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ARTICLE *in* JOURNAL OF MOLECULAR STRUCTURE THEOCHEM · JANUARY 1989

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## SOLVENT INDUCED EMISSION OF MOLECULAR $^1\Delta_g$ OXYGEN

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(Received 11 November 1987; in final form 26 February 1988)

### ABSTRACT

Intensities of  $a^1\Delta_g - X^3\Sigma_g^-$  and  $b^1\Sigma_g^- - X^3\Sigma_g^-$  transitions in an isolated  $O_2$  molecule have been calculated on the basis of the MINDO/3 CI method taking into account spin-orbit coupling (SOC) by perturbation theory. The same method has been used for analysis of the Herzberg I-III and Chamberlain-Slanger bands. In the molecule the  $a-X$  and  $b-X$  transitions are magnetic dipoles in nature, but in collision complexes of  $O_2$  with solvent molecules ( $H_2O$ ,  $NH_3$ ,  $N_2$ ,  $C_2H_4$ ,  $C_{10}H_8$ ,  $CH_3X$ , where  $X = F, Cl, Br$ ) the  $a-X$  and  $a-b$  transitions acquire an electric-dipole character. The complexes have been calculated by the MINDO/3 CI method including double and single excited configurations. The main SOC channel of  $b-X$  mixing in  $O_2$  moiety in collision complexes and the comparatively large  $a-b$  transition electric-dipole moment lead to intensity enhancement of the  $a-X$  transition in solutions. The induced electric-dipole moment of the  $a-X$  transition strongly depends on the intermolecular distance  $R$  in the collision complex  $O_2 + XCH_3$ . The C-X valence bond stretching vibration is able to modulate the  $R$  value. In this way it is possible to explain a new type of singlet oxygen emission, induced by solvent and displaced to the longer wavelength having value  $\omega_{C-X} \approx 600 \text{ cm}^{-1}$ .

### INTRODUCTION

Molecular oxygen has a triplet ground state  $X^3\Sigma_g^-$  and two singlet states  $a^1\Delta_g$  and  $b^1\Sigma_g^+$ , with low energies 0.98 and 1.63 eV respectively, due to the fact that the highest occupied MO of the  $O_2$  molecule is a pair of double degenerate  $\pi_g$  orbitals, which hold two electrons [1]. The red ( $b-X$ ) and IR ( $a-X$ ) transitions can only occur as magnetic dipole radiation [1]. INDO, INDO/S and MINDO/3 [2, 3] CI calculations with inclusion of spin-orbit coupling (SOC) perturbation show, that the  $a-X$  transition is determined by the orbital-momentum operator  $\hat{l}$  [4-6]

$$\begin{aligned} \langle a^1\Delta_g | \beta \sum_i (\hat{l}_i + 2\hat{s}_i) | X^3\Sigma_{g,1}^- \rangle &= \mu_{aX} \\ &= \sum_n \frac{\langle n^3\Pi_{g,2} | \hat{H}_{so} | ^1\Delta_g \rangle}{E(^1\Delta_g) - E(n^3\Pi_g)} \times \langle n^3\Pi_{g,2} | \hat{l}^\perp | ^3\Sigma_{g,1}^- \rangle \\ &\quad + \sum_n \frac{\langle n^1\Pi_g | \hat{H}_{so} | ^3\Sigma_{g,1}^- \rangle}{E(^3\Sigma_g^-) - E(n^1\Pi_g)} \langle n^1\Pi_g | \hat{l}^\perp | ^1\Delta_g \rangle \end{aligned} \quad (1)$$

where  $\hat{\mu}$  is the magnetic-dipole operator  $\hat{\mu} = \beta \sum_i (\hat{l}_i + 2\hat{s}_i)$ ,  $\beta = (e\hbar/2mc)$ , and

$\hat{s}_i$  is spin-angular-momentum operator for electron  $i$  (in  $\hbar$  units),  $\hat{H}_{so}$  is the SOC operator. The main contribution to eqn. (1) produced by  $n=1$ , the first excited  $^3,^1\Pi_g$  states (configuration  $\dots 3\sigma_g\pi_g^3$  at  $r_e = 1.206 \text{ \AA}$ ). In the zero differential overlap approximation the SOC operator can be written as eqn. (2), which has proved to be very useful in the calculation of SOC effects in many diatomic and polyatomic molecules [6]

$$\hat{H}_{so} = \sum_A \zeta_A \sum_i \hat{l}_{iA} \hat{s}_i \quad (2)$$

where  $\zeta_A$  is an SOC constant for the valence shell of atom A. For oxygen O( $^3P$ ) atom  $\zeta_O = 151 \text{ cm}^{-1}$  [6]. Taking into account that  $\pi_g = (1/2^{1/2})(\phi_1 - \phi_2)$ , where  $\phi_1$  and  $\phi_2$  are  $2p_\pi$  AO on oxygen atoms, in the ZDO approximation we obtain the result

$$\mu_{ax} = C_{\sigma\pi}^2 \zeta_O \beta \left( \frac{2^{1/2}}{E(^1\Delta_g) - E(^3\Pi_g)} + \frac{1}{E(^3\Sigma_g^-) - E(^1\Pi_g)} \right) = -0.003\beta$$

where  $C_{\sigma\pi} = 0.63$  is the expansion LCAO coefficient for the  $2p_z$  AO in the  $3\sigma_g$  MO (INDO/S Calculation). The energy of  $1^{3,1}\Pi_g$  ( $3\sigma_g\pi_g^3$ ) state at  $r_e$  distance is the crucial value in this calculation. When the  $r$  value rises the  $1^{3,1}\Pi_g$  state becomes a mixture of ( $\dots 3\sigma_g\pi_g^3$ ) and ( $\dots \pi_u^3 3\sigma_g^2 \pi_g^2 3\sigma_u$ ) configuration at  $r = 1.65 \text{ \AA}$ , where the crossing of attractive ( $3\sigma_g\pi_g^3$ ) and repulsive ( $\pi_u^3 3\sigma_u$ ) configurations is avoided. The same behaviour of  $1^{3,1}\Pi_g$  states has been obtained in ab initio calculations [7, 8], but the MINDO/3 CI method overestimates the binding character of  $1^{3,1}\Pi_g$  states. The vertical excitations of  $1^3\Pi_g$  and  $1^1\Pi_g$  states are equal: 5.03 and 6.72 eV, respectively (MINDO/3 CI); 8.12 and 9.5 eV (INDO/S CI); 8.1 and 9.41 eV [8]. Experimental  $T_e$  values (assumed) are equal to 8.12 and 8.58 eV, respectively. (The last value corresponds to a Rydberg state [9].) Using the experimental and calculated energy differences we have obtained the oscillator strength values  $f_{a-X,1}$  equal to  $(6-2.4) \times 10^{-12}$  [4-6]. The experimental value is  $4 \times 10^{-12}$  [1].

A similar mechanism is acceptable for the  $b^1\Sigma_g^+ - X^3\Sigma_{g,1}^-$  transition [4, 5]

$$\begin{aligned} \mu_{b-X,1} &= C_{\sigma\pi}^2 \zeta_O \beta \left( \frac{1}{E(^3\Sigma_g^-) - E(^1\Pi_g)} - \frac{1}{E(^1\Sigma_g^+) - E(^3\Pi_g)} \right) \\ &= -0.001 \beta \end{aligned} \quad (3)$$

However there is one more additional source of intensity borrowing for the  $b-X,1$  transition. The states  $b^1\Sigma_g^+$  and  $X^3\Sigma_{g,0}^-$  can effectively mix by SOC

$$\begin{aligned} b^1\Sigma_{g,0}^+ &= b^1\Sigma_g^+ + cX^3\Sigma_{g,0}^- \\ \widetilde{X^3\Sigma_{g,0}^-} &= X^3\Sigma_{g,0}^- - cb^1\Sigma_g^+ \end{aligned} \quad (4)$$

where

$$c = \frac{\langle ^3\Sigma_{g,0}^- | \hat{H}_{so} | ^1\Sigma_g^+ \rangle}{E(^1\Sigma_g^+) - E(^3\Sigma_g^-)} = \frac{a_{Xb}}{\Delta E} \quad (5)$$

Thus, the additional contribution to the  $\mu_{bX}$  is equal to  $i2\beta c = -0.021\beta$ , where the experimental energy difference used is  $\Delta E = 13195 \text{ cm}^{-1}$ . The SOC integral  $a_{Xb}$  is equal to  $i\zeta_O$  in a single determinant approximation [4, 5]. When CI is included, the admixture of configuration  $\dots\pi_u^2\pi_g^4$  in the MINDO/3 method diminishes the  $a_{Xb}$  value:  $a_{Xb} = 0.938i\zeta_O = i141.9 \text{ cm}^{-1}$  [6, 10, 11]. The whole moment  $\mu_{b-X,1}$  with inclusion of the orbital magnetic moment (3) and the spin current ( $2i\beta c$ ) contributions (the transition  $b-X,1$  borrows its intensity from a microwave transition between spin sublevels of the ground  $X^3\Sigma_g^-$  states  $X,1-X,0$ ) is equal to  $-0.022\beta$ . The experimental value of the  $b-X$  transition magnetic dipole moment for the O-O band is equal to  $|0.0223|\beta$  [12]. Galkin [12] has determined that the transition moment  $|\mu_{bX}|^2$  depends on  $r$  in an  $r$ -centroid approximation;  $\mu_{bX}^2$  increases linearly when  $r$  increases from 0.7 Å to 1.4 Å [12]. Since the  $\Delta E$  value in the denominator of eqn. (5) decreases approximately linearly with rising  $r$ , it is easy to understand this behaviour. Our MINDO/3 CI calculations of  $|\mu_{bX}|$  dependence on  $r$  are presented in Table 1. The calculated dependence is linear and very close to the experimental one [6]. The good agreement with experiment [1, 12] is not accidental; it is confirmed by calculation of fine structure constants: SOC constants ( $A$ ),  $g$ -factor, spin-rotation ( $\gamma$ ) and spin coupling ( $\lambda$ ) constants (Table 2). The calculated  $A'^3\Delta_u$  state SOC constant is equal to  $-76.7 \text{ cm}^{-1}$ ; the calculation predicts an inverted triplet. This is in contrast to the original conclusion of Huber and Herzberg [1]; in their analysis of the  $A'^3\Delta_u-X^3\Sigma_g^-$  system of absorption bands, Huber and Herzberg assumed that the  $\Omega = 3$  component is the highest and the triplet is regular:  $A = 74.05 \text{ cm}^{-1}$  [1]. More recent experiments [13, 14] and ab initio calculations [15] confirm our prediction of an inverted splitting in the  $A'^3\Delta_u$  triplet [6].

There is also an electric-quadrupole ( $Q$ ) contribution to the intensity of the  $a^1\Delta_g-X^3\Sigma_{g,0}^-$  transition, because of the second part of eqn. (4)

$$Q_{aX} = \langle a^1\Delta_g | \hat{Q} | X^3\Sigma_{g,0}^- \rangle = -c \langle a^1\Delta_g | e(x^2 - y^2) | b^1\Sigma_g^+ \rangle = 0.0059 e\text{Å}^2 \quad (6)$$

TABLE 1

Interatomic distance ( $r$ ) dependence of  $b^1\Sigma_g^+-X^3\Sigma_{g,0}^-$  transition magnetic-dipole moment ( $\mu_{bX}$ ) in  $O_2$  molecule, calculated by MINDO/3 CI method with SOC account

Contributions to $\mu_{bX} = 2ic\beta$		$r$ (Å)			
		1.1	1.206	1.3	1.4
$\langle X^3\Sigma_{g,0}^-   \hat{H}_{so}   b^1\Sigma_g^+ \rangle$	( $i \text{ cm}^{-1}$ )	146.2	141.9	134.4	122.3
$E(^1\Sigma_g^+) - E(^3\Sigma_g^-)$	(eV)	1.084	1.016	0.939	0.846
$ \mu_{bX} ^2$	( $10^{-3}\beta^2$ )	1.119	1.184	1.260	1.285

TABLE 2

Spectroscopic constants for some electronic states of the O<sub>2</sub> molecule

State	$\lambda$ (cm <sup>-1</sup> )		$\gamma$ (cm <sup>-1</sup> )		$g$ -factor	
	Theor.	Exp. <sup>a</sup>	Theor.	Exp. <sup>a</sup>	Theor.	Exp. <sup>a</sup>
$X^3\Sigma_g^-$	1.92	1.97	-0.0075	-0.0084	2.0049	2.0052
$A^3\Sigma_u^+$	-5.04	-4.95	-0.0005	0	2.0026	
$B^3\Sigma_u^-$	1.63	1.5	-0.0287	-0.04	2.0181	

<sup>a</sup>Ref. 1.

which corresponds to oscillator strength  $f_{a-X,0} = 1.8 \times 10^{-13}$ . This value is approximately an order of magnitude smaller than the magnetic dipole contribution  $f_{a-X,1} = 4 \times 10^{-12}$ .

There are electric-dipole transitions in the ultraviolet region of the O<sub>2</sub> spectrum. Electronic configuration  $\pi_u^3\pi_g^3$  produces six bonding states of the O<sub>2</sub> molecule:  $c^1\Sigma_u^-$ ,  $A'^3\Delta_u$ ,  $A^3\Sigma_u^+$ ,  $B^3\Sigma_u^-$  and  $^1\Delta_u$ ,  $^1\Sigma_u^+$ . All are well reproduced in the MINDO/3 CI method [6]. The first three states have approximately the same energy ( $\sim 4.3$  eV) and transitions to them from the ground  $X^3\Sigma_g^-$  state correspond to the Herzberg II, III and I bands. All Herzberg transitions are forbidden in the electric-dipole approximation and the main contributions to their intensity are produced by SOC [6, 11, 15], in spite of the fact that the I and III transitions are triplet-triplet in nature. MINDO/3 CI SOC calculations produced the following results [6]:  $f(A^3\Sigma_u^+ - X^3\Sigma_g^-) = 1.4 \times 10^{-7}$  (the transition borrows its intensity from the Schuman-Runge strong dipole-allowed transition  $B^3\Sigma_u^- - X^3\Sigma_g^-$  by two-centre SOC [11];  $f(A^3\Sigma_u^+ - X^3\Sigma_{g,0}^-) = 0.9 \times 10^{-9}$ ;  $f(A'^3\Delta_{u,1} - X^3\Sigma_{g,0}^-) = 7.1 \times 10^{-9}$ ;  $f(A'^3\Delta_{u,2} - X^3\Sigma_{g,1}^-) = 2.9 \times 10^{-9}$ ;  $f(c^1\Sigma_u^- - X^3\Sigma_{g,1}^-) = 1.9 \times 10^{-9}$  [6]. The Slanger-Chamberlain  $A'-a$  band intensity is large only for the  $\Omega = 3$  spin sublevel transition:  $f(A'^3\Delta_{u,3} - a^1\Delta_g) = 2 \times 10^{-8}$  in accord with experiment [13, 14] and ab initio calculation [15]; the main contribution to its intensity produced by SOC between  $1^3\Pi_{g,2}$  and  $a^1\Delta_g$  states and by transition  $1^3\Pi_{g,2} - A'^3\Delta_{u,3}$  [6]. We have predicted the intensity of a new unknown transition  $A^3\Sigma_u^+ - c^1\Sigma_u^-$ . The states  $c$  and  $A$  are effectively mixed by SOC; the matrix element  $\langle c^1\Sigma_u^- | \hat{H}_{so} | A^3\Sigma_u^+ \rangle = -\zeta_0$  is large and the energy difference is very small:  $E(A) - E(c) = 0.29$  eV. Calculated magnetic dipole transition moment  $\mu_{A-c} = 0.123\beta$  is larger than  $\mu_{b-X}$  and  $f_{A-c} = 1.5 \times 10^{-9}$ .

The knowledge of an intensity borrowing mechanism for the spin-forbidden transitions in the O<sub>2</sub> molecule is necessary for understanding solvent induced emission  $a^1\Delta_g - X^3\Sigma_g^-$  in a variety of solutions.

## MINDO/3 CI SOC CALCULATIONS OF COLLISION COMPLEXES

It is well established, that the  $a$ - $X$  transition is intensity enhanced in a great number of  $O_2$  solutions [16, 17]. The total lifetime of  $O_2(^1\Delta_g)$  decreases from 3890 s (the radiative lifetime of the isolated  $O_2$  molecule in the upper atmosphere [17] to 5  $\mu$ s in aqueous solution [16]. This total lifetime is determined mainly by a nonradiative decay of the  $a^1\Delta_g$  excitation in condensed media [18]. Measurements of quantum yield of photosensitised luminescence and radiative lifetime ( $\tau_r$ ) of singlet  $a^1\Delta_g$  molecular oxygen in solutions show that  $\tau_r$  is practically constant in a large variety of solutions and is equal to  $4.1 \pm 2$  s, while the total lifetime changes on a large scale [16]. So the  $\tau_r$  of  $O_2(^1\Delta_g)$  state decreases in solution approximately 1000 times. The large enhancement of the  $a$ - $X$  radiative transition intensity in solutions [16, 17] and in the foreign gas mixtures [18, 19] can be explained by MINDO/3 CI SOC calculations of the collision complexes of  $O_2$  with solvent molecules ( $H_2$ ,  $N_2$ ,  $H_2O$ ,  $NH_3$ ,  $C_2H_4$ ,  $C_6H_6$ ,  $C_{10}H_8$ ,  $CH_3X$ , where  $X = F, Cl, Br$ ) [6, 10, 20–24, 29].

The characteristic feature of all these complexes is the collision induced electric-dipole moment ( $M$ ) of the  $b^1\Sigma_g^+ - a^1\Delta_g$  transition. For example, in a trapezium-like complex  $H_2 + O_2$ , where the  $z$ -axis is parallel to  $O-O$  and  $H-H$  bonds,  $zx$  is a plane of the trapezium, the lowest component of the slightly splitting  $a^1\Delta_g$  state and the wavefunction of the  $b^1\Sigma_g^+$  state can be written in the form [6, 10]

$$\begin{aligned}\Psi_1(a^1\Delta_g) &= 0.72\Phi(\pi_{g,x}^2) - 0.69\Phi(\pi_{g,y}^2) \\ \Psi_3(b^1\Sigma_g^+) &= 0.69\Phi(\pi_{g,x}^2) + 0.72\Phi(\pi_{g,y}^2)\end{aligned}\quad (7)$$

where  $\Phi(\pi_{g,x}^2)$  means the configuration  $1\sigma_g^2(H_2)\dots\pi_u^43\sigma_g^2\pi_{g,x}^2(O_2)$ ; the height of the trapezium ( $R$ ) is equal to 2 Å. Although the whole complex has  $C_{2v}$  symmetry and the MOs of each component are slightly admixed, it is possible to assign them qualitatively to  $H_2$  and  $O_2$  moieties. The MO  $\pi_{g,y}$  does not change, but the MO  $\pi_{g,x}$  has  $1s$  ( $H$ ) AO admixture ( $C_{1s} = 0.053$ ). The electric-dipole moment of  $b$ - $a$  transition is equal to  $0.5(M_x - M_y)$ , where  $M_x$  and  $M_y$  are the permanent dipole moments of the corresponding configurations. The difference of these dipole moments is determined by a specific interaction of two degenerate oxygen  $\pi_g$  MOs with the orbitals of solvent molecule. Taking into account only two configurations (7), MINDO/3 calculation yields:  $M_{3-1} = 0.0062$  eÅ. Adding two configurations  $\pi_u^2\pi_g^4$ , it yields  $M_{3-1} = 0.0091$  eÅ. CI with 50 configurations produces  $M_{3-1} = 0.0113$  eÅ, which corresponds to the oscillator strength  $f_{b-a} = 7 \times 10^{-6}$ . In an isolated  $O_2$  molecule the  $b^1\Sigma_g^+ - a^1\Delta_g$  transition determines the Noxon emission band at  $5238.5$   $cm^{-1}$ ; it has the absolute transition probability  $2.5 \times 10^{-3} s^{-1}$  [1]. This transition is purely an electric-quadrupole in nature [20]. In INDO approximation the electric-quadrupole  $b$ - $a$  transition moment is equal to  $e\langle r^2 \rangle_{2p} = 0.406$  eÅ [6]; from the experi-

mental intensity of the Noxon band this value is estimated to be  $0.545 \text{ eÅ}$  ( $f_{b-a} = 1.6 \times 10^{-9}$ ) [6]. So the intensity of the  $b-a$  Noxon transition in an  $\text{O}_2 + \text{H}_2$  mixture would be enhanced 4400 times. Since the intramolecular  $\text{O}_2$  structure in collision complex is not altered significantly, the coefficient  $c$  in eqn. (5) does not alter either. So the  $a-X$  transition steals its intensity from a collision-induced  $b-a$  transition:  $M_{a-X} = -cM_{3-1} = 1.22 \cdot 10^{-4} \text{ eÅ}$ , which corresponds to  $f_{a-X} = 1.3 \times 10^{-9}$  [10]. So the  $a-X$  transition is enhanced by three orders of magnitude. The same behaviour is obtained for other complexes [21–24]. Collision-induced transition electric-dipole moments for the complex  $\text{C}_2\text{H}_4 + \text{O}_2$  are shown in Table 3 [6, 22]. The  $b^1\Sigma_g^+ - a^1\Delta_g$  transition in collision complex with the ground state ( $S_0$ ) ethylene molecule (transition 3–1 in Table 3) is greatly enhanced even at the large intermolecular distance  $R = 3.6 \text{ Å}$ . The enhanced oscillator strength  $f_{a-X}$  in collision complex  $\text{C}_2\text{H}_4 + \text{O}_2$  at  $R = 2.8 \text{ Å}$  is equal to  $5 \times 10^{-10}$ . It is also possible to explain the  $T_1-S_0$  transition intensity enhancement in hydrocarbon by  $\text{O}_2(X^3\Sigma_g^-)$  influence (transition 5–0 has the oscillator strength  $1.5 \times 10^{-5}$  at  $R = 2.8 \text{ Å}$ ). So the intensity of excitation to the first excited triplet ( $T_1$ ) state in ethylene is enhanced by  $\text{O}_2$  approximately  $10^4$  times. The cooperative transition 6–0 is also explained; its intensity has the same order of magnitude as the transition 5–0 in accordance with experiment [25, 26]. It is interesting to note that the other cooperative transition  $^1(^3\Sigma_g^- T_1) - (^1\Delta_g S_0)$  has a non-zero intensity and could be observable in emission at high-level detector sensitivity, as in the experiments of Chou and Khan [27]. The  $a-X$  transition in  $\text{O}_2$  molecule perturbed by  $T_1$  excited hydrocarbon is much more enhanced than the previous transitions in Table 3. The  $S_1-T_1$  transition in  $\text{C}_2\text{H}_4$  molecule, perturbed by  $\text{O}_2(X^3\Sigma_g^-)$ , is electric-dipole allowed and has a large transition dipole moment ( $\approx 0.1 \text{ eÅ}$ ) at  $R = 2.8 \text{ Å}$ , because of the charge-transfer contribution to wavefunction  $\Psi_9$  (Table 3).

Using the inductive-resonance energy transfer model for a collision complex

TABLE 3

MINDO/3 CI calculated collision-induced transition electric-dipole moments  $M_{n-m}$  (in  $10^{-3} \text{ eÅ}$ ) for the complex  $\text{C}_2\text{H}_4 + \text{O}_2$

$n-m$	$\Psi_n$	$\Psi_m$	$R (\text{Å})$			
			3.6	3.2	2.8	Polarization
5–0	$^3(^3\Sigma_g^- T_1)$	$^3\Sigma_g^- S_0$	0.05	0.60	4.01	$x$
3–1	$^1\Sigma_g^+ S_0$	$^1\Delta_g S_0$	0.07	0.92	4.06	$z$
4–2	$^1(^3\Sigma_g^- T_1)$	$^1\Delta_g S_0$	0.03	0.29	1.90	$x$
6–0	$^1\Delta_g T_1$	$^3\Sigma_g^- S_0$	0.03	0.56	3.98	$x$
5–6	$^3(^3\Sigma_g^- T_1)$	$^3(^1\Delta_g T_1)$	0.05	1.07	9.65	$z$
5–9	$^3(^3\Sigma_g^- T_1)$	$^3(^3\Sigma_g^- S_1)$	0.07	3.91	92.05	$z$

surrounded by solvent environment, it is possible to explain some quenching processes in oxygen-containing solutions. The energy transfer mechanism of  $O_2(^1\Delta_g)$  quenching in solutions [18, 28] by electronic excitation energy transfer on C-H and O-H vibrations of solvent is examined [20]. The intrinsic quadrupole moment of  $a^1\Delta_g-X^3\Sigma_{g,0}^-$  transition (6), which does not influence the radiative decay determines the quenching by quadrupole-dipole interactions of transition moments (electric-dipole IR overtone transition has an order of magnitude  $3 \times 10^{-4} e\text{\AA}$  [20]).

The additional electric-dipole moment of the  $a-X$  transition, induced in a collision complex, also contributes to the energy transfer from  $O_2(^1\Delta_g)$  on C-H vibrations, but to a lesser extent [6]. This extent rises as the donor property of solvent hydrocarbons strengthens [6]. In saturated hydrocarbons the electric-dipole induced contribution to  $O_2(^1\Delta_g)$  quenching is negligible, but in naphthalene and decapentaene this contribution exceeds the quadrupole quenching [6, 22, 29].

The inductive-resonance energy transfer model can also explain the enhancement of the  $S_1-T_1$  intersystem crossing (5-9 transition dipole moment interacts with ethylene vibration dipoles), quenching of  $T$  states by energy transfer on  $a^1\Delta_g$  state (4-2 transition dipole moment interacts with ethylene vibration transition moments) [6, 22], and other quenching and energy transfer processes [22].

#### SIMULTANEOUS ELECTRONIC-VIBRATIONAL EMISSION OF $O_2(^1\Delta_g)$

Chou and Khan [27] observed a new type of  $O_2(^1\Delta_g)$  emission in halogen containing solvents; besides the O-O band of the  $a-X$  transition (1272 nm) they succeeded in detecting a weak band, shifted to the long-wave edge on a frequency of C-X vibration ( $X = F, Cl, Br$ ) [27]. It is easy to see from Table 3 that the  $a^1\Delta_g-b^1\Sigma_g^+$  (1-3) transition moment strongly depends on the intermolecular distance  $R$ . The same behaviour is predicted for collision complexes  $O_2+XCH_3$  ( $X = F, Cl$ ) by MINDO/3 CI calculation [21]. (The  $XCH_3$  molecule approaches  $O_2$  in the  $zx$  plane at angle  $\angle OOX = 45^\circ$ .) In these collision complexes the C-X valence bond stretching vibration is able to modulate the  $R$  value:  $\partial M_{3-1}/\partial R = -\partial M_{3-1}/\partial q$ , where  $q$  is a normal coordinate of C-X stretching vibration. In accordance with eqn. (3) these derivatives can influence the  $a^1\Delta_g-X^3\Sigma_g^-$  transition intensity, including vibrational excitation of the C-X bond in the solvent molecule

$$\langle a^1\Delta_g S_0^v | M | X^3\Sigma_g^- S_0^v \rangle = -C \left( \frac{\partial M_{3-1}}{\partial q} \right)_0 \langle 0 | q | v \rangle \quad (8)$$

where  $S_0^v$  means vibrationally excited  $S_0$  state. MINDO/3 CI calculations give:  $(\partial M_{3-1}/\partial R)_0 = 0.0077 e$ ,  $\langle 0 | q | 1 \rangle = 0.1626 \text{ \AA}$  for the complex  $ClCH_3 + O_2$  at



$R_0 = 3.2 \text{ \AA}$ . The moment of simultaneous electronic-vibrational transition is equal to  $1.5 \times 10^{-5} e\text{\AA}$  and corresponds to the oscillator strength  $f = 1.6 \times 10^{-11}$ . For the complex  $\text{FCH}_3 + \text{O}_2$  we obtain  $f = 1.25 \times 10^{-11}$ . This new type of singlet oxygen emission, induced by solvent, is approximately 100 times smaller, than O-O transition  $a-X$  in solution; the result is in good agreement with experiment [27].

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