Dioxygen Spectra and Bioactivation

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Intensities of spin-forbidden transitions in electronic absorption and emission spectra of molecular oxygen are analyzed in order to understand the key mechanisms of spin-states mixing induced by spin-orbit coupling (SOC) and the ways to overcome spin prohibition for various photophysical and biochemical processes. Multireference configuration interaction calculations with SOC account are used to generalize spin-selection rules for the oxygen atmospheric and Herzberg bands in free O₂ molecule and in collision complexes. Intensity enhancement of the atmospheric a′Δg → X′Σg⁺, b′Σg⁺ → X′Σg⁻, and Noxon b′Δg⁺ → a′Δg transitions upon bimolecular collisions are compared with those for Herzberg III transitions A′Δu ← X′Σg⁺. Electric quadrupole, dipole, and magnetic approximations are used for transition probability calculations. Intensity distribution in rotational lines is also considered. With this background, we propose some simple spin-selection rules for dioxygen activation in enzymatic reactions. © 2013 Wiley Periodicals, Inc.

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Introduction

The spectra of the O₂ molecule (dioxygen) are a subject of permanent interest because of the great importance of molecular oxygen for the life at our planet.[1–6] The excited states of dioxygen, besides of their obvious impact on chemistry of atmosphere, are involved in oxidative organic photochemistry and a number of photobiological oxygen effects including photosynthesis. Knowledge of dioxygen excited states is important even for dark enzymatic reactions.[6–10] This is getting obvious if one considers the reaction rate in a framework of the full perturbation theory treatment with account of spin-orbit coupling (SOC).[6,11,12] The SOC-induced mixing between states of different multiplicity is the key subject not only for dioxygen spectroscopy and photochemistry but also for oxidation reactions catalyzed by glucose oxidase (GO),[7,9] cytochrome P₄₅₀[13,14] and other enzymes.[12]

It is well established long time ago that the dioxygen molecule has a triplet ground state, X¹Σg⁻, and two singlet excited states, a′Δg and b′Σg⁺, with low excitation energy, 0.98 and 1.63 eV, respectively, above the ground state, which are observed in the visible-near infrared (IR) regions.[15] (Fig. 1). To denote these states in the following, we shall use abbreviations X, a, and b, respectively. Transitions between the states are strictly forbidden by spin and spacial symmetry selection rules and can be observed in the optical absorption spectrum of the Sun light because of a vast amount of dioxygen and a long light pathway through the Earth atmosphere.

The a – X and b – X transitions are induced by SOC perturbation; they occur in the near IR (1.27 μm) and in the red (762 nm) part of the spectrum, respectively.[13] The b – X transition is much more intense; this red atmospheric band is among the bright features in the night-glow and among the Fraunhofer lines in the Sun light absorption spectrum.[16] The reason for large intensity difference between the a – X and b – X transitions is very instructive for understanding of dioxygen chemical and biochemical reactivity.

Spectra and photochemistry of O₂ in the ultraviolet (UV) region below the first dissociation limit O(3P) + O(3P) at 242 nm are also of great interest.[14,17] These spectra are determined by π → π* transitions and connected with the c'Σg⁺, A'Δu and A'3Σg⁺ states.[16] These are weakly bound states lying close below the first dissociation limit at 242 nm; transitions to them from the ground state are forbidden in electric-dipole nonrelativistic approximation and occur as weak Herzberg bands. The Herzberg transitions are also observed in night-glow emission and provide important information on the O(3P) + O(3P) atomic recombination processes in the upper atmosphere.[18] Thus, dioxygen spectra in gas phase demonstrate a number of forbidden transitions which are very weak at zero pressure[19–23], in condensed phases, some of these transitions are strongly enhanced indicating that symmetry of electron distribution in the O₂ molecule is obviously perturbed by weak intermolecular interactions.[24–27] Theoretical studies of such perturbations are also important for dioxygen chemistry analysis, especially for O₂ activation by enzymes.[9,11]

Spin-prohibition: implications in dioxygen chemistry

Because of the paramagnetic nature of the triplet ground state of dioxygen, its chemical reactions with diamagnetic organic molecules are spin-forbidden and O₂ shows sluggish chemical reactivity at the ambient conditions (in the absence of radicals and paramagnetic metals). The majority of organic materials consists of the singlet ground-state molecules; their oxidation by O₂ in living organisms needs very active catalysts (enzymes)

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Almost all oxidation reactions are very exothermic, and it is quite strange from a thermodynamics point of view that our world has not been burnt so far. Occurrence of dioxygen in the Earth’s atmosphere with the first photosynthesis from green algae about 1.4 billion years ago has provided the so-called dioxygen revolution. The advantages of aerobic life and oxidative metabolism were important factors during evolution: these are mainly connected with the high exothermicity of oxidation of organic molecules by dioxygen. At the same time, life strongly depends on the kinetic barriers to the molecular oxygen reactions. O₂ is used as an oxidant in respiration of mammals and oxidative metabolic processes, reducing food to water and carbon dioxide. Although these transformations are equivalent to combustion, the oxygenase enzymes control the specific reaction pathways that store and smoothly release energy by subtle spin selective processes, whereas combustion is a radical chain process. It requires a high temperature initiation step and develops like explosion without strong regulation of energy release. The kinetic constraints, which allow the controlled use of dioxygen by aerobic life in the presence of strong thermodynamic drive, are determined by spin selective interactions between dioxygen and oxygenase enzymes. The first step in understanding of these constraints should be connected with analysis of photophysical processes induced by O₂ interaction with solvents and gases, which provide interesting manifestations in spectroscopy.
which is denoted shortly as ‘...π_u^4 π_g^4’ in the following. A small admixture of the doubly excited configuration ... π_u^2 π_g^4 is also important even at semi-quantitative level for all states under discussion. Transitions between these states (X – a and X – b) provide very weak IR and red atmospheric bands at 1270 and 760 nm, respectively. These transitions are forbidden in the electric-dipole approximation and occur as very weak bands of magnetic and quadrupole nature induced by SOC. The Noxon band b^1Σ_u^+ – a^1Δ_u in the near IR region (1.9 μm) is completely allowed (to the highest possible degree) as quadrupole radiation, but still is not intense. Quadrupole contribution to the a – X transition was predicted to be very weak and has recently been detected by high-sensitivity cavity ring-down spectroscopy.

Despite its biradical character, the O_2 molecule is pretty stable; it needs 5.21 eV excitation energy to reach the first dissociation limit O(2P) + O(2P). The cytochrome-c-oxidase can split the O=O bond in mitochondrial membranes with low activation barrier by special spin- uncoupling through the Fe and Cu ions involvement in dioxygen activation. This spin-catalysis can be understood with account of energy expenses for all possible spin and orbital angular momenta transformations induced by exchange interactions and by internal magnetic perturbations. Analysis of the higher excited states of dioxygen is of great importance for the understanding of such spin-catalysis. In fact, a single electron excitation to the ... π_u^2 π_g configuration provides a series of states with various spin and orbital angular momenta projections: c^1Σ_u^+ (4.1), A^1Σ_u^+ (4.31), A^1Σ_u^+ (4.39), B^3Σ_u^- (6.17), 1Δ_u (8.4), and F^3Σ_u^- (10.1); in parentheses, the 0 – 0 transition energy (in eV) from the ground state is given. Thus, these transitions with single electron excitations cover a wide spectral region from near UV till vacuum UV wavelengths.

In 1903, Schumann first observed a series of discrete absorption bands below 200 nm and Runge in 1921 studied first the B → X emission in a high-voltage arc in dioxygen. Nowadays, there is a huge amount of research of this electric-dipole allowed transition including high-resolution studies in which the zero-field splitting of both triplet states is resolved; for a review, one can see Refs. [37–40]. In the upper atmosphere, a strong absorption of the UV sunlight in the Schumann-Runge (SR) band system (200–130 nm) B^3Σ_u^- ← X^3Σ_g^- leads to O_2 dissociation which prevents our Earth from such deadly radiation. The B^3Σ_u^- state dissociates to the second dissociation limit O(2P) + O(1D) providing a relatively large concentration of the metastable oxygen atoms in such rarefied air. The night-glow from O_2 is confined to the region near the altitude of 95 km, where the maximum oxygen O(1D) atom density is observed. The energy transfer reaction between O(1D) and O_2 generates the ν = 0, 1 levels of the O_2(b^1Σ_u^+) state with high efficiency, which provides the night-glow b^1Σ_u^+ → X^3Σ_g^- transition.

In the lower atmosphere, the main fraction of the ground state oxygen atoms O(3P) arises from dissociation of dioxygen following absorption of the soft UV radiation in the transparent region 200–242 nm known as the Herzberg continuum. Dissociation to the first limit O(3P) + O(1D) through an absorption to this continuum in the stratosphere is an important step in the ozone production. The most intense transition A^3Σ_u^+ ← X^3Σ_g^- in this region was discovered by Herzberg in 1932 being the first of three forbidden absorption band systems of the O_2 molecule studied by him, which led to its designation as ‘Herzberg I’ band. It is forbidden by the ‘+–’ selection rule and this is an example of the triplet–triplet transition induced by magnetic perturbation of the SOC nature.
The next weaker band system \( c^1\Sigma_u^+ \leftarrow c^3\Pi_u \) has been discovered in 1953,[46] and called ‘Herzberg II.’ The set of the excited state vibrational levels that one would now label as \( v' = 6-11[44] \) has been observed in this first absorption measurement by Herzberg, who used a high pressure and long absorption path up to 800 m.[46] Later on, this transition has been detected in the night-glow of Venus by Soviet space-explorer ‘Venera-10’ as a strong emission system including \( v' = 0 \) to \( v'' = 5-13 \) sub-bands.[19,47,48]

The \( A^3\Sigma_u^+ \leftarrow c^3\Sigma_u^+ \) transition called ‘Herzberg III’ was also discovered in the famous absorption experiments of 1953.[46] The \( A^3\Delta_u \) state has both spin and orbital angular momenta and indicates a strong multiplet splitting by SOC. In the first observation of the ‘Herzberg III’ band system,[46] the term sequence for different \( \Omega \) quantum numbers was proposed to be regular. Here \( \Omega = \Lambda + \Sigma \) is the total electronic angular momentum projection on the interatomic axis (\( \Omega \)); \( \Lambda \) and \( \Sigma \) are an orbital momentum and spin momentum projections on \( z \)-axis. Since both the \( \pi_u \) and \( \pi_g \) shells are more than half-occupied in the orbital configuration \( (\pi_u)^3(\pi_g)^3 \) of the \( A^3\Delta_u \) state, the SOC-induced splitting should be inverted; this has been pointed out by Krupenie[16] for the first time in his analysis of the oxygen spectra. The first emission analysis[43] of this system supported the inverted structure of the \( A^3\Delta_u \) multiplet. This means that the \( \Omega = 3 \) state sub-level is the lowest one. This result has been confirmed by semiempirical[43,49] and \( ab \) \( ini\)\( to\) calculations. Recently, a new \( O_2 \) emission band has been observed in the night-sky glow in the blue visible region (430 nm).[42] This very weak band was identified as the forbidden \( c^1\Sigma_u^+ \rightarrow b^1\Sigma_g^+ \) transition, induced by electronic-rotational coupling.[3,45,46]

Nowadays, many rovibronic bands in the Herzberg systems are well studied in gas phase,[1,4,52–54] but information about condensed phase spectra, especially on the ‘Herzberg III’ band system,[17,26,27] is rather confusing.[25,55] Even the regular spin-orbit multiplet splitting for the \( A^3\Delta_u \) state has been inferred from \( O_2 \) spectra in solid deuterium[25,55] in contrast with the accepted scheme in the gas phase,[2,3,41] which seems to be rather strange. In the present paper, we will model the influence of intermolecular interaction on the splitting of the \( A^3\Delta_u \) multiplet and enhancement of all Herzberg bands and oxygen atmospheric bands in water solvent. Photoinduced oxidation of hydrocarbons in supercritical \( CO_2 \) indicates that the formation of primary active oxygen species from \( O_2 \) proceeds at a wavelength longer than 242 nm.[26] The explanation of this result is one aim of our study.

To complete a short review of \( O_2 \) spectra, one has to mention the far UV region. Besides the SR transition, the latter two states from the \( \pi_u^2 \pi_g^2 \) family, \( 1\Delta_u \) and \( f^1\Sigma_u^+ \), are accessible by allowed transitions from the first and second excited singlet states, respectively.[39,56–58] The vertical transitions, which reside in the vacuum UV region, lead to photodissociation. The only allowed transitions from the ground state, \( b^3\Sigma_u^+ \leftarrow c^3\Pi_u \), provides the Schumann-Runge system: it starts at 200–175 nm as a discrete band system and at shorter wavelengths converges to the continuum. The allowed singlet-singlet transitions \( a^3\Delta_u \rightarrow 1\Delta_u \) and \( b^1\Sigma_u^+ \rightarrow f^1\Sigma_u^+ \) are less intense.[57,59] Since they provide the largest contribution to the parallel polarizability component \( (\alpha_{zz}) \) of the low-lying states, the \( x_{zz} \) constant (15.5 \( a_0^2 \)) of the ground triplet \( X \) state is higher than the values \( x_{zz} \) of the low-lying singlet \( a \) and \( b \) states (14.1 and 13.6 \( a_0^2 \), respectively).[60] This is important for the solvatochromic effect on these singlet-triplet \( a,b \rightarrow X \) transitions[60,61]; but in solvents, the polarizability of all these states is changed in a very peculiar manner,[62] which will be discussed later on. We start with a preliminary analysis of the intensity of atmospheric bands in the free \( O_2 \) molecule and then consider their dependence on bimolecular collision in order to understand the general ideas behind the solvent effect on the background of molecular dynamics simulations.

**Analysis of Intensity of the Dioxygen Weak Bands in Gas Phase**

Despite the low transition probability, all weak bands of the \( O_2 \) spectra below the first dissociation limit (above 242 nm) can be observed in absorption owing to the vast amount of molecular oxygen in the terrestrial atmosphere and because of the long-path of the sunlight through this practically transparent optical window.[20,22,23,62] Some of these bands have been seen in night air-glow, day-glow, and Aurora spectra.[4]

Recent studies of the terrestrial night-glow have been carried out by an array of major new telescopes around the world.[14,20] They study a sky spectrum as a correction for astronomers who carry out analysis of stellar spectra. Such telescopes with large echelle spectrometers and CCD detection generate high-resolution data with broad spectral coverage and high sensitivity.[63] Much of the terrestrial night-glow originates from \( O_2 \), and in most cases, the excited \( O_2 \) is pumped by three-body recombination of oxygen atoms.[4] All these phenomena are now well studied experimentally with modern techniques,[4,40] but quantum theory treatment in their analysis is very often still based on rather old approaches.[16,62,64] Besides its great astronomical importance,[20] the night-glow spectrum is now used for monitoring the photochemistry of dioxygen and the whole atmospheric energy budgets.[40,65]

Weak spectral lines of \( O_2 \) are also present in day-glow emission from the stratosphere (\( b \rightarrow X \) and \( a \rightarrow X \) series) originating in the light absorption in the Hartley band of ozone followed by its photodissociation.[40,65] The day-glow spectrum is used for remote measurements of ozone concentration.[4,40] Dioxygen spectra are also used for geophysical control of pressure and temperature. Thus, the \( O_2 \) spectroscopy must not only be good enough for reduction of possible errors in remote sensing,[40] it must be clear in all details being based on consistent theoretical backgrounds. This is the reason for renovated interest to the theory of the dioxygen spectroscopy with high resolution and better detector sensitivity.[14,32,40,66–68]

**Analysis of the atmospheric bands in gas phase**

Both singlet-triplet transitions, \( a \rightarrow X \) and \( b \rightarrow X \), are triply forbidden by symmetry selection rules for electric-dipole radiation. They are doubly forbidden by inversion symmetry rule
(gerade states) and by the spin selection. Behind this, the \( a^1\Delta_g - \chi^3\Sigma_g \) transition is additionally forbidden by the double change of an orbital angular-momentum projection \((\Delta \Lambda = 2)\) and the \( b^3\Sigma_g^- - \chi^3\Sigma_g^- \) transition—by the \( \Sigma^+ - \Sigma^- \) selection rule. All these selection rules are usually very rigorous and strictly forbid the electric-dipole transition.\(^{699}\)

Both these bands, \( a^1\Delta_g - \chi^3\Sigma_g \) and \( b^3\Sigma_g^- - \chi^3\Sigma_g^- \), are allowed in magnetic-dipole approximation with selection rule \((\Delta \Lambda = 0, \pm 1)\) and in quadrupole \((\Delta \Lambda = 0, \pm 1, \pm 2)\) approximation, where \( \mathcal{J} = \mathcal{N} + \mathcal{S} \), and \( \mathcal{N} \) is a rotational moment and \( \mathcal{S} \) is a total spin.\(^{15,30,70,71}\) With quantum-chemical calculations,\(^{31,34}\) the quadrupole contributions have been shown to be practically negligible, and the main intensity of both bands has been explained as magnetic-dipole radiation\(^{31,72,73}\) in agreement with rotational analysis of the most intense observed spectral branches\(^{30,69–71}\). Nevertheless, extremely weak quadrupole contributions to particular rotational lines have been identified recently in both atmospheric bands\(^{32,74,75}\), indicating reliable predictions and success of the old theory.\(^{31,34,43,76}\)

For example, the 0–0 band of the singlet-triplet \( a^1\Delta_g - \chi^3\Sigma_g \) transition has been observed at 1270 nm as a very weak emission band in the night-glow\(^{77,78}\). \( \text{O}_2 \) is a dominant species in the night-glow emission from the upper atmosphere.\(^{40}\) This emission is known as the near IR atmospheric oxygen band.\(^{22}\) The night-glow originates by recombination of the \( \text{O}(^3P) \) atoms created by daytime solar absorption and the \( \text{O}_2 \) cleavage; it covers the UV-visible part (from 240 nm) and extends to IR. Thus, all bound states studied in this paper are presented in night-glow emission.

The Einstein A-coefficient for the \( a \rightarrow X \) spontaneous IR emission is extremely low: laboratory measurements extrapolated to zero pressure gave values from 2.58 \times 10^{-4} \text{ s}^{-1} (Badger et al.\(^{22}\)) to 1.47 \times 10^{-4} \text{ s}^{-1} (Hsu et al.\(^{277}\)). An old atmospheric absorption measurements (Ref. 79)\(^{1}\) gave a value being close to the Hsu’s result; the most recent cavity ringdown spectroscopy studies with a long-path absorption cell provide the Einstein coefficient close to Badger’s result: 2.24 \times 10^{-4} \text{ s}^{-1} - 2.19 \times 10^{-4} \text{ s}^{-1}.\(^{81}\) Despite the difference of results, we can say that \( a \rightarrow X \) transition is the most forbidden one in molecular spectroscopy.\(^{35}\) This transition rate constant is determined mostly by magnetic dipole radiation, which has been estimated for the first time in Refs. \(^{33,82}\) as being induced by SOC mixing between \( a \), \( X \), and \( ^3\Pi_g \) states and by intensity borrowing from magnetic transitions \( X \rightarrow ^3\Pi_g \) and \( b - ^3\Pi_g \). Later, this calculation\(^{33}\) has been supported on \textit{ab initio} level by Klotz et al.\(^{34}\). Intensity of vibronic \( a - X \) \((\mathcal{J} = 0,1)\) band and \((0,0)/(1,0)\) ratio is another important issue connected with a strong intranuclear distance dependence of the magnetic transition moment.\(^{49,62,83}\)

The quadrupole contribution to the IR atmospheric oxygen band radiative probability has been estimated for the first time by Sveshnikova and Mineaev.\(^{31}\) One has to remind here about the IR Noxon band at 1.91 \mu m discovered 50 years ago,\(^{35}\) which is extremely weak and is determined by the \( b^3\Sigma_g^- \rightarrow a^1\Delta_g \) transition. The Einstein coefficient for spontaneous \( b \rightarrow a \) emission (or radiative rate constant \( k_\text{e} \)) was estimated by Noxon to be equal to 0.0014 \text{ s}^{-1}.\(^{33}\) The \( b^3\Sigma_g^- - a^1\Delta_g \) transition is pure electric-quadrupole by nature; analysis of the \( a \) and \( b \) wavefunctions indicates that the Noxon band has a maximum possible quadrupole transition moment, which could exist in the \( \text{O}_2 \) system.\(^{31}\) Sveshnikova and Mineaev\(^{31}\) have shown that the \( a \rightarrow X \) band borrows quadrupole intensity from the Noxon band and found the quadrupole contribution to the IR atmospheric band radiative probability to be practically negligible \((k_\text{e} \sim x = 2.3 \times 10^{-6} \text{ s}^{-1})\).\(^{31,43}\) In fact the recent measurements\(^{32}\) have detected this transition and supported an order of magnitude estimation.\(^{31,43}\)

The red atmospheric oxygen band \( b^3\Sigma_g^- - \chi^3\Sigma_g^- \) transition is much more intense than the \( a \rightarrow X \) system.\(^{4}\) The 0–0 band at 762 nm has the Einstein coefficient for spontaneous emission equal to 0.087 \text{ s}^{-1}.\(^{23}\) This red atmospheric oxygen \( A \) band is among the brightest features in the night-glow and among Fraunhofer lines in the optical absorption spectrum of the Sun light. It was shown\(^{33}\) that the \( b^1\Sigma_g^+ - \chi^3\Sigma_g^- \) transition to the \( \Omega = 1 \) component of the ground state is the most intense and borrows intensity from the “spin current” (spin-flip transition between spin sublevels \( \Omega = 1 \rightarrow \Omega = 0 \) of the ground triple state).\(^{33,73}\) Just this peculiar mechanism is responsible for the observed radiative lifetime of the \( b^1\Sigma_g^+ \) state \((\tau = 12 \text{ s})\) and intensity distribution in rotational structure of the \( A \) band.\(^{33,30,54}\) Radiative rate of vibronic satellites in the red atmospheric system has also found a perfect explanation on the ground of this mechanism.\(^{49,84}\) Recently, both (IR and red) atmospheric oxygen band systems have been detected with high resolution from spectra of the night sky obtained from the echelle spectrographs at large Keck/HIRES telescopes.\(^{4,20}\) Vibronic satellites of these bands are used to determine temperature, pressure, and density profiles in the atmosphere.\(^{4}\) These studies increase the need of theoretical analysis for better understanding of physical nature of atmospheric oxygen bands and their dependence on pressure and collisions. So far, a theoretical analysis of collision effects on Herzberg band was rather limited.\(^{26,52,85,86}\) We shall start with zero pressure oxygen spectra and single \( \text{O}_2 \) molecule internal magnetic perturbations.

The singlet-triplet \( a^1\Delta_g - \chi^3\Sigma_g \) and \( b^3\Sigma_g^- - \chi^3\Sigma_g^- \) transitions in a single nonrotating \( \text{O}_2 \) molecule

The main mechanisms of radiative activity in the atmospheric oxygen bands have been described elsewhere.\(^{33,34,62,84,87}\) Here we recapitulate shortly the essential details of these mechanisms, starting with the \( a \rightarrow X \) band. With account of SOC, both transitions, \( a^1\Delta_g - \chi^3\Sigma_g \) and \( b^3\Sigma_g^- - \chi^3\Sigma_g^- \), (transitions \( \Sigma \) and \( \Sigma \) in Fig. 1, respectively), can borrow intensity from magnetic-dipole transitions of the type \( ^3\Pi \rightarrow ^3\Sigma \). Here the low subscript corresponds to \( \Omega \) (the total electronic angular momentum projection on the interatomic axis). There are also \( a^1\Delta_g \rightarrow ^3\Pi_g \) magnetic-dipole transitions which contribute additionally to the \( a \rightarrow X \) band intensity.\(^{33}\) All these contributions are induced by SOC and by orbital angular momentum projection perpendicular to the molecular axis, which agree with analysis of intensity.
distribution in rotational structure.\cite{30,32,33,75,81,87} We want to remind that the \(\alpha'\Delta g_r - \chi^2\Sigma_{g_r}^2\) component of the \(\alpha - X\) transition (\(\Xi\) in Fig. 1) is magnetic and the \(\alpha'\Delta g_r - \chi^2\Sigma_{g_0}^2\) component (transition \(\Xi\) in Fig. 1) is pure quadrupole by nature.\cite{31,33}

We shall denote nonrelativistic wave functions (without SOC account) in terms of multiplicity (\(\mu = 2\eta + 1\)), spin projection \(\Sigma\), orbital and total angular momentum projections \(\Lambda\) and \(\Omega\), respectively, by \(\Psi_{\Lambda \Sigma \Omega}^\mu\). The main contribution to the triplet ground state wave function of the \(O_{2}\) molecule can be presented by the scheme:

\[
\Psi_0[\chi^2\Sigma_{g_r}^2] = A(1\sigma_r)^2(1\sigma_u)^2(2\sigma_u)^2(2\pi_u)^2(3\pi_u)^2(\pi_{1g})^4(\pi_{-g})^1(\pi_{-g})^1, \tag{2}
\]

where \(A\) indicates the proper antisymmetrization product; \(\pi_{-g}\) and \(\pi_{-g}\) indicate two degenerate \(\pi_g\) molecular orbital (MO) with angular momentum projection \(\lambda = \pm 1\) in units \(h\):

\[
\pi_{g} = \psi(r, \theta)e^{i\phi}, \quad \pi_{-g} = \psi(r, \theta)e^{-i\phi} \tag{3}
\]

Here \(r, \theta, \phi\) are coordinates of electron in the cylindrical system. An open shell of the main configuration, Eq. (2), can be presented by the following part of triplet ground state wave function:

\[
\Psi_0[\chi^2\Sigma_{g_0}^2] = (1/2)[\pi_{g}(1)\pi_{-g}(2) - \pi_{-g}(1)\pi_{g}(2)](\beta(1)\beta(2) - \beta(2)\beta(1)) \tag{4}
\]

For the \(\Omega=1\) components, the spin parts are equal to \(\alpha\) (1) \(\alpha\) (2) and \(\beta\) (1) \(\beta\) (2) functions. All spin parts are symmetrical with respect to permutation and the spatial part is antisymmetrical as the Pauli principle requires. The latter property provides the “minus” sign of the \(\Sigma\) term.

The closed-shell part of all \(\chi^2\Sigma_{g_r}^2, \alpha'\Delta g_r, \) and \(\beta'\Sigma_{g_0}^2\) states is almost the same in a reasonable approximation. Two degenerate states \(\alpha'\Delta g_r\) have a simple open-shell part of the wave function:

\[
\Psi_1[\alpha'\Delta g_r] = [\pi_{g}(1)\pi_{-g}(2) + (1/\sqrt{2})][\alpha(1)\beta(2) - \alpha(2)\beta(1)] \tag{5}
\]

and

\[
\Psi_2[\alpha'\Delta g_r] = [\pi_{-g}(1)\pi_{g}(2) + (1/\sqrt{2})][\alpha(1)\beta(2) - \alpha(2)\beta(1)] \tag{6}
\]

The singlet state \(b\) has a similar configuration as a scheme given by Eq. (4). The main contribution to the open shell of the singlet \(b\) state wave function can be written in a form:

\[
\Psi_b[b'\Sigma_{g_r}^1] = (1/2)[\pi_{g}(1)\pi_{-g}(2) + (1/\sqrt{2})][\alpha(1)\beta(2) - \alpha(2)\beta(1)] \tag{7}
\]

The simple open-shell wave functions, Eqs. (4)–(7), illustrate an important symmetry property, which is essential for SOC analysis and spin selection rules. Reflection in any plane which contains internuclear axis corresponds to interchange (\(\phi\)) \(\rightarrow (-\phi)\). For molecular orbitals in Eq. (3), this corresponds to transformation \(\pi_{+g} \rightarrow \pi_{-g}\). Thus, the spatial part of the triplet state wave function, Eq. (4), changes the sign, and the spatial part of the singlet state wave function, Eq. (7), does not change the sign upon reflection in molecular plane. These properties of the \(\Sigma_g^2\) and \(\Sigma_{g_0}^2\) spatial wave functions are very important for SOC analysis and explanation of optical spectra of oxygen molecule in the whole visible and near-IR regions.\cite{43,88} Not only the \(b - \chi\) and \(X - \chi\) transitions intensity, but also the \(b'd'\Sigma_g^1 - b'\Sigma_{g_0}^1\) transition probability,\cite{88,89} and some other optical phenomena in diluted gases and solvents containing molecular oxygen\cite{43,61,90,91} depend on the SOC-induced mixing between \(b'\Sigma_g^1, X^2\Sigma_{g_0}^2\) states. Because of the symmetry of the SOC operator,\cite{43} the spatial wave functions of the triplet and singlet \(\Sigma_g^2\) and \(\Sigma_{g_0}^2\) states are connected by the z-component of \(H_{so}\):

\[
H_{so} = B_x S_x + B_y S_y + B_z S_z, \tag{8}
\]

where \(S_z = \sum_{i} S_{z_i}\) and the orbital part can be presented in a simple approximation\cite{43,92}

\[
B_z = \sum_{n} c_n^2 \sum_{i} f_{z_i}^n \tag{9}
\]

Orbital part of the \(B_z S_z\) operator provides spatial rotation around z-axis; thus, it changes sign in respect to reflection in molecular plane and can mix the spatial parts of the wave functions of the \(\Sigma_g^2\) and \(\Sigma_{g_0}^2\) states. The spin operator \(S_z\) provides mixing of the spin functions in Eqs. (7) and (4). If one denotes the SOC-perturbed wave functions in the first order of perturbation theory by \(\Psi_{\eta, n}\), where \(n\) is a spectroscopic term notation, then it follows:

\[
\Phi_{\eta} = \Psi(b'\Sigma_g^1) + C_{b,\eta} \Psi(X^2\Sigma_{g_0}^2) + \sum_{n} C_{b,\eta} \Psi(n^2\Pi_{g_0}^n), \tag{10}
\]

\[
\Phi_{\eta, 0} = \Psi(X^2\Sigma_{g_0}^2) - C_{b, 0} \Psi(b'\Sigma_g^1), \tag{11}
\]

\[
\Phi_{\eta, 1} = \Psi(X^2\Sigma_{g_1}^1) + \sum_{n} C_{b, \eta} \Psi(n^2\Pi_{g_1}^n), \tag{12}
\]

where, for example:

\[
C_{b, \eta} = \frac{\langle \Psi(X^2\Sigma_{g_0}^2)|H_{so}|\Psi(b'\Sigma_g^1) \rangle}{E_{b} - E_{\chi}}. \tag{13}
\]

In an effective one-electron approximation, Eqs. (8) and (9), the SOC matrix element in the numerator of Eq. (13) is equal to

\[
<\pi_{x}|B_z|\pi_{y}> = i\epsilon^0, \tag{14}
\]

where \(\epsilon^0 = 153\text{ cm}^{-1}\), as it is derived from the multiplet splitting for the \(O(\Omega)\) atom.\cite{92} \(Ab\ initio\) calculations\cite{34,50,84} have given a larger value of 176 cm\(^{-1}\). If we put this value into the numerator of Eq. (13) and submit the experimental energy gap \((E_b - E_{\chi} = 13195\text{ cm}^{-1})\) into the denominator, the admixture coefficient will equal to \(C_{b, \chi} = 0.0134\). This small coefficient is very important for dioxygen spectroscopy and photochemistry. It plays a crucial role in explanation of many optical phenomena, reactivity, magnetic, and radiative properties of dioxygen at zero pressure in the upper atmosphere\cite{33} in real mixture of gases,\cite{43,76} and even in solvents and solids.\cite{31,49,93}
The singlet oxygen emission from the $b^1\Sigma_g^+$ state and a great enhancement of the $O_2(a^3\Delta_g)$ oxygen emission in solvents are entirely determined by the coefficient of Eq. (13).

First, we explain the pure magnetic transitions from the $b^1\Sigma_g^+$ and $a^1\Delta_g$ states to the ground $X^3\Sigma_g^-$ sublevels in a free (nonrotating) $O_2$ molecule.

These spin sublevels of the ground triplet state ($\Omega = 1$ and $\Omega = 0$) are split in the absence of external magnetic field by the value $D = 3.96 \text{ cm}^{-1}$.[16] This zero-field splitting (ZFS) is determined by an expectation value of spin-spin coupling ($D_{ss} = 1.44 \text{ cm}^{-1}$) and by the second-order contribution of perturbation theory with SOC account ($D_{ao} = 2.32 \text{ cm}^{-1}$). Thus, the calculated value ($D = 3.76 \text{ cm}^{-1}$) is in a reasonable agreement with the EPR and optical measurements.[16,36] In Figure 1, this ZFS is exaggerated (the doubly degenerate levels with $\Omega = 1$ and $\Omega = 0$ are presented in the split form for convenience). The five optical transitions, shown in Figure 1, have to be considered in a nonrotating oxygen molecule. Transitions $1 - 4$ are doubly degenerate; only transition $5$ is a single one.

An additional EPR transition $6$ between the ZFS spin sublevels, which occurs in the microwave region, is also shown in Figure 1. It is observed in the solid oxygen[37] and is important for analysis of the optical absorption and emission of dioxygen.[33,38]

The Noxon transition $3$ is a pure quadrupole by nature and transition $6$ (being an ordinary EPR transition) is a pure magnetic dipole in nature induced by the spin operator in Eq. (15) with perpendicular projection on the molecular axis.

The magnetic dipole operator, $\mu$, as given in Eq. (15),

$$\mu = \frac{\mu_0}{h}(L + g_s S),$$  \hspace{1cm} (15)

includes $L$ and $S$—the orbital and spin angular momenta, respectively; here $\mu_0$ is the Bohr magneton and $g_s = 2.0023$ is a $g$-factor of free electron. Transitions $3$ and $6$ in Figure 1 are pure magnetic and have been considered as the following.[33,38]

The magnetic dipole transition moment between $b^1\Sigma_g^+$ and $X^3\Sigma_g^-$ states (transition $T$, Fig. 1)

$$\mu_{b - X,1} = \langle \Phi_b | \mu | \Phi(X^3\Sigma_g^-) \rangle,$$  \hspace{1cm} (16)

includes both spin and orbital angular momenta contributions. Now we consider first the spin contribution, $S$, from Eq. (15). In this case, we can take into account that the $\Phi_1 \ldots \Phi_4$ substates, Eq. (12), is almost pure, since the $C_{K\mu}$ admixtures are not important here. They are small and do not influence much the normalization constant; thus, we take for simplicity an approximation $\Phi_1 \sim \Psi(X^3\Sigma_g^-,\Omega = 1)$. Perturbations of the $\Omega = 1$ spin sublevels are important for the orbital, but not for the spin part of the transition moment Eq. (16) calculated with the total magnetic dipole operator (15). In a similar manner, we can neglect here the $\Pi_{g,o}$ substates admixtures in the total $b$ state expansion, Eq. (10), since they do not contribute to the spin part of the magnetic transition moment, Eq. (16).

Thus, we can neglect for simplicity the $C_{K\mu}$ and $C_{K\mu}$ coefficients in Eqs. (10) and (12), respectively. Only the $C_{K\mu}$ coefficient in Eq. (10) produces contribution to the spin part of magnetic dipole transition moment[76]:

$$\mu_{b - X,1} = C_{gX} \frac{\mu_0}{h} \langle \Psi(X^3\Sigma_g^-) | g_s S_{z,1} | \Psi(X^3\Sigma_g^-) \rangle$$

$$= C_{gX} \frac{g_s h}{\mu_0} = 0.0268 \mu_0.$$  \hspace{1cm} (17)

Here $S_{z,1}$ is the lower and increase operator. In fact we have found that the optical transition $T$ (Fig. 1) of the atmospheric oxygen band in the red region of visible light can borrow intensity from the EPR transitions $3$ (Fig. 1) in the terahertz microwave region. This is the first example in molecular spectroscopy, when the spin-flip magnetic dipole transition between spin sublevels of the ground triplet state $M_s = 0$ and $M_s = 1$ (spin current) ‘produces’ the visible light. In the following, we can see that this is the largest contribution to the atmospheric red band intensity.[73,76]

Of course, there is also an orbital angular momentum $L$ contribution of the magnetic dipole operator (15) to the $b^1\Sigma_g^+ - X^3\Sigma_g^-$ transition moment $\mu_{b - X,1} = \langle \Phi_b | (L \cdot \Phi(X,1)) | \Phi(X,1) \rangle$ (transition $T$ in Fig. 1)[33,38]:

$$\mu_{b - X,1} = \frac{\mu_0}{h} \left[ \sum L_i \langle \Psi(n^1\Pi_{g,1}) | H_{so} | \Psi(n^3\Pi_{g,1}) \rangle \right]$$

$$= \left[ \langle \Psi(n^3\Pi_{g,1}) | X \cdot L | \Psi(n^1\Pi_{g,1}) \rangle \right]$$

$$= \left[ \langle \Psi(n^3\Pi_{g,1}) | L \cdot \Psi(n^1\Pi_{g,1}) \rangle \right]$$

$$= \left[ \langle \Psi(n^3\Pi_{g,1}) | L \cdot \Psi(n^3\Pi_{g,1}) \rangle \right].$$  \hspace{1cm} (18)

The first semiempirical estimation[33] based on INDO/S-type theory[33,73] has taken into account the lowest singlet and triplet $1^1\Pi_g$ states, produced by $3\sigma_g \rightarrow \pi_g$ excitation. In order to see an essential feature of the intensity-borrowing mechanism is worse to consider the orbital contribution to magnetic transition moment Eq. (18) in terms of the old theory.[33,73] In fact the most important contributions to the sum Eq. (18) are proved by the later ab initio[34,84,88] to be produced with the lowest $1^1\Pi_g$ states. It is shown[49,50] that in the vicinity of the equilibrium internuclear distance, 1.15–1.35 Å, the $1^1\Pi_g$ states are really connected with the single electron excitations $3\sigma_g \rightarrow \pi_g$ which provide the main contribution to the orbital magnetic transition moment Eq. (18). Thus, they can be approximated by a simple expression[43]:

$$\mu'_{b - X,1} = C_{gX} \frac{\mu_0}{h} \left[ \frac{1}{E(X^3\Sigma_g^-) - E(1^1\Pi_g)} - \frac{1}{E(b^1\Sigma_g^+) - E(1^1\Pi_g)} \right]$$

$$= 3.92 \times 10^{-4} \mu_0.$$  \hspace{1cm} (19)

Here $C_{gX} = 0.653$ is the LCAO-coefficient in the $3\sigma_g$ molecular orbital expansion for the $2p_x$-AO in the INDO/S approximation. It is an essential feature of Eq. (19) that both singlet and triplet contributions come with opposite signs and indicate a trend to cancel each other. The total $b - X,1$ transition magnetic dipole moment $\mu_{b - X,1} = \mu_{b - X,1} + \mu'_{b - X,1}$ is almost equal to the spin current, Eq. (17), which provides a radiative lifetime.
(τ₀ = 12 s) in a good agreement with observations. The magnetic b ← X transition T (Fig. 1) determines practically all intensity of the atmospheric oxygen red band at 762 nm. Since the first observation in a solar atmospheric spectrum, recorded with the air absorption path up to 150 km and its first analysis of rotational structure, the oxygen red band b′σg ← X′σg is known to be magnetic by nature. The spin current contribution was only recognized a half century later.

After the red atmospheric oxygen b ← X band, let us consider the infra-red a′Δg ← X′σg transition band. The magnetic dipole transition moments for the red and infra-red atmospheric band, let us consider the infra-red a′Δg ← X′σg transitional probability. Comparison between these two atmospheric oxygen band systems provides an illustrative lesson for spin catalysis in chemistry and biophysics of O₂ activation. Especially important is comparison of magnetic transitions in Fig. 1 and quadrupole intensity (transitions S and Q, Fig. 1) in order to clarify the nature of big differences for all transitions in the red and IR atmospheric oxygen bands. The magnetic a ← X,1 band intensity (transition 2, Fig. 1) in nonrotating oxygen molecule has only orbital angular momentum contributions. The structure of perturbation theory expression for the a′Δg ← X′σg transition moment is generally similar to Eqs. (18) and (19)

\[ \mu_{a \rightarrow X} = \frac{\mu_B}{\hbar} \left[ \sum_n \left( \frac{\langle \Psi(n^1\Pi_g) | H_{SO} | \Psi(X^3\Sigma_g^-) \rangle^2}{E(X^3\Sigma_g^-) - E(n^1\Pi_g)} \right) \times \langle \Psi(a^1\Delta_g, L_1 | \Psi(n^1\Pi_g) \rangle \right] + \sum_n \left[ \frac{\langle \Psi(n^1\Pi_g) | H_{SO} | \Psi(a^1\Delta_g) \rangle^2}{E(b^1\Sigma_g^-) - E(n^1\Pi_g)} \right] \times \langle \Psi(n^1\Pi_g, L_1 | \Psi(X^3\Sigma_g^-) \rangle \right] \]

(20)

where \( \mu_{a \rightarrow X} = \frac{\mu_B}{\hbar} \langle \Phi_a | \Phi(X, 1) \rangle \). An obvious difference between Eqs. (18) and (20) is that in the former equation the decreasing \( L_1 \) and increasing orbital angular momentum operator \( L_1 \) are involved and in the later—only increasing operator contributes. In a similar simple approximation mentioned above in Eq. (21), one has an analogous expression for the infra-red atmospheric band:

\[ \mu_{a \rightarrow X} = \frac{C^2_{a \rightarrow X}}{\hbar} \left[ \frac{1}{E(X^3\Sigma_g^-) - E(1^1\Pi_g)} + \frac{\sqrt{2}}{E(a^1\Delta_g) - E(1^1\Pi_g)} \right] \]

= \(-2.48 \times 10^{-3}\) μ₀

(21)

The magnetic dipole transition moments for the red and infra-red oxygen bands determined by the orbital magnetism are induced by the SOC mixing with the same \( \Pi_g \) states. In both transitions b ← X and a ← X, the orbital angular momentum expressions (19) and (21) are similar except the sign and value of the second term.

The multiplet mixing induced by SOC is rather small for all orbital magnetic contributions because of the large energy difference between the 1^3Π_g and X_ab states near the equilibrium. The vertical excitation energy from the ground state to the 1^3Π_g and 1^1Π_g states are estimated in these expressions to be equal to 8.06 and 9.33 eV, respectively.

The semiempirically estimated value, Eq. (19), is in a good agreement with ab initio results of the quadratic response (QR) calculation with large active space at the multiconfiguration self-consistent field (MC SCF) level (4.6 × 10⁻⁴ μ₀). The semipirical value (21) is also in a reasonable accord with the vertical transition moment \( |\mu_{a \rightarrow X}| = 0.0025 \) μ₀ calculated by QR method. The \( |\mu_{a \rightarrow X}| \) term is larger than the \( |\mu_{b \rightarrow X}| \) magnetic orbital contribution by 6.3 times. The square of transition moment correlates with the corresponding intensity; with account of the transitions energy, the ratio of the corresponding oscillator strength for the \( X \rightarrow a \) and \( X \rightarrow b \) absorptions, determined by orbital magnetism, is equal to 24.3.

But still the a ← X,1 transition is very weak; the radiative rate constant for spontaneous emission (or Einstein A coefficient) calculated with the magnetic dipole transition moment, Eq. (21), provides \( k_a \rightarrow X = 8.3 \times 10^{-2} \) s⁻¹, being close to results of QR methods. The ab initio calculations of Klotz et al. give \( |\mu_{a \rightarrow X}| = 0.00376 \) μ₀ and \( k_a \rightarrow x = 1.897 \times 10^{-4} \) s⁻¹, which is in a reasonable agreement with the most recent experimental value of Newman et al. (2.19 × 10⁻⁴ s⁻¹).

An internuclear distance (r) dependence of the magnetic dipole transition moments, Eqs. (16) and (20), is calculated in Refs. [43,83,84,99]. The main b ← X,1 spin transition moment, Eq. (17), increases with r, because the energy gap in the denominator of the C₀X expression, Eq. (13), decreases with the internuclear distance going to zero at the dissociation limit. This behavior explains pretty well the vibronic lines intensity; for all known (1,0), (1,1), (2,0) and (3,0) bands, the deviation from the experimental measurements does not exceed 5%, though the radiative rate constants themselves differ by four orders of magnitude. Simple account of the Franck-Condon ratios cannot provide such accuracy.

Deviations from the Franck-Condon approximation are now known for the (0,0)/(1,0) band ratio of the atmospheric infrared a ← X,1 transition. The calculated r-dependence of the magnetic dipole transition moments, Eq. (20), indicates an increase in the range 0.8–1.6 Å, Table 1, from 0.001 to 0.006 μ₀ and decrease at larger distances. The (0,0)/(1,0) intensity ratio still strongly depends on the complete active space (CAS) intensity self-consistent field (MC SCF) level (4.6 × 10⁻⁴ μ₀). The semipirical value (21) is also in a reasonable accord with the vertical transition moment \( |\mu_{a \rightarrow X}| = 0.0025 \) μ₀ calculated by QR method. The \( |\mu_{a \rightarrow X}| \) term is larger than the \( |\mu_{b \rightarrow X}| \) magnetic orbital contribution by 6.3 times. The square of transition moment correlates with the corresponding intensity; with account of the transitions energy, the ratio of the corresponding oscillator strength for the \( X \rightarrow a \) and \( X \rightarrow b \) absorptions, determined by orbital magnetism, is equal to 24.3.

<table>
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<th>r (Å)</th>
<th>CAS-I</th>
<th>CAS-II</th>
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<tr>
<td>0.8</td>
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<td>0.000727</td>
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account in the MC SCF calculations.\textsuperscript{[83]} In Table 1, the internuclear distance dependence for the $a - X_1^1$ transition calculated at two different CAS is presented. Both CAS are reasonable; they have no frozen orbitals in the 1s core. But CAS-II includes much larger number of empty orbitals, thus it is better fitted for the Rydberg states. Account of the Rydberg potential curves increases the calculated $a - X_1$ transition magnetic moments only slightly near the equilibrium ($r_e = 1.207$ Å). Thus, the much stronger enhancement at larger distances (Table 1) can be ascribed to the better description of state mixing at the way to dissociation limit.\textsuperscript{[36]} Both calculated $r$-dependences start to diverge after $r = 1.4$ Å; CAS-II provides higher magnetic transition moments at larger interatomic distances because of better description of the excited $^3\Pi_g$ states.

Rotational structure of vibronic IR bands has been considered in some details with account of the main magnetic intensity.\textsuperscript{[83,101]} Recently, a weak quadrupole contribution became available from very sensitive measurements with high spectral resolution.\textsuperscript{[32,75]} We shall start to consider this contribution with nonrotating molecule. This traditional application of quantum chemistry provides an integrated intensity source which depends entirely on electronic wave functions in the Born-Oppenheimer approximation.\textsuperscript{[69]} Next, we shall consider molecular rotation in order to clarify more carefully all reasons for differences in intensity distribution within rotational branches between the magnetic and quadrupole transitions which will be also useful in spin-catalysis of dioxygen reactivity.

The electric-quadrupole transition moments for the atmospheric oxygen bands

It is well known that the electric-quadrupole transitions are not so effective as dipole transitions in radiative processes\textsuperscript{[69]} and this explains the weakness of the $b^1\Sigma^+_g - a^1\Delta_g$ Noxon band at 1.91 mm (transition $\tilde{3}$ in Fig. 1), which is pure quadrupole by nature. The $b - a$ quadrupole transition moment is equal $Q_{b - a} = 1.351 \text{ Debye} \times \text{Å}$, which is approximately comparable with the permanent electric-quadrupole moment of the low-lying dioxygen states.\textsuperscript{[31,34]} The corresponding radiative rate constant for the spin-allowed singlet-singlet $b \rightarrow a$ Noxon transition ($k_b \rightarrow a = 0.00139 \text{ s}^{-1}$)\textsuperscript{[31,34]} is much smaller than that for the spin-forbidden singlet-triplet $b \rightarrow X$ transition (the $k_b \rightarrow X$ value is about 20 times larger).

The quadrupole component of the red band (transition $5$, Fig. 1) is very weak: it has not been carefully identified until recent time, when Naus et al.\textsuperscript{[74]} and later Long et al.\textsuperscript{[75]} have made cavity ring-down spectroscopic measurements of high sensitivity. In the classical study by Herzberg,\textsuperscript{[69]} it was mentioned that rotational lines of the red $b \leftarrow X$ system should in principle be accompanied by the thousands-time weaker lines of quadrupole nature. Some of these rotational lines ($^3\Omega$ and $^3\Pi$ branches) coincide with much more intense magnetic transition branches and are overlapped and masked, but the $^3\Omega$ and $^3\Pi$ rotational branches are widely shifted.\textsuperscript{[74]} The $^3\Sigma$ lines are relatively easy to detect\textsuperscript{[102]} since they lie beyond the main $R$ branch band head. Long et al.\textsuperscript{[75]} have determined the band strength of the quadrupole lines of the red $b \leftarrow X$ system to be $8 \times 10^{-6}$ weaker than the magnetic dipole intensity, determined by Eq. (17). From Eqs. (10) and (11), it follows that electric quadrupole tensor operator component along z-axis ($Q_{zz}$) provides the nonzero matrix element between the $X^1\Sigma^+_g$ and $b^1\Sigma^+_g$ states in the form\textsuperscript{[34,43]}:

$$Q_{b - X,0}^z = \langle \Phi_0 | Q_{zz} | \Phi(X,0) \rangle = C_{b,0} \langle \Psi(b^1\Sigma^+_g) | Q_{zz} | \Psi(X^1\Sigma^+_g) \rangle - \langle \Psi(b^1\Sigma^+_g) | Q_{zz} | \Psi(b^1\Sigma^+_g) \rangle \rangle \quad (22)$$

In a nonrotating molecule, the only allowed quadrupole transition moment of the red system ($\tilde{5}$, Fig. 1) is determined by the difference of the permanent electric quadrupole moments of the $X^1\Sigma^+_g$ and $b^1\Sigma^+_g$ states.\textsuperscript{[34,43]}

This difference is quite essential, because the wave functions calculated with account of configuration interaction are not exactly equal to the simple approximations, Eqs. (4) and (7). Instead of the simple $...\pi^2_{2s} ...\pi^2_{2p}$ configurations, presented in these equations and denoted by square brackets like $\Psi_0[\Sigma^+_g,0]$, there are essential admixtures of the doubly excited terms $...\pi^2_{2s} \pi^2_{2p}$ in the $\Psi[\Sigma^+_g]$ state, this admixture is larger than in the $\Psi[\pi^2_{1g}]$ states and even much larger than in the ground triplet state. The corresponding contributions are equal to 6.4%, 4.3%, and 2.1%, respectively. The doubly excited configuration $...\pi^2_{2s} \pi^2_{2p}$ results in a larger quadrupole component; Thus for the $b$ state, the calculated electric quadrupole moment is equal to 1.746 Debye $\times$ Å, and for the ground state $X_1$, it is smaller, 1.37 Debye $\times$ Å. Similar results have been calculated by Klotz et al.\textsuperscript{[34]}

The calculated quadrupole $b \rightarrow X_0$ transition moment is equal to 0.0051 Debye $\times$ Å, which corresponds to the radiative rate constant $K' = 4.7 \times 10^{-7}$, where degeneracy of both states is accounted\textsuperscript{[32]} (this result is approximately three times larger than the result of Klotz et al.).\textsuperscript{[34]} The integrated electric quadrupole band intensity determined by Long et al.\textsuperscript{[75]} is $1.8 \times 10^{-27} \text{ cm/molecule}$, which corresponds to the radiative rate constant $K' = 7 \times 10^{-7}$.\textsuperscript{[32]} Thus, the agreement between the theory, Eq. (22), and experiment\textsuperscript{[75]} for quadrupole intensity of the $b \rightarrow X_0$ transition ($\tilde{5}$, Fig. 1) seems to be satisfactory, though few additional arguments of Refs. [32,103] provide some complications.

Now we need to consider quadrupole contributions to infrared oxygen bands at 1.27 mm and 1.91 mm simultaneously. In order to calculate the quadrupole $a^1\Delta_g - X^1\Sigma^+_g$ transition moment, one has to submit into the integral $\langle \Phi_0 | Q_{zz} | \Phi(X) \rangle = Q_{a - X,0}$ the perturbed wave function of Eq. (11). Because of the nonzero admixture of the singlet $^1\Sigma^+_g$ state character into the ground triplet $\Phi(0)$ spin-sublevel, Eq. (11), the $a - X_0$ transition $\tilde{4}$ (Fig. 1) can borrow intensity from the $b^1\Sigma^+_g - a^1\Delta_g$ Noxon band.

$$Q_{a - X,0} = -C_{b,0} \langle \Psi(a^1\Delta_g) | Q_{zz} | \Psi(b^1\Sigma^+_g) \rangle \quad (23)$$

Since the $b - a$ transition has an appreciable electric-quadrupole moment, this mechanism of intensity borrowing, Eq. (23), induces a nonvanishing quadrupole transition moment for the
The \( \Delta g - \chi^4 \Sigma_g^+ \) atmospheric oxygen band at 1.27 mm: \( Q_a - \chi_0 = -C_{b,3}Q_{b,a} = 0.018 \) Debye \( \times A^{[31,34]} \) This corresponds to the \( \Delta g - \chi^4 \Sigma_g^+ \) transition radiative rate constant \( k_a - \chi_0 = 5 \times 10^{-7} \) s\(^{-1}\)[38] Semiempirical calculations by this scheme, Eq. (23), had provided a larger value of \( 2 \times 10^{-6} \) s\(^{-1}\).\(^{[31]} \) All the above conclusions concern the nonrotating \( O_2 \) molecule; they could be applied to the oxygen molecule frozen in a noble gas matrix, if the matrix does not perturb the internal \( O_2 \) structure. But this is not a case even for \( N \)e matrix.\(^{[110]} \) The total band intensity estimations are not changed if the molecule rotates, but some additional details connected with intensity distribution among rotational branches occur. In that case, spin sublevels (\( \Omega \) equals 1 and 0) are mixed by rotation and the prediction of different intensity of the \( a - X,0 \) and \( a - \chi,1 \) transitions cannot be verified directly. In order to check fine details of intensity distribution and make comparison with the observed rotational lines strength, we have to consider molecular rotation.

**Molecular rotation**

In 1934, Van Vleck\(^{[30]} \) has considered the nature of the atmospheric oxygen bands, just discovered that time, and presented short table for rotational line-strength formula for magnetic dipole radiation in the \( 1 \Delta - 3 \Sigma \) transition. He has also discussed different combinations of symmetries for both, red and IR atmospheric oxygen bands and concluded that the \( 3 \Sigma_g^+ - 3 \Sigma_g^+ \) symmetry is a proper assignment for the red band, accounting that the same rotational structure would possess the \( 1 \Sigma_u - 3 \Sigma_u^+ \) transition. (Now it is known as the \( c - A \) band calculated in Ref. [49] to have much higher magnetic transition moment 0.123 \( \mu_b \) than the red band. Because of small \( c - A \) transition energy, 0.29 eV, its radiative rate constant is negligible, \( k_a - c = 0.0054 \) s\(^{-1}\) and cannot compete with other type of deactivation through Herzberg bands).\(^{[110]} \) Van Vleck\(^{[30]} \) tried to explain the great difference in intensity of the red and IR bands by qualitative account of SOC-induced borrowing schemes, which correspond to those, presented in Eqs. (18) and (20) at a qualitative level. He has argued that the second term in Eq. (18) should be more important than the other possible contributions, which is absolutely correct, but he neglected the signs. Now we know that without account of spin-current contribution, Eq. (17), one cannot explain the red and infra-red bands intensity ratio.

The main achievement of Van Vleck’s classical paper\(^{[30]} \) is determined by his rotational analysis and magnetic-dipole nature assignment of the atmospheric oxygen bands. The Van Vleck’s formulas have been generalized by Bellary and Balasubramanian\(^{[70]} \) with account of spin splitting and centrifugal distortion in the ground state.\(^{[70]} \) Quantum chemical calculations in terms of this theory\(^{[70]} \) provide an agreement with fine details of rotational intensity distribution.\(^{[70]} \) In the following, we shall consider molecular rotation in order to clarify connections between magnetic and quadrupole intensity, the question which become quantitatively important in recent time.

The \( \Delta g - \chi^4 \Sigma_g^- \) system of oxygen in the absence of electric-quadrupole branches with \( \Delta J = \pm 2 \) can be entirely ascribed to a magnetic dipole radiation with \( k_a - \chi_0 = 2 \times 10^{-4} \) s\(^{-1}\)[33,34,81] This is in a good agreement with predictions of the old theoretical models for quadrupole radiation: \( k_a - \chi_0 = (2-0.5) \times 10^{-6} \) s\(^{-1}\).\(^{[31,34]} \) Thus, the electric-quadrupole contribution to the intensity of the \( a - X,0 \) transition in nonrotating \( O_2 \) molecule was considered before\(^{[31,83]} \) as being practically negligible. But recently, a very weak electric quadrupole contribution to the \( \Delta g - \chi^4 \Sigma_g^- \) transition rate constant has been identified and measured to be equal to \((1.02 \pm 0.10) \times 10^{-6} \) s\(^{-1}\).\(^{[32]} \) Such weak bands have been detected in the ground-based solar absorption spectra,\(^{[32]} \) thanks to a long absorption path through the atmosphere. Subsequently, the rotational analysis of the quadrupole-induced branches in the \( \Delta g - \chi^4 \Sigma_g^- \) transition has been performed with the high-sensitivity cavity ring-down spectroscopy experiments.\(^{[32]} \) The peculiar rotational structure of these branches has been interpreted because of a good understanding of more intense magnetic dipole rovibronic transitions\(^{[32,34,81,84]} \), and because of exact knowledge of the nature of quadrupole intensity borrowing scheme.\(^{[31,35,41]} \) Thus, a short discussion of the atmospheric oxygen bands in a rotating \( O_2 \) molecule is necessary here.

The rotational levels of the \( a \) and \( X \) states can be considered in terms of Hund’s case (b) coupling approximation, though the lower levels of the ground state obey the intermediate \( \chi \) Hund’s coupling case.\(^{69-71,103} \) The spin sublevels of the \( \chi^4 \Sigma_g^- \) state, Eqs. (11) and (12) in rotating molecule, are mixed and can be presented in a form:\(^{[70]} \)

\[
\left| F_1(J) \right| = s_J|\Phi_{X,1}(J)e_J| + c_J|\Phi_{X,0}(J)e_J| \quad (24)
\]

\[
\left| F_2(J) \right| = |\Phi_{X,1}(J)| \quad (25)
\]

\[
\left| F_3(J) \right| = c_J|\Phi_{X,1}(J)e_J| - s_J|\Phi_{X,0}(J)e_J|, \quad (26)
\]

where the \( F_1 \) component corresponds to \( J = N + S \) rotational sublevel, \( F_2 \) to \( J = N \) and \( F_3 \) to \( J = N - S \), the \( e \) and \( f \) labels denote rotational-vibrational levels with rovibronic parity \( \pm(-1)^J \). The \( e \) parity rotational sublevels of the \( \chi^4 \Sigma_g^- \) and the \( \chi^4 \Sigma_g^- \) states are mixed in spin-rotational terms \( F_1(J) \) and \( F_3(J) \), while the \( f \) parity rotational sublevel \( \chi^4 \Sigma_g^- \) corresponds to the \( F_2(J) \) spin-rotational term.\(^{[16,70]} \) The wave functions in Eqs. (11) and (12) now depend on \( J \) because of additional account of Coriolis coupling, which includes \( BL \) terms (\( B \) is a rotational constant) besides the known SOC-induced corrections.\(^{[70,83]} \) The \( J \)-dependent coefficients \( c_J \) and \( s_J \) for the \( \chi^4 \Sigma_g^- \) state of \( O_2 \) molecule are well known\(^{[32,70]} \) for the intermediate and Hund’s (b) coupling cases.

\[
S_J = \left| F_3(J) - F_2(J)/F_2(J) - F_1(J) \right|^{1/2} \quad (27)
\]

\[
C_J = \left| F_3(J) - F_1(J)/F_2(J) - F_1(J) \right|^{1/2}
\]

In the Hund’s (b) coupling limit, these coefficients are \( s_J = [(J + 1/2J + 1)]^{1/2} \) and \( c_J = J/(2J + 1)]^{1/2} \). Account of rotation, Eqs. (24)-(26), SOC, Eqs. (11)-(13), and Coriolis perturbation terms, Eq. (29), following Refs. [70,103] and omitting...
some minor terms leads to the expression for the ground \(X^2\Sigma_g^-\) state, which has only \(e\) parity:

\[
\Phi_{x,0}(Je) = \Psi(X^2\Sigma_g^-;e) - C_{xx} \Psi(b^2\Sigma_g^+;e) + \sum_n x_{x,n} [J(J+1)]^{1/2} \Psi(n^3\Pi_g;e),
\]

where the Coriolis coefficient accounts the triplet–triplet states mixing with the \(n^3\Pi_g\) terms:

\[
x_{x,n} = \frac{\langle \Psi(n^3\Pi_g_2) | \mathbf{B} | \Psi(X^2\Sigma_g^-) \rangle}{E_x - E_n}.
\]

The \(C_{xx}\) coefficient given in Eq. (13) is still a crucial value of the whole rovibronic intensity theory. In a similar manner, the upper \(2\) spin-sublevel \(X^2\Sigma_g^-\) should also be accounted for quadrupole \(a - X\) transition in rotating molecule:

\[
\Phi_{x,1}(Jf) = \Psi(X^2\Sigma_g^-;f) + \sum_n C_{x,n} \Psi(n^3\Pi_g;f) + \sum_n x_{x,n} [J(J-1)]^{1/2} \Psi(n^3\Pi_g;f) + \sum_n x_{x,n} [J(J+1)]^{1/2} \Psi(n^3\Pi_g;f),
\]

where the Coriolis coefficient accounts the triplet–triplet states mixing with the \(n^3\Pi_g\) terms:

\[
x_{x,n} = \frac{\langle \Psi(n^3\Pi_g_2) | \mathbf{B} | \Psi(X^2\Sigma_g^-) \rangle}{E_x - E_n}.
\]

Comparison with the observed lines intensity for the \(RQR\) branches of the \(a^1\Delta_g - X^3\Sigma_g^- (F)\) transitions can be done using these eigenfunctions of rotational spin-sublevels and similar wave function for the upper \(\Phi_p(F)\) states \({}^{83} \); the effective rotational transition moments in the Hund’s (a) case are tabulated elsewhere. \({}^{71,101} \)

Gordon et al. \({}^{32} \) have used the measured weak quadrupole lines intensities for calculation of complete list of quadrupole \(a - X\) transitions which obey the selection rule \(\Delta J = \pm 1, 0\). These calculations have been performed for the intermediate Hund’s coupling case, assuming that these transitions are possible only through the SOC-induced mixing of the \(X^2\Sigma_g^-\) and \(b^1\Sigma_g^+\) states, as it is shown in Eq. (11) and through intensity borrowing from the Nuxon band Eq. (23). The calculated complete list of lines agrees well with the experimental data and has been used to improve the residuals of the fitted solar atmospheric absorption spectrum. \({}^{32} \) The most intense lines are those that obey the selection rule \(\Delta J = \pm 2\); namely these are lines in the \(5\S\) and \(6\S\) branches. \({}^{32} \)

Thus, we come to important conclusion that in free \(O_2\) molecule the \(a - X\) emission band (1270 nm) consists practically only from magnetic radiation (transition \(a - X1\) to the \(\Omega = 1\) spin sublevel). This IR emission (transition \(\mathbf{F}, \mathbf{I}\) Fig. 1) is determined by the SOC-induced orbital magnetism, Eq. (20). The quadrupole \(a - X0\) transition is observable with very sensitive CRD spectrometer and its rotational structure supports the old mechanism, Eq. (23), proposed in Ref. (31). The SOC-induced mixing between the \(b\) and \(X0\) states, Eq. (13), determines all peculiarities of the atmospheric oxygen bands.

Intensity of forbidden UV oxygen bands in gas phase

Rotational branch intensities in the “Herzberg” bands and in other UV spectra in the 240–400 nm region are more uncertain. \({}^{4,19,20,50,53,63} \) There are many attempts to fit the mechanism of their intensity borrowing to the observed intensity distribution in the rotational lines. \({}^{4,19,20,50,54,63,105} \) All “Herzberg” bands are electric-dipole allowed if SOC is taken into account, but without SOC perturbation they are spin-forbidden (even the triplet–triplet transitions, \(X - A\) and \(X - A\) \({}^{43,45} \). Thus, their photoabsorption cross-sections are 4–6 orders of magnitude smaller than that in the SR continuum. Since the “Herzberg” bands absorption is very weak, it affords the near UV sunlight to penetrate deep into the Earth atmosphere, where dioxygen concentration is quite large. The absorption in the “Herzberg” band systems is a key step in the stratospheric ozone formation; the most intense and important is the Herzberg I band. Its analysis has a long history.

In 1935, Present \({}^{63} \) considered rotational branch strengths for the \(A^3\Sigma_g^+ - X^3\Sigma_g^-\) Herzberg I transition through possibility of mixing of either \(A\) or \(X\) states with a \(3\II\) states by SOC or rotational Coriolis coupling. His simulations of strong \(Q\)-branch and weaker \(O\)- and \(S\)-form branches neither were satisfactory. \({}^{63,64} \) Huesitz and Sanger, in their paper on the \(A^3\Delta_g - X^3\Sigma_g^-\) Herzberg III band \({}^{48} \) mentioned on simulation of the \(A^3\Sigma_g^+ - X^3\Sigma_g^-\) transition that included a new additional source of intensity borrowing, that is the SOC-induced mixing of the
transition in the Herzberg I band system is transition \( \Sigma \) (Fig. 2), which includes in fact four degenerate transitions between sublevels with \( \Omega = 1 \) in both states, each one has an electric dipole moment \( D(X,1 - A,1) = 0.00041 \) a.u. as follows from our direct multireference configuration interaction (MRCI) + SOC calculations. The perpendicular polarized transition \( \Sigma \) (Fig. 2) has only 0.00013 a.u. transition moment as well as the transition \( \tilde{\Pi} \) (Fig. 2), having very close to this value electric dipole moment.

The perpendicular polarization occurs because of intensity borrowing from the parallel \( A^3\Sigma_u^+ \rightarrow X^3\Sigma_g^- \) transitions by SOC-allowed transition moment (0.774 a.u.). Since the upper and lower states of this transition have rather similar ZFS parameters (3.96 and 3.26 cm\(^{-1}\)), respectively),\(^{49,96}\) each intense line in the SR bands could have very weak satellites which all together look like a triplet. Because of predissociation in the upper \( B^3\Sigma_u^- \) state, the SR lines are wide and weak satellites are overlapped and have not been nonobservable so far.

Transitions from metastable states

Absorption from the metastable \( b \) state to the upper state of the SR system is one of the most interesting finding in...
dioxgen spectroscopy in recent time.\textsuperscript{108} The $b^3\Sigma^+_0 \leftarrow b^1\Sigma^+_0$, absorption has been detected in two-step photo-dissociation experiment with the fragment $\text{O}^+(\text{D})$ atom recoil measurements.\textsuperscript{108} Electric dipole transition moment for this absorption can be explained by the same coefficient Eq. (13), which provides the ground triplet state admixture to the $b$ state, Eq. (10).\textsuperscript{88} Thus, the $B - b$ transition borrows intensity from the intense $SR$ band, which provides the largest singlet-triplet transition moment in dioxygen ($D(B,1 - b) = 0.0089$ a.u.)\textsuperscript{17,88,89} In the present review, we give our new direct CI $+$ SOC calculations which include aug-ccPVTZ basis, small CAS-$i$, and 27 spin states. This calculation provides the parallel component of the electric dipole transition moment $D(B,1 - b) = 0.00973$ a.u. being also in a good agreement with experiment.\textsuperscript{89,108} The calculated oscillator strengths for the $B(v') - b(v' = 0)$ bands are in the range $f(B - b) \sim 10^{-8}$ for the most intense ($v' = 10$) ($v' = 16$) vibronic bands, thus explaining the observed absorption cross-section and recoil direction of the aligned $\text{O}^+(\text{D})$ fragment.\textsuperscript{89,108} The perpendicular component of the $b^3\Sigma^+_0 \leftarrow b^1\Sigma^+_0$ transition moment is determined by the SOC-induced mixing with the $\Pi$ states ($D(B,1 - b) = 0.0009$ a.u.) and also agree well with the previous results.\textsuperscript{88,89}

We have to mention that a new possible transition from the metastable $b$ state to the split $A$ triplet is predicted in our MRCI $+$ SOC calculations to be relatively active. It touches only the $\Omega = 1$ spin-component of the $A^3\Delta_u$ state (the calculated vertical transitions moment $D = 0.00019$ a.u. provides expectation that this transition could be observable; for the most intense ($\nu' = 9$) ($\nu' = 0$) vibronic band, the calculated oscillator strength equal to $f(A',1 \leftarrow b)27 \times 10^{-10}$).

In Ref. [17], a set of spin-allowed transitions from the triplet $A^3\Pi_u$ states to the quasistable $1^3\Pi_g$ state have been calculated and predicted to be observable. The $1^3\Pi_g$ state is irregular when the SOC splitting equal to 88 cm$^{-1}$. Thus, the $\Omega = 2$ spin-component is the lowest one.

The $1^3\Pi_g$ triplet state has a very shallow (if any) minimum on the potential curve produced by avoiding crossing $^{17,105}$ and the above-mentioned $1^3\Pi_g \leftarrow A^3\Pi_u$ transitions can provide the narrow continuum bands in the visible ($\sim 470$ nm) region. With our new direct CI $+$ SOC calculations, we support this prediction; for example, we get $D(1^3\Pi_{g,2} \leftarrow A^3\Pi_{u,3}) = 0.173$ a.u. at 1.21 Å. In the short-wavelength edge of same region, we obtain a relatively intense singlet-triplet transition $1^3\Pi_{g,1} \leftarrow c^1\Sigma^+_g$ with the SOC-induced perpendicular transition dipole moment $D(1^3\Pi_g - c) = 0.013$ a.u. Intensity ratio for the nearest bands (0.0057) provides a weak but still detectable singlet-triplet transition ($f \sim 10^{-7}$). These visible absorption can be detected in electric discharge in the air when the $c^1\Sigma^+_g$ and $A^3\Delta_u$ states are formed by the $\text{O}^+(\text{P})$ atoms recombination.

Transitions from the $A^3\Delta_u$ states

Now we shall concentrate attention on the Herzberg III band (transitions $\Sigma \rightarrow \Sigma, \Pi$ in Fig. 2) and on the Chamberlaine $A^3\Delta_u \leftarrow a^1\Delta_g$ band, transitions $\Pi$ (Fig. 2),\textsuperscript{210} which show a specific spin-selectivity.\textsuperscript{43,49}

The Herzberg III band, $A^3\Delta_u \leftarrow \Xi^3\Sigma^+_g$, being rather weak, is the most important from the instructive point of view in connection with dioxgen chemical reactivity and spin-catalysis. The spin-sublevels of the $A^3\Delta_u$ state are highly split by the first-order SOC effect.\textsuperscript{69} This inverted splitting (Fig. 2) is equal to $\Delta \Omega$ in a simple theory,\textsuperscript{43} which is now supported by all experimental dioxgen spectra in gas phase. The reassignment of the regular splitting of the $A^3\Delta_u$ state, originally used in Ref. [69], has been first proposed by Krupenie\textsuperscript{160} and supported on the ground of the Chamberlaine $A^3\Delta_u \leftarrow a^1\Delta_g$ band analysis.\textsuperscript{44} That means that the $\Omega = 3$ spin-component is the lowest one (Fig. 2) and is the most intense in the Chamberlaine band emission. In fact our calculations provide for the Chamberlaine band system the largest electric dipole moment for the transition $\Pi$, each of four degenerate components is equal to 0.00019 a.u. (All other transitions moments are calculated to be less than 10$^{-5}$ a.u.) Transition $\Pi$ in Fig. 2 is also predicted to show a relatively large intensity ($D(A - a) = 0.00013$ a.u.)

In condensed phase, all spin-prohibition selection rules are changed dramatically because intermolecular interactions reduce the high symmetry of the electron cloud inside the $O_2$ species.\textsuperscript{43,93} Even nonreactive collisions at low pressure and temperature provide important deformations in the electronic shell of dioxgen. Of course, these deformations become more important when the collision energy will be comparable with activation barrier of chemical reaction.

It is well-known that all forbidden transitions (especially the $a \rightarrow X, b \rightarrow a, A \rightarrow X$ and $a \rightarrow X$) are possible only when the collision energy will be comparable with activation barrier of chemical reaction.

In this review, we are going to consider intermolecular perturbations in dioxgen spectra by direct CI $+$ SOC calculations of some complexes between $O_2$ and nitrogen and water containing environment.

Collision-Induced Transition Intensity

A theory developed 30 years ago\textsuperscript{93,94} was grounded on a prediction of a great enhancement of the Noxon $b^3\Sigma^+_g \rightarrow a^1\Delta_g$ transition probability ($\Xi$, Fig. 1) by intermolecular interaction. In order to recapitulate it shortly, let us consider the $O_2 + H_2$ collision with the $C_{2v}$ symmetry and analyze the singlet excited states of the oxygen moiety in such a system. The electronic structure of both molecules at a typical intermolecular distance (R = 2.6 Å) is almost not perturbed; there are no big changes in their wave functions and the molecular orbitals are almost completely localized on each molecule. Thus, we can use MO notations following the intrinsic symmetry of each...
species. Instead of complex MOs, Eq. (3), we have to use real wave functions for the two quasidegenerate $\pi_{xg}$ and $\pi_{yg}$ MO in the collision complex, since there is no molecular axis and thus the orbital angular momentum projection is quenched. If the collision complex, since there is no molecular axis and thus the expectation value of electric dipole moment for the $D_x$ now acquires a form of $D_x = \sum_{z} r_{z}$. This prediction is supported by all calculations including our relativistic approach. Thus, the $a - X0$ band enhancement is explained by intensity borrowing from the collision-induced $b - a$ transition. In the following calculations of the complex between the $O_2$ and $N_2O$ molecules, we shall concentrate on some important sequences of the previous qualitative consideration.

The collision-induced transitions in the complexes $O_2 + N_2$, $O_2 + N_2O$ and in water

We have optimized geometry of two collision complexes $O_2 + N_2$ and $O_2 + N_2O$ in the ground triplet state by density functional theory (DFT) with the B3LYP functional and also by multiconfiguration self-consisted field (MCSCF) method in a CAS for the singlet and triplet states. A well-known $2p$-CAS has been used for $O_2$ and $N_2$ molecules; similar CAS has been implemented for NNO species. The $b^1 \Sigma^+_g \rightarrow a^1 \Delta_g$ transition probability has been calculated by QR function at the excitation frequency of the first S-T transition. A total scheme of this approach is described elsewhere and the DALTON code has been used.

The optimized geometry of the $O_2-N_2O$ complex is presented in Figure 3. The $O_2-N_2$ complex is close to similar structure with the optimized N(4)-N(3)-O(2) angle equal to $112^\circ$ and larger N(3)-O(2)-O(1) angle ($132^\circ$). The nearest intermolecular distances are 3.14 and 3.23 Å for the complexes with $N_2$ and $N_2O$ molecules, respectively.

In Figure 4, the result of water + $O_2$ aggregate simulation is given. Hyper-fine coupling (HFC) constants at the $^{17}$O and $^{14}$N nuclei and Mulliken atomic population analysis are presented in Tables 2 and 3. Calculated IR and Raman spectra in the ground triplet state of the $O_2 - N_2$ complex are given in Table 4. Similar IR spectrum is obtained for the $O_2 - N_2O$ system. As it follows from Table 2, the spin density of paramagnetic oxygen only slightly penetrates to diamagnetic $N_2$ molecule during collision. Isotropic HFC constant at the nearest nitrogen atom N(3) is higher than at the terminal one, but the total atomic spin density has an opposite trend. This is connected with spin polarization and negative spin density at atom N(3). Anisotropy of spin dipole couplings is very similar for both

Table 2. Anisotropic ($B_{ij}$) and isotropic ($\alpha$) hyper-fine coupling constants (spin-dipole and Fermi contact couplings, MHz) in the the ground triplet state of the $O_2-N_2$ complex at the $^{17}$O and $^{14}$N nuclei, Mulliken atomic spin densities ($\rho$), and Mulliken charges ($Q$).

<table>
<thead>
<tr>
<th>Atom</th>
<th>$B_{aa}$</th>
<th>$B_{ab}$</th>
<th>$B_{ac}$</th>
<th>$\alpha$</th>
<th>$\rho$</th>
<th>$Q$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(1)</td>
<td>167.579</td>
<td>-83.743</td>
<td>-83.836</td>
<td>-42.308</td>
<td>1.00149</td>
<td>0.00196</td>
</tr>
<tr>
<td>O(2)</td>
<td>167.067</td>
<td>-83.294</td>
<td>-83.772</td>
<td>-42.357</td>
<td>0.99799</td>
<td>-0.00175</td>
</tr>
<tr>
<td>N(3)</td>
<td>-0.246</td>
<td>-0.229</td>
<td>0.474</td>
<td>0.017</td>
<td>-0.00002</td>
<td>0.000104</td>
</tr>
<tr>
<td>N(4)</td>
<td>-0.225</td>
<td>-0.210</td>
<td>0.435</td>
<td>0.005</td>
<td>0.00054</td>
<td>-0.00125</td>
</tr>
</tbody>
</table>

Figure 3. Optimized structure of the collision complex NNO + $O_2$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 4. A snapshot of oxygen molecule and solvent molecules in the first solvation shell. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
nuclei. In the IR spectrum of the O2−N2 complex, the oxygen bond stretching vibration gets higher intensity than the N-N vibrational mode (Table 3). These intramolecular vibrations are active in Raman spectrum but IR-forbidden in isolated molecules. Collisions induce some small electric polarization and corresponding IR activity, including nonzero dipole moment derivatives for some intramolecular modes. Intermolecular vibrations provide rather weak far-IR bands except the ν4 = 52.5 cm−1, which could be observable.

The orbitals of the complexes are mostly localized on each partner of collision, thus all excited states can be classified in terms of local excitations and charge-transfer excitations. The calculated Einstein coefficient for the b1Σg+ → a1Δg transition as a function of the O2−N2O distance (R) indicates a strong increase at the distances slightly shorter than the equilibrium value (R0 = 3.14 Å). At R = 3.2 Å, the calculated Einstein coefficient is equal to 23.5 s−1 and at R = 2.9 Å it exceeds 100 s−1. (For collision with hydrogen, this value has been obtained at shorter distance, 2 Å[91]). This strong intermolecular distance dependence for the b1Σg+ ↔ a1Δg transition moment is obvious and natural. But we have found quite unexpected result that the collision-induced b → a transition dipole moment depends on the intramolecular O–O bond distance. Accounting an expansion of the collision-induced b → a transition dipole moment Db → a as a function of the bond length (r) in a series in a vicinity of the equilibrium bond distance (r0(Db → a(r) = Db → a(r0) + (dDb → a/dr)(r − r0) + · · ·), one can predict a strong enhancement of the (0,1) vibronic band in the Noxon transition. This band is in a typical IR region (about 3700 cm−1), which is difficult for detection in kinetic transient spectroscopy, since both states are strongly metastable. This specific intramolecular O=O bond distance dependence of the Db → a transition dipole moment in the collision complexes immediately transfers into similar dependence for the Da → X0 transition, because of their connections through Eq. (23) and its dipole moment analog. The Eq. (23) leads to the proportional electric dipole transition moment for the a → X singlet oxygen emission. Thus, we come to conclusion that not only the 0–0 a → X transition is strongly enhanced, but also 0–1 band has a particular enhancement which deviates from the Franck-Condon ratio.

We need to pay attention to the fact that in a free nonrotating O2 molecule the final state of magnetic a → X spontaneous emission is the Ω = 1 sublevel (transition Ω in Fig. 1), while the collision-induced emission is connected with other spin sublevel (Ω = 0, transition Ω in Fig. 1). We have simulated O2 in water solvent in isothermal-isobaric ensemble using molecular dynamics simulation. From the simulation trajectory, we have chosen a single snapshot (see Fig.4) of oxygen and its first solvation shell of water (containing 24 water molecules) for analysis. The results of molecular dynamic simulation in the time scale of 5 ps qualitatively reproduce scenario of transition enhancement for a simple collision complex in gas phase. The collision-induced b → a and a → X emission at low gas pressure (2.5 Torr) in electric discharge through O2 and addition of foreign gases has been studied in Refs. 1[09,113]. Fink et al.[113] have produced the excited O2(b1Σg+) state by microwave discharge and studied the emission by Fourier transform IR spectrometer. The detected collision-induced transition appears as a continuum emission under the discrete lines of pure quadruple b → a and pure magnetic a → X1 rotational branches[109,113]. Upon addition of a few Torr of PCl3 vapor, the integrated intensity of the continuum becomes much higher than that of the discrete lines, which explain strong increase in intensity of the unresolved band in the spectra of low resolution. From the pressure dependence of observed emission, Fink et al.[109,113] have determined the second-order rate constants k^c_b−a and k^c_b−X for collision-induced transitions. They have stressed that the values of k^c_b−a strongly depend on the nature of collider. These values increase by a factor of about 400 on going from noble gas Ne to the polar PCl3 molecules, but the ratio k^c_b−a/k^c_b−X remains almost constant for all studied gases and quite close to the result predicted by Eq. (33).[49,93,94,109,122] which is derived from the quantum theory described above. Exactly from Eq. (23), it follows that the ratio of the collision-induced b → a and a → X radiative rate constants does not depend on the buffer gas collision because both transition moments are connected through the crucial C_bX coefficient determined by Eq. (13), which is an entirely dioxygen property:

\[ k^c_b−X/k^c_b−a = |C_bX|^2K_{Ya−a}^3/\nu_{Ya−a}^3 \]  

where \( K = d_0/d_a \) depends on the degeneracy factors (d), which need some additional comments. Formally K=1/2, but the choice of degeneracy ratio in the dioxygen transitions is complicated by spin-multiplicity change[6] and by nuclear spin statistics effect on rotational energy levels.[81] It was shown[20] that the degeneracy ratio for the A and B Einstein

**Table 3.** Anisotropic (β) and isotropic (α) hyper-fine coupling constants (spin-dipole and Fermi contact couplings, MHz) in the ground triplet state of the O2-N2O complex at the 17O and 14N nuclei.

<table>
<thead>
<tr>
<th>Atom</th>
<th>β_a</th>
<th>β_b</th>
<th>β_c</th>
<th>a</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(2)</td>
<td>182.609</td>
<td>−91.205</td>
<td>−91.404</td>
<td>−25.626</td>
</tr>
<tr>
<td>O(3)</td>
<td>180.093</td>
<td>−89.703</td>
<td>−90.309</td>
<td>−26.264</td>
</tr>
<tr>
<td>N(1)</td>
<td>3.254</td>
<td>−0.500</td>
<td>0.504</td>
<td>0.131</td>
</tr>
<tr>
<td>N(4)</td>
<td>0.363</td>
<td>0.293</td>
<td>−0.656</td>
<td>0.005</td>
</tr>
<tr>
<td>O(5)</td>
<td>0.225</td>
<td>−0.210</td>
<td>0.435</td>
<td>0.005</td>
</tr>
<tr>
<td>O(1)</td>
<td>167.579</td>
<td>−83.743</td>
<td>−83.836</td>
<td>0.005</td>
</tr>
</tbody>
</table>

**Table 4.** Calculated IR and Raman spectra in the the ground triplet state of the O2-N2 complex.

<table>
<thead>
<tr>
<th>C_b</th>
<th>ν (cm⁻¹)</th>
<th>f</th>
<th>IR intensity</th>
<th>Raman activity</th>
<th>Depolar (P)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a₀</td>
<td>7.41</td>
<td>0.001</td>
<td>0.002</td>
<td>2.479</td>
<td>0.744</td>
</tr>
<tr>
<td>a₁</td>
<td>22.11</td>
<td>0.001</td>
<td>0.000</td>
<td>0.976</td>
<td>0.745</td>
</tr>
<tr>
<td>a₀</td>
<td>27.46</td>
<td>0.001</td>
<td>0.001</td>
<td>2.479</td>
<td>0.750</td>
</tr>
<tr>
<td>a₀</td>
<td>52.52</td>
<td>0.024</td>
<td>0.003</td>
<td>1.387</td>
<td>0.724</td>
</tr>
<tr>
<td>a₀</td>
<td>165833</td>
<td>25.916</td>
<td>0.015</td>
<td>12.822</td>
<td>0.295</td>
</tr>
<tr>
<td>a₀</td>
<td>2457.70</td>
<td>49.834</td>
<td>0.011</td>
<td>15.669</td>
<td>0.254</td>
</tr>
</tbody>
</table>

Frequencies (ν, cm⁻¹), force constants (f, mDyne/A), IR intensities (K/Mole), Raman scattering activities (A²/amu), depolarization ratios for plane polarized incident light.
In the following chapter, we shall move to the bioactivation of dioxygen by some enzymes and try to explain the origin of spin multiplicity changes being based on the similar spin and spin-orbital interaction ideas, which have been described above in the spectroscopic chapters.

We are not going to say that the same pure molecular oxygen wave functions which have been considered before in Eqs. (2)–(7) can be used for description of O₂ reactions with enzymes. Instead, some new atomic and molecular orbitals and their overlaps come into play. Nevertheless, it was shown that at particular stages of enzymatic dioxygen activation, where redox processes occur, the same SOC integrals, which operate in the O₂ spectroscopy, are responsible for the triplet–singlet transition in the active center of enzyme.[8,7,10–12,28]

Interaction of such small molecules like O₂ with metalloproteins is of coordination nature which is well described in coordination chemistry.[126] Though the structure of O₂ and of the central iron metal in cytochrome or in myoglobin can change and acquire various redox forms during dioxygen activation process, one can still use some common ‘finger-print rules’ implemented in molecular spectroscopy of dioxygen.[28,83] In the following chapter, we shall show how these common rules can be used in a number of enzymes.

### Enzymatic Reactions

Spin-forbidden organic oxidation reactions of dioxygen are effectively activated by enzymes. GO catalyzes the triplet ground state dioxygen reduction into H₂O₂ by effective overcoming of spin prohibition.[7]

GO is a homodimeric protein mostly found in fungi; in the graphical abstract taken from the structure of the enzyme[127] from Aspergillus niger,[128] we present only one protein subunit.

In the GO active center, there is noncovalently bound flavin adenine dinucleotide (FAD) shown inside and outside the GO protein chains. GO catalyzes the oxidation of D-glucose into D-glucono-1,5-lactone in reductive half-reaction (i) in Figure 5, which then hydrolyzes to gluconic acid (Fig. 5, iii). At the stage (i), FAD is reduced to FADH₂. Thus, GO mediates hydrogen

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**Figure 5.** General reaction mechanism of glucose oxidase.
transfer from glucose to FAD in the reductive half-reaction (i) and then GO catalyzes the peroxide H₂O₂ production by concerted electrons and protons transfer in the systems of FADH₂ + O₂ giving FAD + H₂O₂, which is illustrated by oxidative half-reaction (ii) in Figure 5. This half-reaction is spin-forbidden[9] since GO, H₂O₂, and GOH₂ are in singlet ground states; it overcomes spin prohibition because of specific SOC inside dioxygen.[7]

The oxidation mechanism proposed[7–9] started when O₂ occupies a cavity between histidine residue (His516 shown by green color in the graphical abstract) and the flavin moiety of FAD. The measured limiting rate constants at high and low pH[128] indicate that only one prototropic form of GO with protonated histidine (at low pH) is working. At the first step of oxidation, a fast electron transfer from the reduced cofactor FADH₂ to dioxygen occurs in the small cavity. This is exothermic process as follows from DFT calculation including dielectric effect; the reason for such easy electron transfer is that electron affinity (EA) of dioxygen is extremely high (5.1 eV) in the presence of the protonated histidine at low pH. The EA for free dioxygen is only 0.45 eV[16,69] and strong attraction of the ‘jumping electron’ to the protonated histidine His516 is of fundamental importance for spin-catalysis by GO. The electron jump is initiated just by occurrence of O₂ at the active site of GO and by intermolecular and O–O vibration (see Table 4 for typical values of the modes frequency). The zero vibrational level of O₂ is almost isoenergetic with the ν=3 level of the O₂⁻ and the corresponding Franck-Condon factor is relatively large.[9]

The generated ion-radical pair FADH⁺₂ – O₂⁻ is obviously in the triplet state. In order to trigger the subsequent nonradical-chain chemistry, the triplet–singlet transition has to be induced in the ion-radical pair. If the system occurs on the singlet potential energy surface (PES), a simultaneous 2H⁺ + e⁻ transfer to superoxide O₂⁻ anion can generate the final product—hydrogen peroxide. DFT calculation of the transition state for such reaction on the singlet PES in the radical pair FADH⁺₂ – O₂⁻ provides the free-energy barrier equal to 6.6 kcal/mol. This corresponds to the rate constant of 10⁷ s⁻¹.[19] In the electron-coupled protons transfer, 2H⁺ + e⁻ from the GO active center, FADH⁺₂ + His516H⁺, both protons reach the superoxide O₂⁻ anion almost simultaneously. The new nascent radical O₂H⁻ attracts proton very fast and this process can occur only on the singlet state PES. The final step of reaction cycle FADH⁺₂ + His516 → FAD + His516H⁺ includes back proton transfer to histidine through water and protein environment, which is calculated to be essentially thermoneutral,[9] after which the product O₂H₂ leaves the cavity and the catalytic GO cycle is completed.

The DFT/B3LYP calculation of the Hessian at the transition state on the singlet state PES provides the imaginary frequency of 567 cm⁻¹. From this Hessian, a clear deuterium isotope effect is predicted (and no ¹⁸O isotope effect)[9] which is exactly opposite to experimental study.[128] Because the predicted isotope effects do not match the experimental observations, the calculated singlet state reaction with the discussed transition state cannot be the rate-limiting. Such conclusion is supported by the calculated barrier and the rate constant of 10⁶ s⁻¹[19] which is much higher than the experimental rate of only 10⁴ s⁻¹.[128] Since the first electron transfer from cofactor to dioxygen is predicted to be exothermic process without activation barrier, we come to a conclusion that the triplet–singlet transition has to be the rate-limiting step.[7,9]

In order to compete with other chemical processes (back electron transfer, radical-chain reactions), the triplet–singlet transition could be induced by relatively large SOC matrix element. In such cases, a typical intersystem crossing rate constant can reach a high limit of 10⁶ s⁻¹[17,92] which is in agreement with experimental kinetics of GO.[128] The mechanism of strong SOC in this system was prompted by analysis of the famous integral in Eq. (13), the orbital part of which is similar to the <₁π(x) |B₂y|₁π(x) matrix element in Eq. (14). In other words, the large SOC integral, Eq. (13), which determines states mixing, Eqs. (11) and (10), and intensities of various spin-forbidden transitions in dioxygen spectrum, at the same time determines dioxygen activation in GO and in other flavonoid enzymes.[6,7]

In order to explain the rate-limiting step in GO reaction cycle, we need to consider the mechanism of singlet O₂(¹Σg) quenching by amines.[6,8] It has been shown that the quenching rate constant (Kq) increases upon going from primary to secondary and to tertiary amines, i.e., with a decrease in the ionization potential (IA) of the amine. The dependence of Kq on temperature and pressure indicates a purely ‘collisional’ character for the quenching. The observed linear dependence of logKq on IA led to conclude that the charge-transfer states (CT) should affect the quenching mechanism. With account of two CT states, one is a singlet state with transfer of an electron from the lone pair n-MO of the amine to the incompletely filled πₓ-MO of the dioxygen (¹CTₓ) while the second charge-transfer state (¹CTy) is a triplet with transfer of an electron from n-MO of the amine to the πₙ-MO, it was shown that small admixtures of these CT states to the singlet and triplet dioxygen states, respectively, lead to increase of the quenching Kq rate constant.[6] This is because the SOC matrix element <²CTₓ |Hₘ₀|¹CTₚ > = (1/2) <₁π(x) |B₂y|₁π(x) > is determined by the same orbital integral, Eq. (14), which enters the important spectroscopic expression Eq. (13). It entirely depends only on oxygen, since the amine lone pair n-MO is the same in both CT states and does not contribute to the S-T matrix elements of the single-electron SOC operator, Eq. (14).

This is in agreement with the observed ¹⁸O isotope effect and an absence of the deuterium isotope effect in the GO catalytic cycle.[128] In order to provide T-S crossing between the charge-transfer states (¹CTₓ and ¹CTₚ) inside the ion-radical pair FADH⁺₂ – O₂⁻ (which actually corresponds to degeneracy of the ²Πₓ state in free O₂⁻), vibration and rotation of dioxygen moiety in the GO active site should occur. This is an additional prerequisite for the T-S transition besides the SOC, which explains the observed ¹⁸O isotope effect.

Other significant effects of spin change on biochemical functions are connected with dioxygen binding to heme proteins and to hemoglobin (Hb) in particular. They have the similar charge-transfer nature of SOC perturbation. The heme unit commonly includes an iron-protoporphyrin-IX complex linked
to globular protein by amino acid residue (an axial ligand) to
the heme iron. One coordination position at the iron
heme active site is empty and can be used for dioxygen
binding, like in myoglobin (Mb).

It is often assumed that one can overcome the spin prohi-
bition to oxidation of organic substrates with atmospheric oxy-
gen by successive addition of a single electron and proton in
the successive reduction of the O2 molecule. It is assumed
that the removal of spin prohibition in such reactions pro-
cceeds as in the case of radical chain oxidation, where the spin
prohibition can be removed upon formation of primary rad-
cals. One has though to stress a fundamental difference
between the enzymatic reactions and the radical reactions in
chain oxidation processes. In the latter case, radicals go to the
bulk and do not save the spin memory about their precursors.
In contrast, all participants of biochemical oxidation reactions,
including dioxygen and electron transfer agents, are confined within
the same active site of the enzyme. The electron transfer to
the oxygen molecule from a diamagnetic enzyme produces a
triplet ion-radical pair. In such triplet precursor, all spins remain
correlated, the spin memory is saved, and the spin prohibition
is valid and cannot lead to a singlet product. For example, the O2 reaction
with GO involves flavine adenine dinucleotide (FAD) and includes
two states; namely, glucose oxidation to gluconolactone with
reduction of FAD to FADH2 and the reverse cycle
FADH2 → FAD, with reduction of O2 to hydrogen peroxide. It is
interesting to consider only the second stage. After forma-
tion of a triplet radical pair, FADH2/O2, the T–S transition
needs to occur in order to provide the final products FAD +
H2O2. The last phase of the catalytic cycle accompanied by the
formation of hydrogen peroxide can occur only in the singlet
state. The T–S transition has been explained by a relatively
large SOC between the S and T states of the radical
pairs, which have different orbital structures inside the
superoxide ion.

It has been shown that a similar mechanism of SOC
enhancement by charge transfer can be applied for spin depen-
dent reaction of dioxygen binding to heme. At the inter-
mediate distances 2.5 Å, the starting 3A2 (2) state from the en-
trance channel transfers to the triplet Fe3+...O2 radical pair. In this
region, there are few crossing points between S and T
states, including the 3A2 (2) → 1A1 (1) states crossing, where
spin change could occur. The both radical pairs could be in
T and S states; all four states are almost degenerate at the in-
termediate distances.

The starting triplet radical pair corresponds to a charge
transfer (CT) state described by 3A wave function and the final
singlet radical pair also represent CT state but with other
space symmetry 1A. Both are similar to charge-transfer states
Fe3+...O2 of the 1CTg and 3CT, type described above.

The SOC matrix element between these states is equal to
half of the integral shown in Eq. (13) as it was shown in the case
of the singlet oxygen quenching by amines and in the
GO catalytic cycle. It entirely depends only on oxygen, since
the Fe orbital is the same in both CT states and does not con-
tribute to the S-T matrix elements of the single-electron SOC
operator, Eq. (14). Account of more sophisticated CAS CI can
lead to nonzero SOC contribution from Fe ion as well. It is im-
portant to stress that contributions from dioxygen and from
the iron cannot quench each other. In principal, these SOC
contributions interference could be destructive but it is not so
in dioxygen binding to Hb. The reason is that the orbital angu-
lar momentum quantization axes for Fe ion and for O2 do not
coincide in hemoglobin. The porphyrin macrocycle in heme
is characterized by significant electron and spin delocalization
including charge transfer to the Fe ion. This mobility of
unpaired spin density is important for various heme functions.
A high probability of spin transitions between close lying
states of different multiplicity in heme proteins deter-
mines their reactivity in respect to O2 and spin-catalysis of var-
ious enzymatic oxidation processes. Such spin-capacity in Hb
and Mb provides fast spin transformations during dioxygen
binding to heme Fe(II) site. The enzymatically active heme
species in horse reddish peroxidase and in cytochrome
P450 family include so-called compound I as a key intermedi-
ate. On the way to "compound I," the dioxygen insert-
ion into substrate bound ferric and ferrous species leads to the
oxy-ferrous form, which is similar to oxy-myoglobin. Numerous
spin changes in these reactions are now well-established by ki-
netic spectroscopy and quantum-chemistry methods.

The reaction of the ferrous heme quintet ground state with
the triplet dioxygen provides a number of spin multiplets in
the entrance channel, but none of them can lead to the oxy-
heme product, which has an open-shell singlet ground state
structure. Analysis of wave function of this product at the
oxygen moiety indicates that it is similar to the upper
state of the Herzberg III A3Δu ← XgΣg transition in O2. This is
not a simple O2 superoxide anion with the πg open shell;
there is also a hole in the πu orbitals, which interact with the
3d-AOs of the iron. From such analogy, we can apply various
spin-selection rules, developed during analysis of the Herzberg
III bands intensity distribution. The Chamberlein bands inten-
sity ratio can also be instructive. On this back-
ground, we can predict semiqualitatively the relative rate con-
stants for different spin transitions during the O2 – heme reac-
tion and in the oxy-heme productL. We come to a
conclusion that the SOC in dioxygen moiety is the most im-
portant in these reactions. Of course, the SOC in the iron 3d
shell can also contribute to the spin-selective reaction rate
constants, but both SOC contribution can be considered sepa-
rately, since the dioxygen and iron quantization axes do not
coincide in the oxy-heme product (the angle between Fe–O
and O–O axes is about 134°). Thus, one cannot anticipate that
the Fe and O2 SOC contributions are able to interfere; in the
case of the parallel axes, the destructive quenching of both
contributions is possible.

The A3Δu spin substrates are doubly degenerate in free
O2 molecule and show the inverted character (Ω = 3 is the
lowest state and the Ω = 2 is the middle one, Fig. 2). In colli-
sion with N2 and Fe-ion, the A3Δu ← s spin substrate is not
doubly degenerate, but strongly split by about 200 cm−1,
while the general multiplet SOC splitting (142 cm−1) is only
slightly reduced. The Herzberg III A3Δu ← XgΣg transition in
collision complex is strongly increased only for the $^1\Delta_g - 2\pi^g$ spin substrate ($D=0.004$ a.u.). At the same time, the Chamberlein band for the same spin substrate is predicted to be completely allowed ($D=0.259$ a.u.) in our MRCI + SOC calculation of the $O_2 + N_2$ collision complex (in spite the fact that this is a singlet-triplet transition). From this finding, we can conclude that spin-forbiddenness can be effectively overcome in dioxygen activation by enzymes, if the open shell $\pi^u\pi^g$ configuration is admixed during exchange perturbation with the catalyst.

Conclusions

The $a^1\Delta_g$ state is doubly degenerate in free $O_2$ molecule, but this degeneracy is slightly shifted in $O_2$ collisions with $N_2$, NNO, and water. The splitting is very small; it is about 3 cm$^{-1}$ for the optimized geometry of the $O_2 + N_2O$ complex. This splitting has nothing in common with the band width of singlet oxygen emission in solutions, which depends on collision-induced polarizability changes in the $a$ and $X$ states. The enhancement of the Noxon band, $b^1\Sigma^+_g - a^1\Delta_g$, is about $10^4$ times, which induces the corresponding $a^1\Delta_g \rightarrow \chi^1\Sigma^+_g$ ($M_s = 0$) transition enhancement. Vibronic intensity response to intermolecular interactions is very peculiar. Additional enhancement of the $(0,1)$ vibronic band in the $a \rightarrow X$ emission is explained by a rather strange collision-induced transition-moment dependence on the O=O bond distance in dioxygen. Such dependence is completely unexpected from the general principles of intermolecular interactions. This is in qualitative agreement with the collision-induced $(0,1)$ band intensity of the $a \rightarrow X$ phosphorescence in dense gases. The ratio of the collision-induced radiative rate constants for the $a \rightarrow X$ and $b \rightarrow a$ emission does not depend on the solvent or on the nature of the colliding gas particle.

Intensity distribution in rovibrionic lines of the red atmospheric oxygen band systems has been calculated and analyzed by ab initio methods for a free $O_2$ molecule and its complexes with $N_2$, NNO, and water. We have to mention some additional enhancement of the $(0,1)$ vibronic band of the $b^1\Sigma^+_g - \chi^1\Sigma^+_g$ system. It depends on collision-induced electric dipole moments of the $b$ and $X$ states. Calculations show that their difference strongly depends on the O=O bond length vibration during the $O_2 + N_2O$ collision.

From our MRCI + SOC calculations, we have found that the Schumann-Runge band system can include besides the very intense bands, like $\chi^1\Sigma^+_g \rightarrow b^3\Sigma^+_u$, also a very weak transition with different $\Omega$ values in the both states. Thus, our calculation with the aug-ccPVTZ basis set (small CAS) provides a perpendicular component of the electric dipole transition moment $\chi(\Delta \Omega = 0) \rightarrow b(\Delta \Omega = 1)$ equal to 0.00008 a.u. The same result is obtained for the $\Delta \Omega = -1$ spin component.

Since the ZFS parameters in both states are rather close (3.96 and 3.26 cm$^{-1}$ in the ground and upper states, respectively), the intersystem transitions could not be overlapped by the intense $\Delta \Omega = 0$ transitions. For the lower $\nu$ values, the Schumann-Runge linewidths are not very wide and the $\Delta \Omega = \pm 1$ intersystem transitions could be observable, despite their low intensity.

All these spectroscopic details are important for $O_2$ reactivity and for biochemical activation of dioxygen by enzymes. The same SOC integrals which are responsible for spin-forbidden transitions in dioxygen spectra do occur in the key steps of the $O_2$ reactions catalyzed by oxidases and cytochromes. FAD is a common component in biological oxidation-reduction reactions. The redox reactions involve a gain or loss of electrons. In the GO-catalyzed redox reaction, FAD works as the initial electron acceptor and is reduced to FADH$_2$. Then FADH$_2$ is oxidized by the final electron acceptor, dioxygen, which can do so because it has a higher reduction potential and a special arrangement of protonated protein residue in GO. $O_2$ is then reduced to hydrogen peroxide ($H_2O_2$) transforming triplet ground state to the singlet. In GO, the triplet–singlet transition occurs at the ion-radical stage and is determined by SOC matrix element in the superoxide ion, which is known from dioxygen spectroscopy. Thus, the key step of the oxidative half-reaction in GO (Fig. 5, ii) is an electron transfer and the triplet–singlet transition inside the $O_2$ anion, being bound with the FADH$^+_2$ cation. This is in agreement with the observed $^{18}O$ isotope effect in GO oxidative half-reaction and a strange absence of deuterium isotope effect. The rate constants estimations also support the predicted spin-flip mechanism of the rate-limiting step in GO catalytic cycle. Similar SOC parameters are applicable for the most important biochemical reaction—dioxygen binding to hemoglobin. The $\pi_u - \pi_g$ excitations in the Herzberg bands simulate in some way an electron promotion during dioxygen activation by cytochrome P450. Thus, the analysis of spin-forbidden transitions in dioxygen spectroscopy provides some useful information for the enzymatic spin-catalysis.

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Keywords: dioxygen spectra · bioactivation · spin-orbit coupling · multireference configuration interaction · Herzberg and Noxon bands

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