Magnetic phosphorescence of molecular oxygen. A study of the 
b\(^1\Sigma^+_g\)−\(X\ ^3\Sigma^+_g\) transition probability using multiconfiguration 
response theory

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Received 24 January 1996

Abstract

Multiconfigurational response function calculations of the magnetic dipole transition moment for the red atmospheric 
emission band \(b\ ^1\Sigma^+_g\)−\(X\ ^3\Sigma^+_g\) in \(O_2\) have been performed at different internuclear distances. Spin and orbital angular 
momentum contributions are calculated as residues of the linear and quadratic response functions using the full Breit-
Pauli spin-orbit coupling operator. Vibronic band intensities are calculated by vibrational averaging of the magnetic dipole 
transition moments and compared with experimental data. The Einstein coefficient for the 0,0 transition probability (0.079 
s\(^{-1}\)) is obtained 10% smaller than the most recent experimental result of Ritter and Wilkerson (0.089 s\(^{-1}\)), but in fair 
agreement with previous experimental data (0.077–0.0825 s\(^{-1}\)), while an excellent agreement for all other known vibronic 
transition probabilities for the red atmospheric band is obtained.

1. Introduction

In accordance with Mulliken's prediction [1] the oxygen molecule possesses a triplet ground state, \(X\ ^3\Sigma^+_g\), 
and two low-lying singlet excited states, \(a\ ^1\Delta_g\) and \(b\ ^1\Sigma^+_g\), (shortly X, a and b in the following). Although 
transitions between the triplet ground state and the two singlet states are strictly forbidden in the electric dipole 
approximation, both by orbital and spin selection rules, they have been observed in the red (762 nm, b–X transition) [2] and in the near-infrared (1270 nm, a–X transition) regions [3,4]. Rotational structure of these 
bands clearly reveals a magnetic dipole nature of both transitions [4,5]. The lowest excited \(a\ ^1\Delta_g\) state is highly 
metastable; its radiative lifetime at the zero pressure limit is more than one hour [6,7]. The probability of the 
a–X transition is determined by the electronic orbital angular momentum in a free \(O_2\) molecule [8–12] and 
is extremely sensitive to collisions [6,11,13,14]. The radiative lifetime of the \(a\ ^1\Delta_g\) state diminishes by 3–4 
orders of magnitude upon collisions in solvents [15–20] and in dense gases [21]. The observed lifetime of the 
a\(^1\Delta_g\) state is mainly determined by non-radiative quenching in solvents and ranges from 4 \(\mu\)s in water to 0.3 
\(s\) in perfluorodecalin [22]. The \(a\ ^1\Delta_g\) state, now often referred to as "singlet oxygen", has been shown to be 
important in many applications [23–25], and particularly in biochemistry, including the mechanisms of certain 
human diseases, cell aging and laser cancer treatment [26–32]. The singlet \(a\ ^1\Delta_g\) state oxygen emission is the
main direct tool for monitoring this important metastable and chemically active intermediate. The theory of the
"singlet oxygen" radiative lifetime in condensed media depends on the radiative properties of both the singlet
$^1\Delta_g$ and $^1\Sigma_g^+$ states [11,13,14,33–35]. This is one of the reasons for repeating the b–X transition intensity
calculation [8,12] at a new level of theory.

The b–X transition itself is very important in molecular spectroscopy. The atmospheric red emission is among
the brightest features of the air-glow. Because the 0,0 band ("A band") lies in a relatively transparent part of
the atmospheric spectrum, it is well studied for atmospheric spectroscopy applications [36]. Apart from being
of interest in itself, this emission provides an important method of remotely studying and the dynamical and
chemical processes of the middle and upper atmosphere. $\text{O}_2$ ($^1\Sigma_g^+$) is generated in the terrestrial atmosphere
both directly and from energy-transfer processes. It is seen in the night-glow, the day-glow and in aurorae,
in each case with a different production mode [37]. The the A-band intensity is widely used now in precise
atmospheric measurements by lidar systems [36]. The b–X emission has been detected recently in solvent
[18,22] in spite of very efficient non-radiative quenching of the b state.

$\text{O}_2$ ($^1\Sigma_g^+$) can be monitored by luminescence spectroscopy via two emissions, b $\rightarrow$ a and b $\rightarrow$ X. The b $\rightarrow$ a
emission (1910 nm, the "Noxon band") is a pure electric quadrupole transition in the free oxygen molecule
and has a low transition probability $\approx 0.0014$ s$^{-1}$ [11,12,38,39]. It was predicted by CI calculations that this
transition should be sensitive to a very weak intermolecular interaction [11,13] and observations in solvents
[40,41] and in matrices [42] supported this prediction quantitatively. The b $\rightarrow$ a transition enhancement can
directly contribute to the intensity borrowing by the a $\rightarrow$ X transition through the spin–orbit coupling (SOC)
mixing (1)–(3).

The b–X magnetic dipole transition has the largest probability (0.089 s$^{-1}$) [36,43] among the family of
these forbidden red and infrared transitions. Although being magnetic dipole- and spin-forbidden by nature it
is 64 times more intensive than the spin-allowed b $\rightarrow$ a electric quadrupole radiation and is 345 times more
intensive than the a $\rightarrow$ X transition of the same magnetic nature. The explanation of these peculiarities have
been obtained on the basis of semi-empirical calculations almost twenty years ago [8,9]. The key idea comes
from a comparatively large spin–orbit coupling between the b $^1\Sigma_g^+$ state and the lowest spin sublevel of the
ground X $^3\Sigma_g^-$ state (shortly X,0). In the framework of perturbation theory it corresponds to the mixing of these two states

$$
\Phi_b = \mid b \mid ^1\Sigma_g^+ \rangle + C \mid X^3\Sigma_g^-,M_s=0 \rangle,
$$

$$
\Phi_{X,0} = \mid X^3\Sigma_g^-,M_s=0 \rangle - C^* \mid b \mid ^1\Sigma_g^+ \rangle,
$$

where

$$
C = \frac{\langle X^3\Sigma_g^-,M_s=0 \mid H_{so} \mid b \mid ^1\Sigma_g^+ \rangle}{E_b - E_X}.
$$

In the semiempirical approximation the absolute value of the SOC matrix element is equal to the SOC
constant for the O($^3P$) atom (153 cm$^{-1}$) [8]. Ab initio calculations by Klotz et al. [12,44] gave 176 cm$^{-1}$.
This SOC is the highest possible perturbation of this type, which in principle can occur in unionized oxygen
[11]. By using the experimental energy difference in the denominator of Eq. (3), the admixture coefficient
equals 0.0134i. This appreciable admixture of singlet $^1\Sigma_g^+$ character into the triplet $\Phi_{X,0}$ state (2) produces an
additional contribution to the a–X,0 transition amplitude

$$
\langle \Phi_a \mid \hat{T} \mid \Phi_{X,0} \rangle = \langle a \mid ^1\Delta_g \mid \hat{T} \mid X^3\Sigma_g^-,M_s=0 - C^*b \mid ^1\Sigma_g^+ \rangle = -C^*\langle a \mid ^1\Delta_g \mid \hat{T} \mid b \mid ^1\Sigma_g^+ \rangle,
$$

where $\hat{T}$ is a multipole in the expansion of the radiation field. Because the Noxon transition a–b acquires electric
dipole character upon collisions, it contributes to the intensity of the a–X radiation by Eq. (4) [13,33,35]. In
the $\text{O}_2 + \text{H}_2$ collision the induced electric dipole transition moment $\langle a \mid ^1\Delta_g \mid \hat{T} \mid b \mid ^1\Sigma_g^+ \rangle$ is of the order 0.02
which corresponds to the $a$–$X$ spontaneous emission Einstein coefficient equal to $0.26 \, \text{s}^{-1}$. This means three orders of magnitude enhancement of the $^1\Delta_g$ singlet oxygen emission probability in comparison with the collision-less zero pressure limit. The enhancement of the $a$–$b$ (and hence the $a$–$X$) transition probability depends on the nature of the solvent and obviously depends on its ionization potential and polarizability [11,45], since the collision-induced electric dipole transition moment is determined by the difference in permanent dipole moments [13]. These features are in agreement with many experimental findings [17,18,20,21,40,42,46,49]. It is necessary to stress that intermolecular interactions in lower states of the collision complexes between $O_2$ and solvent molecules are very weak and are determined mostly by dispersion forces [35,50]. At the same time the charge-transfer interactions are very sensitive to the symmetry of states; this leads to preferential enhancements of some appropriate transitions and to their specific polarization [35,50]. The SOC mixing (1)–(3) also explains the large $b$–$X$ transition magnetic dipole moment in free oxygen. Taking account of the perturbation of the $b^1\Sigma_g^+$ state (1), the magnetic transition moment to the unperturbed $M_5 = \pm 1$ spin sub-levels of the $X^3\Sigma_g^-$ state

$$M(\text{b-X},1) = \langle \Phi_b | M | X^3\Sigma_g^-, M_s=\pm 1 \rangle$$

(5)

has a large contribution from the spin part of the magnetic dipole operator

$$M = \frac{\mu_B}{\hbar} (L + g_e S).$$

(6)

So it borrows intensity from the magnetic dipole transitions between spin sub-levels of the ground triplet state $X$ (spin current) [8,10]

$$M(\text{b-X},1) = C^* \frac{\mu_B}{\hbar} (X^3\Sigma_g^-, M_s=0 | g_e S_T | X^3\Sigma_g^-, M_s=\pm 1) = \sqrt{2} g_e \mu_B C^*.$$

(7)

In Eqs. (6)–(7) $\mu_B$ is the Bohr magneton, $g_e = 2.0023$ is the electronic $g$-factor, $L$ and $S$ are orbital and spin angular momenta, respectively. The $L$ contribution to the magnetic dipole transition moment (5) is 60 times smaller than the spin contribution (7) in the vicinity of the equilibrium geometry, $r_e \approx 1.21 \, \text{Å}$ [8,12], so its influence on the calculated $b$–$X$ (0,0) transition probability is almost negligible. The $a$–$X$,1 transition in free oxygen has only orbital angular momentum contributions, induced by SOC mixing with $\Pi_g$ states, which is very small because of a huge energy difference between the $^1\Sigma^+_g$ and $X_a$ states near the equilibrium [8]. Electric-quadrupole contributions to the $a$–$X,0$ transition intensity is practically negligible [11,39]. This leads to small $a$–$X$ transition probability ($0.00015 \, \text{s}^{-1}$) [7] and extremely high radiative lifetime of free $^1\Delta_g$ oxygen. In solvents the $a$–$X$ transition borrows intensity from the collision induced $a$–$b$ transition, as described above, and is greatly enhanced. In contrast, the $b$–$X$ transition, being comparatively intensive in free molecules, have no effective sources of intensity borrowing upon collision [10,11,13], so its radiative probability is not much enhanced in condensed media (especially in the absence of heavy atom solvents) [6]. The semi-empirical theory of singlet-triplet transitions in free oxygen molecules [8–11] was supported by MRCI calculations [12,44]. Klotz et al. [12] have calculated the $b$–$X$ and $a$–$X$ transition probabilities at the equilibrium internuclear distance ($r_e$) in the ground state. Because the $r_e$ values in the $X_a$ and $b$ states do not differ much (1.207, 1.217 and 1.227 Å, respectively) the authors [12] refer the probabilities calculated at $r_e = 1.207 \, \text{Å}$ to the 0,0 bands. But the $M_{b,X}$ transition moment dependence on $r$ can be easily predicted on grounds of a simple analysis of Eqs. (3)–(7); the energy denominator in Eq. (3) strongly depends on $r$ [11]. It means that a proper estimation of the $b$–$X$ transition probability must include vibrational averaging of $M_{b,X}(r)$. Taking account of the Franck–Condon factor for the (0,0) band ($q_{0,0} = 0.931$) would destroy the excellent agreement between theory ($F_{0,0} = 0.0858 \, \text{s}^{-1}$) [12] and experiment ($F_{0,0} = 0.0887 \, \text{s}^{-1}$) [36] for the spontaneous emission Einstein coefficient ($F$) (it should be mentioned that the theoretical value [12] has been obtained with account of the experimental energy difference in the denominator of Eq. (3)).
In this paper we are presenting for the first time an ab initio calculation of the magnetic dipole transition moment dependence on the internuclear distance for the red atmospheric band of oxygen and a theoretical estimation of its vibronic probabilities.

2. Preliminary remarks on the relative vibronic transition intensities in the red atmospheric band

In contrast to a great amount of the electric dipole transitions in diatomics, the number of studied magnetic dipole transitions is scarce [51]. It was supposed [43] that magnetic dipole transition moments do not depend on the internuclear distance, as it was observed in the Layman–Berdge–Hopfild system \( \alpha {\Pi}_g - \chi \Sigma_g^+ \) in the nitrogen molecule [51,52]. The orbital magnetic dipole transition moments for the spin-allowed transitions of the \( \alpha {\Pi}_g - \chi \Sigma_g^+ \) type are not much dependent on \( r \) in the \( \text{N}_2 \) and \( \text{P}_2 \) molecules (and neither in \( \text{O}_2 \)) in the vicinity of the equilibrium distances \( (r_e \pm 0.2 \ \text{Å}) \) because the upper state is determined mostly by the one-electron \( 3\sigma_g \rightarrow 1\tau_g \) excitation with large permanent contribution of \( 2\sigma \) atomic orbitals to the \( 3\sigma_g \) molecular orbital (MO) [11]. In the INDO CI approximation it means that the \( L \) transition moment (perpendicular to the axis) is quite constant in the mentioned range of \( r \) [11]. But this is not the case for the oxygen \( b \)-\( X \) transition. As it follows from Eq. (7), the main contribution to the magnetic dipole moment of this transition is determined by the SOC-induced mixing coefficient (Eq. (3)). The energy difference in the denominator of Eq. (3) is a well known strong function of \( r \) [53]. At the dissociation limit the energy difference \( E_b - E_X \) goes to zero, so the spin contribution to the transition moment, Eq. (7), rises with \( r \). The orbital contribution in Eqs. (5) and (6) has the opposite sign to the spin contribution and depends on the denominators (for example, \( E({\Pi}_g) - E_X \), which also goes to zero at the dissociation limit. But in the region of chemical bonding \( (r \leq 1.8 \ \text{Å}) \) the spin contribution is much larger than the orbital one [11], so a steep increase of the magnetic transition dipole moment for the \( b \)-\( X \) band has been predicted on the background of semiempirical calculations [11,33]. The assumption of a distance independent \( b \)-\( X \) transition magnetic moment was often used for estimations of different vibronic band intensities in the red atmospheric emission in night afterglow and in aurora [54]. Galkin showed that experimental data do not agree with this assumption [54] and determined the \( M_{b,X} \) dependence on \( r \) from the measurements of integrated absorption coefficients for the \((0,0), (1,0), (2,0), (3,0)\) and \((1,1)\) vibronic transitions [43]. He found a linear dependence of \( |M_{b,X}(r)|^2 \) in the region \( 0.66 \ \text{Å} < r_{X,\tau} < 1.37 \ \text{Å} \); the \( |M_{b,X}(r)|^2 \) value increases with \( r \). A qualitative explanation of such behavior has been obtained at a semiempirical MINDO/3 CI level [11,33], though the transition energies and the SOC matrix elements were underestimated. In the following, quadratic response theory has been applied for calculation of the magnetic phosphorescence \( b \)-\( X \) radiative lifetime and the corresponding absorption probability for few vibronic bands.

3. Theory

We are considering the spontaneous rate of decay from an initial state \( |i\rangle \) to a final state \( |f\rangle \), where the emitted radiation is of magnetic dipole character:

\[
\Gamma_{i \rightarrow f} = \frac{\alpha^2 \omega^3 g_i}{3} |\langle f | L + g_e S | i\rangle|^2, \tag{8}
\]

where \( \alpha \) is the fine-structure constant, \( \omega \) the transition frequency, \( g_e \) is the electronic \( g \)-factor, \( g_i \) is the degeneracy of the final states. \( L \) and \( S \) are the electronic orbital and spin angular momenta respectively. For the pure spin states \( \chi \Sigma_g^- \) and \( \beta \Sigma_g^+ \) of oxygen this transition is magnetic dipole forbidden. We now consider the first-order corrections of the initial and final states due to spin–orbit coupling. This gives a matrix element of the form
which is the famous phosphorescence formula where we replace the electric dipole operator with the magnetic dipole operator. The mechanics of this radiative transition may therefore be called magnetic phosphorescence.

Eq. (9) represents a sum over triplet and singlet $\Pi_g$ states for the orbital angular momentum part of $M$ (Eq. (6)). The orbital angular momentum components (and also the spin–orbit components) transform according to the irreducible representations $\Sigma_g^-$ and $\Pi_g$ of the symmetry group $D_{ohn}$. From symmetry selection rules, the only combination of $L$ and $H_{so}$ operators which couple the $b^1\Sigma_g^+$ and the $X^3\Sigma_g^-$ states is the combination with symmetries $\Pi_{gx}$, $\Pi_{gy}$. This mechanism thus only allows transitions to the $x, y$ ($M_S=\pm1$) spin sub-levels of the $X^3\Sigma_g^-$ state. The rate of decay to the $y$ sub-level is thus governed by the matrix element

$$
\langle \Phi_{x,y} \mid L_x \mid | \Phi_b \rangle = \sum_k \frac{\langle X^3\Sigma_{g,y}^+ \mid L_x \mid \Sigma_{g,y}^+(k) \rangle \langle \Pi_{g,y}^+(k) \mid L_y S_y \mid b^1\Sigma_g^+ \rangle}{E_b - E_k},
$$

where state subscripts $x, y$ refer to Cartesian spin projection sub-levels (e.g., $X^3\Sigma_{g,y}^+$ is the spin component with zero spin projection along the $y$-axis) and superscripts to the Cartesian components of the degenerate irreducible representation $\Pi_g$ (in a SCF representation of $\Pi_g^+$ the $\pi_{g,y}$ orbital is singly occupied). $L_y S_y$ is to be seen as a shorthand notation for the $y$-component of the full Breit–Pauli spin–orbit interaction operator.

For the spin angular momentum only one term survives in Eq. (9); since $S$ can at most change the spin-projection of a given state, the only non-vanishing term is the $k = X^3\Sigma_g^-$ term of the first sum. Furthermore, since the spin–orbit component of $\Sigma_g^-$ symmetry is the $z$-component, the intermediary state can only be the $z$ ($M_S=0$) sub-level, which in turn only decays to the $x, y$ ($M_S = \pm 1$) final state sub-levels, as allowed by the corresponding spin angular momentum components. The spin analogue of Eq. (10) is (cf. Eq. (7))

$$
\langle \Phi_{x,y} \mid S_x \mid | \Phi_b \rangle = \sum_k \frac{\langle X^3\Sigma_{g,y}^+ \mid S_x \mid X^3\Sigma_{g,z}^- \rangle \langle X^3\Sigma_{g,z}^- \mid L_z S_z \mid b^1\Sigma_g^+ \rangle}{E_b - E_k} = -\frac{1}{E_b - E_X} \langle X^3\Sigma_{g,z}^- \mid L_z S_z \mid b^1\Sigma_g^+ \rangle.
$$

Since two sublevels ($M_S = \pm 1$) of the final state equally participate in the $b-X$ emission, we must account in Eq. (8) for the degeneracy factor $g_t = 2$. We must note that the square of the transition moment values inferred by Galkin [43] must be multiplied by the factor $3/2$ because he used a wrong statistical weight factor $g_t = 3$ in a formula of the type Eq. (8). In Tables 1–3 the calculated transition moments for one sublevel are presented.

Transition matrix elements may be calculated as residues of response functions. They are defined by the expansion of an expectation value in powers of a (in general time-dependent) perturbation $V$.

$$
\langle A \rangle = \langle 0 \mid A \mid 0 \rangle + \int d\omega e^{-iw_{\omega}t+\epsilon t} \langle A; V \rangle_{\omega} + \int d\omega_1 \int d\omega_2 e^{-i(\omega_1+\omega_2)t+2\epsilon t} \langle A; V; V \rangle_{\omega_1,\omega_2},
$$

where the first term is the expectation value in the unperturbed (reference) state, the second term defines the linear response function and the third the quadric response function. In general, a matrix element $\langle 0 \mid A \mid k \rangle$ can be evaluated as the residue

$$
\langle 0 \mid A \mid k \rangle = \lim_{\omega \to \omega_k} (\omega - \omega_k) \langle A; V \rangle_{\omega} \langle k \mid V \mid 0 \rangle.
$$
If the matrix element \( \langle 0 | A | k \rangle \) is zero in the absence of a perturbation, but can be induced by the static perturbation \( W \), we may obtain to first order in perturbation theory a matrix element of the form (10) which is evaluated as a residue of a quadratic response function

\[
\langle 0 | A | k \rangle = \lim_{\omega \to \omega_k} (\omega - \omega_k) \langle A(W,V)\rangle_{\omega,\omega_k} \langle k | V | 0 \rangle.
\]

In general, calculations involving the electronic orbital angular momentum bring up the question of gauge-origin invariance. Gauge invariance can only be guaranteed in the limit of a complete basis set. To obtain results which are independent of the gauge origin we must either employ a basis set which is sufficiently large to render the gauge effects negligible, or use orbitals or basis functions which eliminate the gauge dependence. The most successful of the latter method appears to be the London orbital method [55] where each atomic basis function undergoes a gauge transformations such that all atomic integrals are independent of the gauge. This method has been implemented by Ruud et al. [56] for the calculation of magnetic properties. For the special case we are considering, origin dependence is eliminated by pure symmetry selection rules. A change of origin \( r \to r - R \) gives the following correction to the calculated transition moments,

\[
\langle A | L | B \rangle \to \langle A | L | B \rangle - R \times \langle A | p | B \rangle,
\]

but since the transitions we are considering are electric dipole forbidden, the last term of Eq. (15) vanishes even to first order in perturbation theory when spin–orbit coupling is included.

4. Calculations

At first we only considered the electronic degrees of freedom, that is to calculate the transition amplitude and transition rate at the equilibrium geometry. Three different levels of correlation and three basis sets, were employed to establish a sufficiently accurate level. The basis sets are the 3s2p1d/4s3p2d1f/6s5p3d2f contractions of the atomic natural orbitals of Widmark et al. [57]. For each basis set, calculations were carried out at the Hartree–Fock (HF) level and for two complete active spaces (CAS): 10 electrons in 7 active orbitals \((3\sigma_g, 1\pi_u, 2\sigma_u, 1\pi_g)\) and 10 electrons in 12 active orbitals \((3\pi\sigma_g, 1\sigma_u, 2\pi_u, 2\sigma_u, 2\pi_g)\), denoted by CAS I and CAS II respectively. These active spaces were used in Ref. [58] for studying the spin–orbit coupling matrix element in Eq. (3). All electronic structure calculations were performed using the DALTON program [59], the vibrational wave functions were obtained from the program VIBROT of the MOLCAS [60] program package.

The results of the equilibrium geometry rate calculations are given in Table 1. We conclude from this table that the highest level of correlation is required for the calculation of transition rates. Our assumption that CAS II is a sufficiently large active space is based on the results of Ref. [58] where the spin–orbit matrix element was studied. In Ref. [58], a comparison between a sequence of configuration interaction (CI) and complete active space multi-configuration self-consistent field (CASSCF) calculations, indicated that the spin–orbit matrix element converged to the same value at the the CAS II and the SDTQ-CI (up to quadruple excitations) levels. The data presented in Table 1 also suggest that the results have practically converged at the \((4s3p2d1f)\) basis set level. The change in the total transition rate, going from \(4s3p2d1f\) to \(6s5p3d2f\), is less than half a percent which certainly is less than the experimental standard deviation [36].

Next we carried out a vibrational averaging of the magnetic dipole transition moment amplitudes to obtain the transition rate for the lowest vibronic bands of the red atmospheric system. The singlet \(b^1\Sigma_g^+\) state was first optimized for internuclear distances in the range 1.6–3.5 bohr \((a_0)\). This state singlet was then used as the reference state in a linear response calculation, which gives the deexcitation energies to the ground state (and thereby the triplet \(X^3\Sigma_g^-\) state energies). The potential energy curves are listed in Table 2 and plotted in Fig. 1. The calculated \(X\) and \(b\) state equilibrium bond distances are equal to 2.295 and 2.342 bohr, respectively,
Table 1
Excitation energy \( \omega \), spin–orbit coupling \( H_{so} \), spin \((g_s S)\), orbital \((L)\), and total magnetic dipole transition amplitude \((M)\), total spontaneous emission transition rate \( I'(s^{-1}) \) for various basis sets and active spaces at internuclear distance \( r_c = 2.281 \) bohr

<table>
<thead>
<tr>
<th>Basis</th>
<th>CAS</th>
<th>( \omega (E_h) )</th>
<th>( H_{so} (cm^{-1}) )</th>
<th>( 2S (\mu_B) )</th>
<th>( L (\mu_B) )</th>
<th>( M (\mu_B) )</th>
<th>( I'(s^{-1}) )</th>
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<td>186</td>
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<td>0.0144</td>
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Table 2
CASSCF energies for the \( b^1\Sigma^+ (E_h) \) and \( X^3\Sigma^- (E_X) \) states, spin–orbit coupling \( (X^3\Sigma^-) | H_{so} | b^1\Sigma^+ \), spin \((g_s S)\), orbit \((L)\), and total magnetic dipole transition amplitudes as functions of the internuclear distance \( r \)

<table>
<thead>
<tr>
<th>( r ) (( a_0 ))</th>
<th>( E_h (E_h) )</th>
<th>( E_X (E_h) )</th>
<th>( H_{so} (cm^{-1}) )</th>
<th>( g_s S (\mu_B) )</th>
<th>( L (\mu_B) )</th>
<th>( M (\mu_B) )</th>
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</thead>
<tbody>
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<td>-149.367</td>
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<td>0.0224</td>
<td>0.000359</td>
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<tr>
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<td>170</td>
<td>0.0230</td>
<td>0.000291</td>
<td>0.0227</td>
</tr>
<tr>
<td>1.8</td>
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<td>-149.680</td>
<td>174</td>
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</tr>
<tr>
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</tr>
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</tr>
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<td>0.0234</td>
</tr>
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<td>0.0242</td>
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<tr>
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<td>177</td>
<td>0.0256</td>
<td>0.000478</td>
<td>0.0251</td>
</tr>
<tr>
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<td>0.000536</td>
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</tr>
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<td>0.001164</td>
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</tr>
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<tr>
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<td>-149.721</td>
<td>148</td>
<td>0.1099</td>
<td>0.002936</td>
<td>0.1070</td>
</tr>
</tbody>
</table>

in good agreement with experimental values (2.282 and 2.318 bohr, respectively) [51]. Both the calculated and experimental RKR potentials are presented in Fig. 1; they are plotted with common ground state minima. The linear response calculation also gives the SOC matrix element \( H_{so} \), Table 2, Fig. 2) and spin current contribution \( (g_s S \) entry in Table 2, and Fig. 3); the quadratic response calculation gives the orbital angular momentum transition amplitudes \( (L \) in Table 2 and Fig. 3). It can be seen that the SOC matrix element is relatively constant along the potential energy curve compared to the angular momentum values. The SOC matrix element has a maximum at \( r = 2.1 \) bohr (177.6 cm\(^{-1}\)) and diminishes slowly with increasing internuclear distance. At \( r = 3.5 \) bohr the SOC matrix element equals 148.4 cm\(^{-1}\). The calculated SOC dependence on \( r \) is quite close to the results of Klotz and Peyerimhoff [44]. At \( r = 2.3 \) and 2.9 bohr, Klotz and Peyerimhoff obtained 176.5 and 162.4 cm\(^{-1}\), respectively, which is in good agreement with our values (176.8 and 164.8
Fig. 1. Potential energy curves for the singlet $b\Sigma_g^+$ and triplet $X\Sigma_g^-$ states of O$_2$. Calculated curves (solid lines) and RKR curves (dashed lines) are plotted with a common ground state minimum.

Fig. 2. Spin-orbit coupling matrix element between the $b\Sigma_g^+$ and $X\Sigma_g^-$ states of O$_2$.

Fig. 3. Orbital ($L$) and spin ($S$) angular momentum contributions to the magnetic transition moment $b\Sigma_g^+ - X\Sigma_g^-$ of O$_2$.

Fig. 4. Total magnetic dipole transition moment $b\Sigma_g^+ - X\Sigma_g^-$ of O$_2$ calculated ab initio and by account of the experimental energy differences (from RKR potentials) in the denominator (3) of the spin contribution (7).

cm$^{-1}$ respectively).

In Fig. 3 the spin magnetic moment appears to show much larger variation with internuclear distance than the orbital angular momentum on the same scale. The fact is that both quantities show a relative increase by an order of magnitude towards the high $r$ end of the curve, mostly because the energy differences decrease. These enter as denominators in the perturbation expansions. The vibronic transition intensities $b\Sigma_g^+, \nu' \rightarrow X\Sigma_g^-, \nu''$ were calculated by vibrational averaging of the magnetic dipole transition moments. We used two approaches for calculations of the transition probability. One is completely ab initio, the other uses the experimental energy differences in the denominator of Eq. (11) for calculation of the most important spin contribution to the transition moment and also for the transition probability estimation. Both methods gave quite similar results, but the latter has spectroscopic accuracy. Since the fine details of transitions intensity are very sensitive to exact energy differences it is better to use well established RKR potentials for the spectroscopic predictions. The total
magnetic transition moment curves are given in Fig. 4.

The potential energy curves (theoretical or experimental) were then used to calculate vibrational wavefunctions \((\chi_n)\) numerically. As a second step the vibrational wavefunctions are used to calculate an averaged transition matrix element between different vibrational levels:

\[
M_{\ell',\ell''} = \langle \chi_{\ell',\ell''} | M_{b-X,1}(r) | \chi_{\ell',\ell''} \rangle.
\] (16)

In the case of the RKR potentials this integration is restricted to the region where we have experimental data, \(\sim 2.1-2.6\) bohr.

5. Results and discussion

Considering the case of a non-rotating molecule, we obtain in the ab initio approach the 0,0 transition frequency

\[
\omega_{00} = 0.06213 \text{ hartree } (E_h) = 13636 \text{ cm}^{-1},
\] (17)

vibrationally averaged (0,0) magnetic dipole transition moment

\[
M_{b-X} = 0.0241 \mu_B,
\] (18)

and a transition rate of

\[
\Gamma_{0,0} = 0.0792 \text{ s}^{-1}
\] (19)

for the oxygen \(A\) band, which is a reduction of the total rate by 13\%, compared with the equilibrium geometry rate. Ritter and Wilkerson reported a value of 0.0887 s\(^{-1}\), and our result falls in the range of previous experiments: 0.073–0.085 s\(^{-1}\) (reported in Ref. [36]). Transition rates for other vibronic bands calculated by the complete ab initio method deviate somewhat from experimental data (Table 4). Most of known vibronic band intensities are smaller by factor of two (or even by factor of 4 for the (3,0) transition) than the calculated transition intensities. Account of the RKR potentials improves the quality of vibrational wave functions for the higher vibrational quantum numbers and also improves the spin contribution to the transition moment, making agreement with experimental vibronic intensities good (Table 4).

Klotz et al. [12] employed CI expansions of a small selected set of intermediate states for all transitions in molecular oxygen between the three lowest states at the equilibrium ground state geometry. The response functions permit us to evaluate the sum over all possible intermediate states. This feature is not, however, crucial for the calculation of the \(b-X\) transition since it is the spin-flip mechanism, Eqs. (5) and (7), that dominates. Their result, 0.0858 s\(^{-1}\), is based on a smaller basis set (no f-functions, and for the spin–orbit matrix elements no d-functions either), being on par with our 3s2p1d results. At this level, Klotz et al. [12] also used the experimental energy of the vertical \(b \leftarrow X\) transition (13195 cm\(^{-1}\)) for the transition rate estimation \((\omega^3\) dependence in Eq. (8)) and the (0,0) transition energy (13120 cm\(^{-1}\)) for the calculation of the spin contribution. So the latter value (Eqs. (3) and (7)) was estimated by Klotz et al. [12] as

\[
\text{ge} \mu_B C = \frac{175.6}{13120} \text{ge} \mu_B = 0.0268 \mu_B.
\] (20)

The orbital contribution (10) [8], which has only minor influence, was obtained equal to \(-0.00046 \mu_B\) [12]. This is in good agreement with our value \((-0.000467 \mu_B\), Table 1) obtained by the sum over all possible intermediate states. Though the calculations of Klotz et al. [12] were undertaken at the experimental equilibrium bond distance \(r_e = 2.28\) bohr, it is difficult to refer the value (20) to this equilibrium. In our ab initio calculation
Table 3
RKR energies for $b^1\Sigma_g^+$ ($E_b$) and $X^3\Sigma_g^-$ ($E_X$) states, spin ($g_sS$) and total ($M$) magnetic dipole transition moments as functions of the internuclear distance ($r$)

<table>
<thead>
<tr>
<th>$r$ (a₀)</th>
<th>$E_b$ ($E_h$)</th>
<th>$E_X$ ($E_h$)</th>
<th>$g_sS$ (μB)</th>
<th>$M$ (μB)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>0.0804</td>
<td>0.0160</td>
<td>0.0252</td>
<td>0.0248</td>
</tr>
<tr>
<td>2.2</td>
<td>0.0653</td>
<td>0.00283</td>
<td>0.0259</td>
<td>0.0255</td>
</tr>
<tr>
<td>2.3</td>
<td>0.0602</td>
<td>0.000121</td>
<td>0.0268</td>
<td>0.0263</td>
</tr>
<tr>
<td>2.4</td>
<td>0.0620</td>
<td>0.00453</td>
<td>0.0278</td>
<td>0.0273</td>
</tr>
<tr>
<td>2.5</td>
<td>0.0681</td>
<td>0.0136</td>
<td>0.0291</td>
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</tr>
<tr>
<td>2.6</td>
<td>0.0770</td>
<td>0.0258</td>
<td>0.0306</td>
<td>0.0299</td>
</tr>
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</table>

Table 4
Calculated and experimental Einstein coefficients $I'_{v',v''}$ (s⁻¹) for different vibrational bands of the $b^1\Sigma_g^+ (v') \rightarrow X^3\Sigma_g^- (v'')$ system

<table>
<thead>
<tr>
<th>$v', v''$</th>
<th>Ab initio</th>
<th>RKR</th>
<th>[43]</th>
<th>[54]</th>
<th>[63]</th>
</tr>
</thead>
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<td>0, 0</td>
<td>0.0792</td>
<td>0.0794</td>
<td>0.084</td>
<td>-</td>
<td>0.06</td>
</tr>
<tr>
<td>0, 1</td>
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<td>-</td>
<td>0.0047</td>
<td>-</td>
</tr>
<tr>
<td>1, 0</td>
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<td>0.0069</td>
<td>-</td>
<td>0.0056</td>
</tr>
<tr>
<td>1, 1</td>
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<td>0.0667</td>
<td>0.067</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2, 0</td>
<td>0.000645</td>
<td>0.0003</td>
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<td>-</td>
<td>0.0027</td>
</tr>
<tr>
<td>3, 0</td>
<td>0.0000307</td>
<td>0.000007</td>
<td>0.0000067</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

the spin transition moment at the equilibrium is 0.025 μB, which is 6% smaller than the combined estimation (20).

In order to obtain spectroscopic accuracy we must include experimental energies from RKR potentials [53] for calculation of the spin contribution, Eqs. (3) and (7), to the transition moment dependence on $r$ (Table 3). Comparison between complete ab initio values of the spin contribution with those calculated by RKR potentials for the most important internuclear distance region (Fig. 4) shows that the “semi ab initio” values are few percents higher, especially at small distances (at $r = 2.1$ bohr it is 7% higher). At the RKR equilibrium, $r = 2.281$ bohr, we have spin contribution $g_sS = 0.0269$ μB, which is very close to the result (20) of Klotz et al. [12]. The total transition moments are also close at this distance, but the vibrational averaged (0,0) transition moment values differ by 7.7%. Our final prediction for the (0,0) transition spontaneous emission rate is

$$I_{0,0} = 0.0794 \text{ s}^{-1},$$

which accidentally coincides with the complete ab initio value (Eq. (19)). (The cubic dependence on $\omega$ in Eq. (8) leads to slightly overestimated ab initio $I$ value and the smaller transition moment gives an accidental coincidence.)

The use of the RKR potentials improves also the vibrational averaging procedure and our final vibronic transition rates are in excellent agreement with experiment [43] (Table 4). The results for transitions (0,1) ($\omega_{0,1} = 11564 \text{ cm}^{-1}$) and (3,0) ($\omega_{3,0} = 17251 \text{ cm}^{-1}$) cover a wide range of internuclear distances (from $r = 1.370$ Å to 0.656 Å in the $r$-centroid approximation). Very good agreement with experimental rates for these and for other vibronic bands shows that the calculated transition moment dependence on $r$ is correct. Wallace and Hunten [61] measured the airglow photon intensity ratio of (0,0):(0,1) bands as 17 ± 2. Our “RKR”-calculated ratio is 16.93 (Table 4). A simple account of the Franck–Condon factors, based on RKR potentials gives 14 [53]. This shows the importance of the $M(r)$ dependence even in the vicinity of the equilibrium. This analysis indicates that the calculated $I_{0,0}$ value (Eq. (21)) is more appropriate than the latest result of Ritter and Wilkerson (0.0887 s⁻¹) [36]. The previous values (0.077–0.082) cited by Galkin [43] seem to be
In order to calculate the radiative lifetime of the \( v' = 0 \) state we take into account, besides the 0,0 and 0,1 transitions from Table 4, also the values of \( \Gamma_{0,2} = 0.000140 \text{ s}^{-1} \) and \( \Gamma_{0,3} = 0.000002 \text{ s}^{-1} \) calculated by our RKR “semi ab initio” procedure. Finally, the calculated radiative lifetime of the \( b^1\Sigma_g^+, v = 0 \) state with account of RKR data is 11.87 s which is in a good agreement with the experimental value of 12 s [6].

An excellent agreement for the 0,0 transition (“A-band”) probability between the theoretical result of Klotz et al. [12] (0.0858 s\(^{-1}\)) and the most recent experimental data of Ritter and Wilkerson [36] (0.0887 s\(^{-1}\)) needs some additional comments. The agreement seems to be somewhat fortunate because the \( r \)-dependence of the transition moment and vibrational averaging was not considered by the authors of Ref. [12]. Even using their approach (20) and considering the transition moment to be distance independent it is necessary to take the Franck-Condon factor (\( q_{0,0} = 0.931 \)) into account. Then it is more consistent to account for the same 0,0 transition energy as used in Eq. (20) for the Einstein coefficient estimation. This leads to the value \( \Gamma_{0,0} = 0.0785 \text{ s}^{-1} \), which is even smaller than our best estimation (21).

In the experimental work of Ritter and Wilkerson [36] absorption profiles of 54 spectral lines of the A-band have been measured with a high-resolution spectrometer at different pressures up to one atmosphere. Quantitative measurements of individual absorption line strengths have been made earlier by many authors at lower resolution which resulted in \( \Gamma_{0,0} \) values in the range 0.073–0.082 s\(^{-1}\) (a review of these papers is given in Ref. [43]). In the other relatively recent experiment by Grossmann [62] the high resolution spectrometer has also been used and this analysis resulted in \( \Gamma_{0,0} = 0.077 \text{ s}^{-1} \). All these data are in a good agreement with our calculation.

6. Conclusions

The magnetic dipole transition moment for the red atmospheric band system of the oxygen molecule \( b^1\Sigma_g^+ - X^3\Sigma_g^- (M_S = \pm 1) \) has been studied by MCSCF linear and quadratic response methods. Large basis sets including s,p,d and f functions and the complete form of the spin–orbit coupling operator have been used. The results show a good convergence with respect to the basis set and the size of the active space. The transition moment dependence on internuclear distance and vibrational averaging of the vibronic band intensities have been calculated. The orbital angular momentum contribution to the transition moment was studied by quadratic response calculations. It increases an order of magnitude with the internuclear distance from 0.9 till 1.9 Å, but constitutes only one percent of the total transition moment value, which mostly is determined by the spin–flip in the ground state; it borrows intensity from the spin operator induced \((M_S = \pm 1) - (M_S = 0) \) microwave band. The spin contribution rises approximately 5 times in the same region of internuclear distances. The complete ab initio study has been supplemented by “semi ab initio” calculations which take account of the transition energies from experimental RKR potentials. These RKR-corrected transition probabilities are in very good agreement with all known experimental vibronic band intensities: the radiative lifetime of the \( b^1\Sigma_g^+, v = 0 \) state with account of four vibronic bands is 11.87 s which is in good agreement with the experimental value 12 s [6]. The calculated Einstein spontaneous emission coefficient for the 0,0 band (0.0794 s\(^{-1}\)) agrees with many experimental data obtained in 1969–1979, including the high resolution measurement of Grossmann (0.077 s\(^{-1}\)) [62], but is 10% smaller than the most recent result of Ritter and Wilkerson (0.0887 s\(^{-1}\)) [36]. An excellent agreement between the latter value and the earlier calculation by Klotz et al. [12] (0.0858 s\(^{-1}\)) seems to be somewhat fortunate, since there was no account of the internuclear distance dependence and vibrational averaging. At the equilibrium distance our results are quite close to the quantities calculated by Klotz et al. [12].
Acknowledgements

This work was supported by a grant from INTAS-94-4089 and from the Swedish Royal Academy of Science (B.F.M.).

References