

# The impact of oxygen encounter complexes on photophysics of molecular oxygen and some other atmospheric molecules

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A weakly bound environment has crucial influence on the photophysics and photochemistry of molecular oxygen. The photoabsorption of “isolated” oxygen molecules is very weak within the whole UV-IR spectral region where all electronic transitions of ground state O<sub>2</sub> molecule are spin and/or orbital symmetry forbidden. But the interaction of oxygen molecules with molecular environment provides the strong enhancement of UV-absorption by oxygen and other molecules. This drastic effect is governed by encounter complexes X-O<sub>2</sub> and takes place when molecules collide in the gas phase. Thus for example isoprene C<sub>5</sub>H<sub>8</sub> (the most widespread biogenic organic compound in the Earth atmosphere after methane), being transparent at wavelengths  $\lambda > 240$  nm, absorbs in the presence of molecular oxygen due to collision-induced absorption in C<sub>5</sub>H<sub>8</sub>-O<sub>2</sub> encounter complexes [1].

Collision-induced absorption of oxygen encounter complexes also dramatically changes oxygen photochemistry causing new photochemical processes such as formation of singlet oxygen species O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>) which possess high chemical reactivity and play important role in nature. In our recent investigations we found out a new process of singlet oxygen O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>) formation that was unknown before [1,2]. Singlet oxygen molecules were detected by their IR-luminescence centered at 1.27 μm after UV-photoexcitation of pure oxygen and N<sub>2</sub>+O<sub>2</sub> or C<sub>5</sub>H<sub>8</sub>+O<sub>2</sub> gas mixtures by laser radiation. We have established that this new photochemical process proceeds via UV-photoexcitation of O<sub>2</sub>-O<sub>2</sub>, N<sub>2</sub>-O<sub>2</sub> and C<sub>5</sub>H<sub>8</sub>-O<sub>2</sub> encounter complexes and measured the spectral dependence of singlet oxygen quantum yield for the first time. The maximum quantum yield values are provided to be rather high and close to 2. Relying on the obtained data we made estimations of the role of this new process in the Earth atmosphere.

We suggest the probable mechanism to consist of two processes responsible for singlet oxygen formation. One results from collision-induced absorption of O<sub>2</sub> giving rise to excited triplet oxygen molecules X-O<sub>2</sub>+hν→X+O<sub>2</sub>(A'<sup>3</sup>Δ<sub>u</sub>) with their further annihilation in collisions with the ground state O<sub>2</sub> molecules giving rise to singlet oxygen. Another process consisting in cooperative X-O<sub>2</sub> encounter complex excitation with further simultaneous change of the both partner spins <sup>3</sup>(<sup>1</sup>X-<sup>3</sup>O<sub>2</sub>)+hν→<sup>3</sup>(<sup>3</sup>X-<sup>1</sup>O<sub>2</sub>)→<sup>3</sup>X+<sup>1</sup>O<sub>2</sub> is one of peculiar interest. We suppose that this process may cause changes in the absorption spectrum of X molecules and result in O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>) formation in widespread wavelength region including visible spectral region depending on oxygen collisional partner X. We also assume singlet oxygen generation to follow the excitation of any encounter complexes X-O<sub>2</sub> in any oxygen-containing media.

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## References

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