle M1 \rangle_{0,0}^2$$

where $Q(T)$ is the total partition sum. The fit of the experimental intensities to Eq. (11) yielded the value $C\langle M1 \rangle_{0,0}^2 = 1.1910(37) \times 10^{-28}$ cm^2/molecule, from which, taking $Q(T = 296) = 215.774$, we arrive at the value $\langle M1 \rangle_{0,0} = 0.02679(4)\,\mu_B$. This is close to the *ab initio* value $0.02552\,\mu_B$ deduced from the theoretical transition rate $\Gamma_{0,0} = 0.0794\,s^{-1}$ computed by Minaev et al. [8]. The value $\langle M1 \rangle_{0,0} = 0.02679\,\mu_B$ derived here from the experimental data, when inserted in the relation

$$\Gamma_{0,0} = \frac{64\pi^4}{3h} \nu_{0,0}^3 \left[2\langle M1 \rangle_{0,0}^2 \right],$$

given in [6], leads to $\Gamma_{0,0} = 0.0874\,s^{-1}$, which is 10% larger than the theoretical value but is close to the value $0.0869\,s^{-1}$ deduced in [5].

Turning now to the E2 part of the calculation, the entries in the last column of Tables 1–4 show that the E2 contribution to the transition intensities is 4 to 6 orders smaller than the $M1$ contribution. Thus the E2 mechanism is far too weak to influence the transition rate $\Gamma_{0,0}$ in any

perceptible way. In passing we call attention to the abrupt drop in the E2 intensity of the $P(5)Q(4)$ transition (Table 2), which happens due to near cancellation of the contributions from the two moments Q_{20} and Q_{2-1}.

4. Conclusion

The recent extensive and accurate experimental data relating to the $P(N)P(J)$ and $P(N)Q(J)$ ($3 \leq N \leq 51$), $R(N)R(J)$ and $R(N)Q(J)$ ($1 \leq N \leq 41$) of $M1$ transition intensities in the O_2 A-band reported in [3–5] are analyzed using the theoretical framework developed in [6] modeled on the mutual perturbations between the b and X states. The measured intensities carry clear signatures of rovibronic perturbation effects. Very small N-dependent residuals could be accounted for by invoking the Herman–Wallis (HW) effect. A theoretical treatment of the HW effect from first principles shows that the HW correction factor, in the context of A-band branch intensities, takes the form $(1 + \xi_1 m + \xi_2 m^2)^2$. The theoretical analysis of the experimental data leads to the value $\langle M1 \rangle_{0,0} = 0.02679(4)\,\mu_B$ for the transition moment. The E2 contribution to line intensities are also calculated and listed.

Acknowledgments

References

[1] Long DA, Havey DK, Okumura M, Pickett HM, Miller CE, Hodges JT. Laboratory measurements and theoretical calculations of O$_2$ A band electric quadrupole transitions. Phys Rev A 2009;80:042513.
[2] Gordon IE, Kassi S, Campargue A, Toon GC. First identification of the a$^1\Delta_g$–X$^3\Sigma_g^-$ electric quadrupole transitions of oxygen in solar and laboratory spectra. J Quant Spectrosc Radiat Transfer 2010;111: 1174–83.
[3] Havey DK, Long DA, Okumura M, Miller CE, Hodges JT. Ultra-sensitive optical measurements of high-J transitions in the O$_2$ A-band. Chem Phys Lett 2009;483:49–54.
[4] Robichaud DJ, Hodges JT, Brown LR, Lisak D, Masłowski P, Yeung LY, et al. Experimental intensity and lineshape parameters of the oxygen A-band using frequency-stabilized cavity ring-down spectroscopy. J Mol Spectrosc 2008;248:1–13.
[5] Long DA, Havey DK, Okumura M, Miller CE, Hodges JT. O$_2$ A-band line parameters to support atmospheric remote sensing. J Quant Spectrosc Radiat Transfer 2010;111:2021–36.
[6] Balasubramanian TK, Narayanan O. Magnetic dipole and electric quadrupole linestrengths for the atmospheric oxygen (b$^1\Sigma_g^+$–X$^3\Sigma_g^-$) system. Acta Phys Hung 1994;74:341–53.
[7] Balasubramanian TK, Mishra AP. Comment on "Laboratory measurements and theoretical calculations of O$_2$ A-band electric quadrupole transitions". Phys Rev A 2011;84:056501.
[8] Minaev B, Vahtras O, Ågren H. Magnetic phosphorescence of molecular oxygen. A study of the b$^1\Sigma_g^+$–X$^3\Sigma_g^-$ transition probability using multiconfiguration response theory. Chem Phys 1996;208: 299–311.
[9] Watson JKG. Rotational lineintensities in $^3\Sigma$–$^1\Sigma$ electronic transitions. Can J Phys 1968;46:1637–43.
[10] Klotz R, Marian CM, Peyerimhoff SD, Hess BA, Buenker RJ. Calculation of spin-forbidden radiative transitions using correlated wavefunctions: lifetimes of b$^1\Sigma^+$, a$^1\Delta$ states in O$_2$, S$_2$ and SO. Chem Phys 1984;89:223–36.
[11] Herzberg G. Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules. New York: Van Nostrand Reinhold; 1950.
[12] Watson JKG. Quadratic Herman–Wallis factors in the fundamental bands of linear-molecules. J Mol Spectrosc 1987;125:428–41.

[13] Yang S, Canagaratna MR, Witonsky SK, Coy SL, Steinfeld JI, Field RW, et al. Intensity measurements and collision-broadening coefficients for the oxygen A band measured by intracavity laser absorption spectroscopy. J Mol Spectrosc 2000;201:188–97.

[14] Stefano GD. Linestrength of the visible oxygen atmospheric transition. Chem Phys 2004;302:243–9.

[15] Stefano GD. Linestrength of oxygen's atmospheric transitions from absorption data. I. The A, B, and γ bands. Chem Phys Lett 2006;426: 33–8.

[16] Anderson B, Brecha RJ. Tunable diode laser absorption measurement of oxygen A-band line strengths. Appl Phys B 2007;87:379–85.