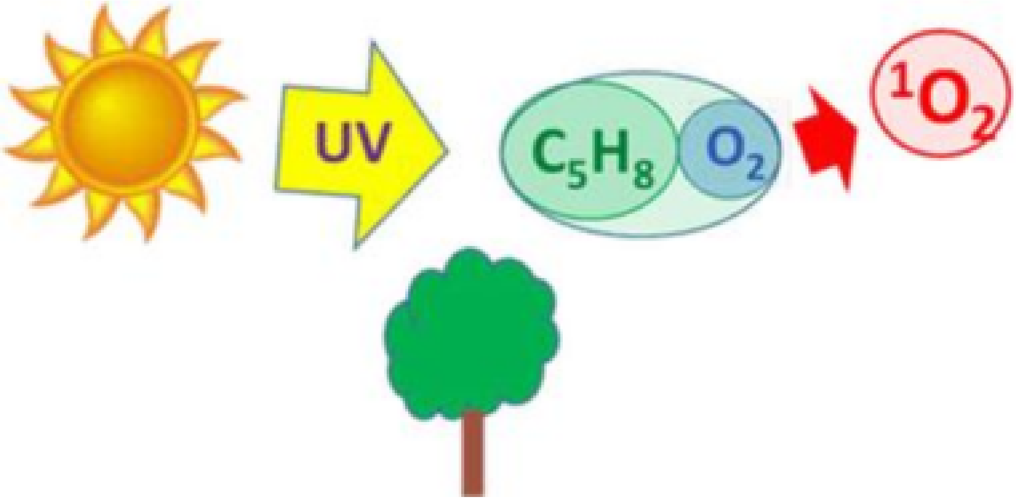
UV-photoexcitation of oxygen-isoprene collision complexes as a source of singlet oxygen

Pyryaeva Alexandra P., Ershov Kirill S., Kochubei Sergei A., Baklanov Alexey V.



Voevodsky Institute of chemical kinetics and combustion SB RAS

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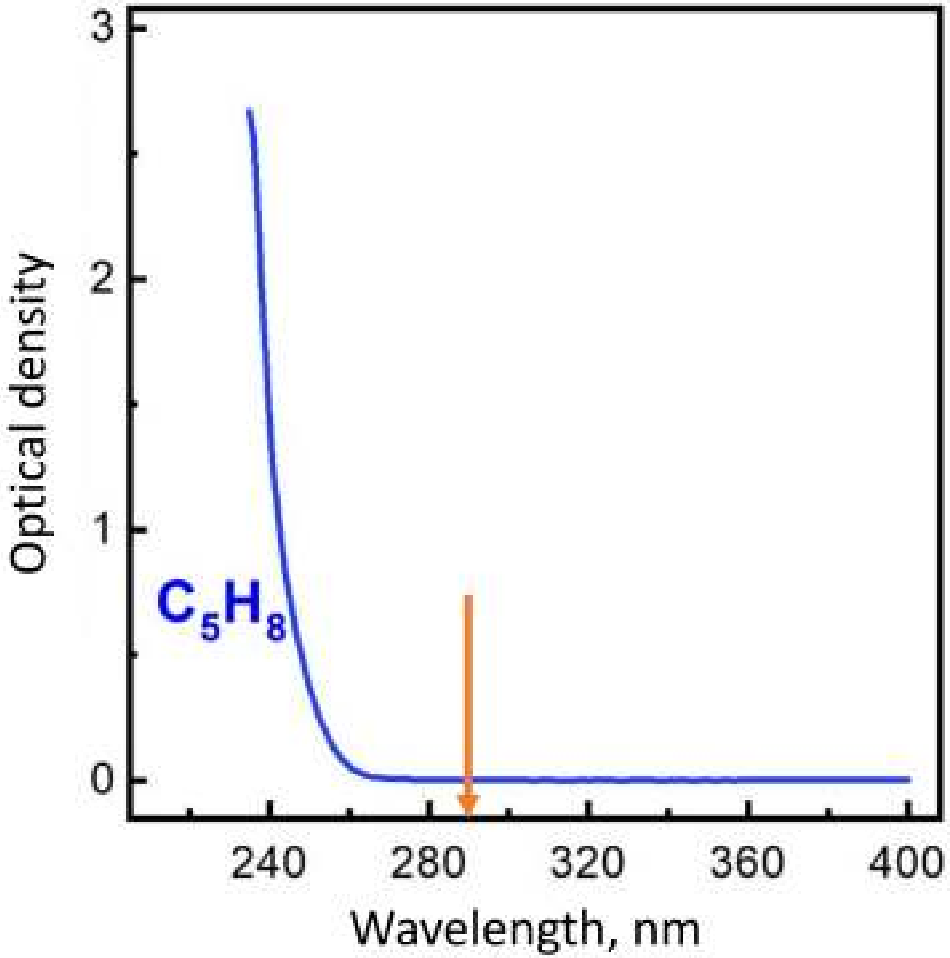
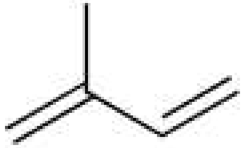
X International Voevodsky Conference «Physics and Chemistry of Elementary Chemical Processes»
Novosibirsk - 2022

«Isolated» isoprene molecules



Isoprene C_5H_8 (2-methyl-1,3-butadiene)

C_5H_8



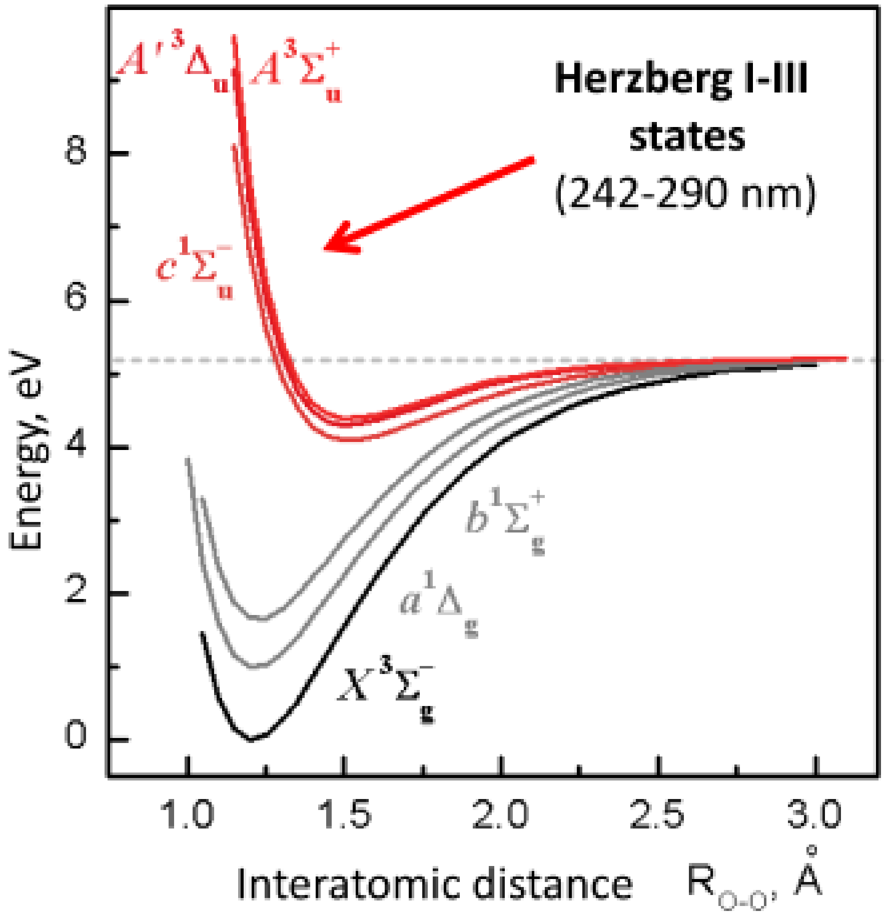
the second most abundant biogenic volatile organic compound in the Earth's atmosphere

one of the most important molecules for the atmospheric photochemistry

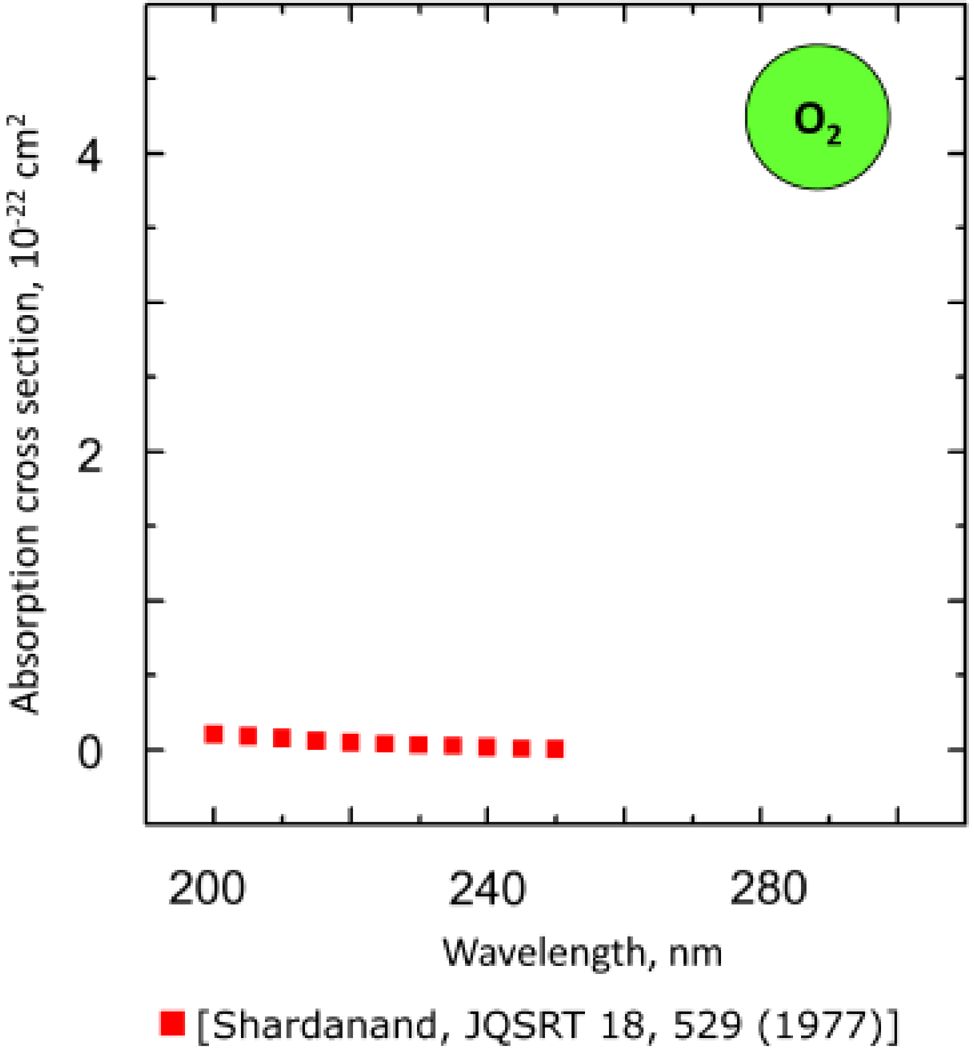
participates in several atmospheric oxidative processes

completely transparent for the solar radiation that passes through the Earth's troposphere (λ>290 nm)

«Isolated» oxygen molecule

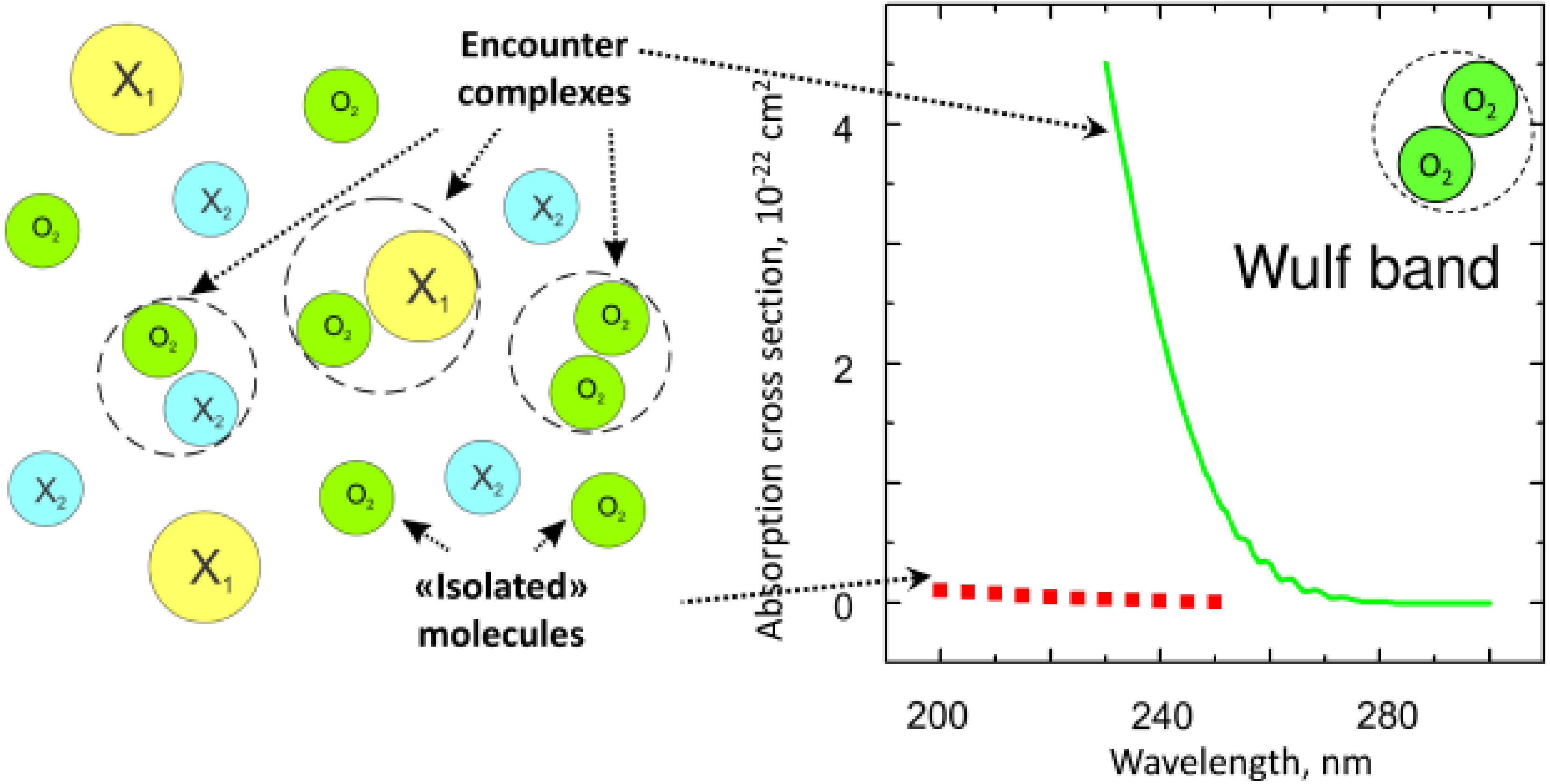


Herzberg I-III states (242-290 nm)



🟥 [Shardanand, JQSRT 18, 529 (1977)]

Influence of molecular environment

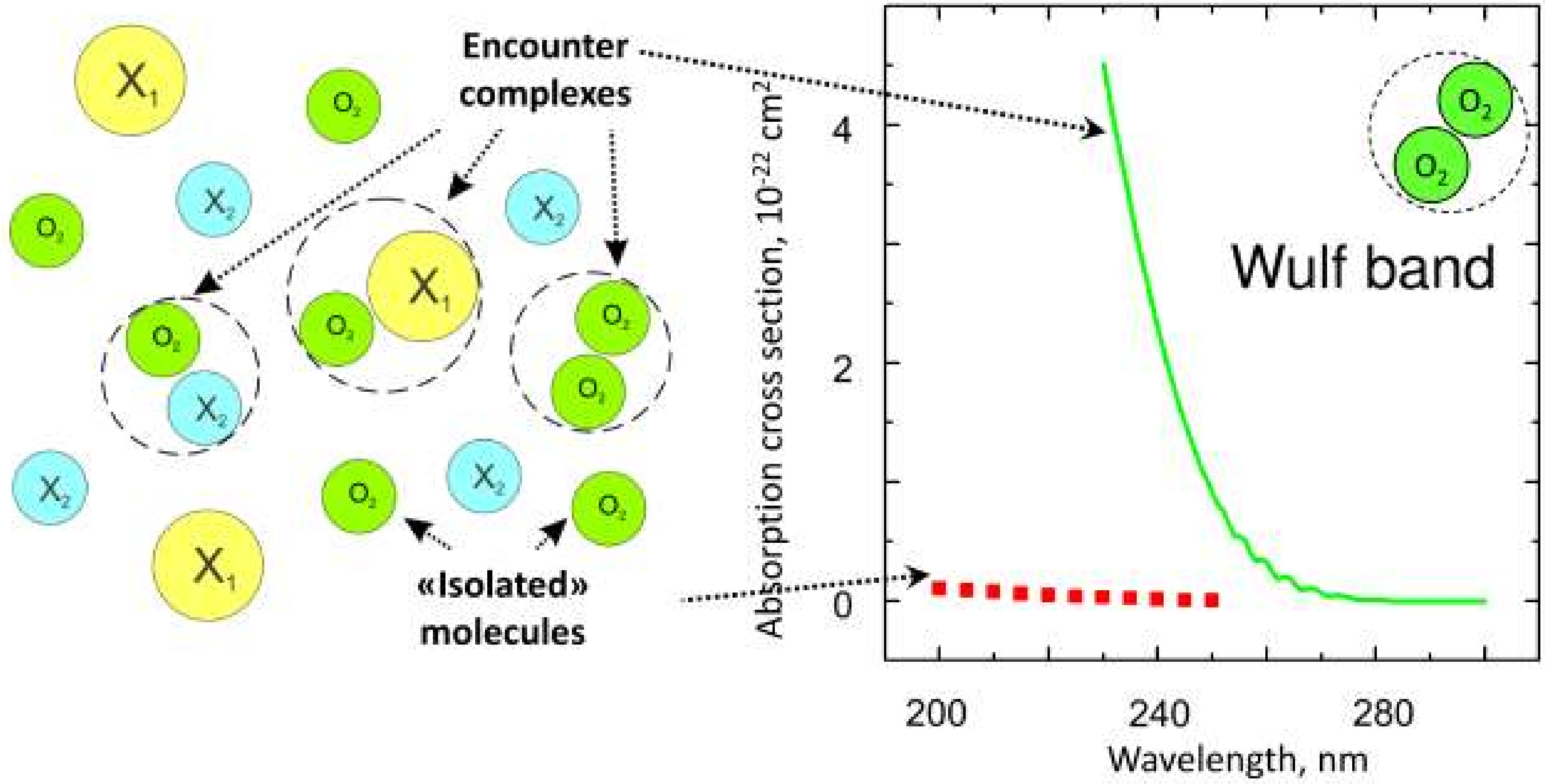


Encounter complexes

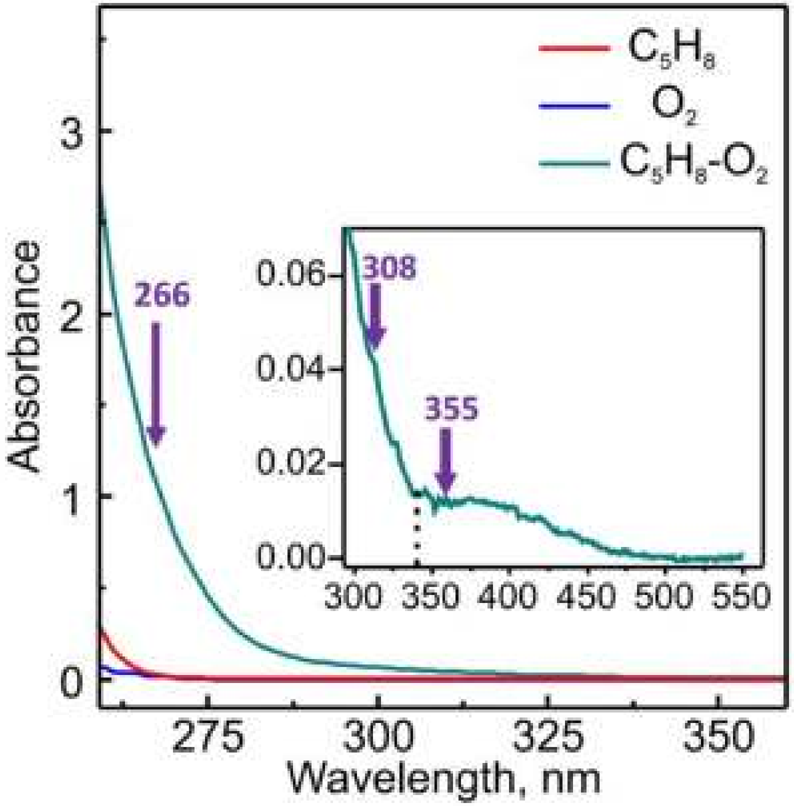
«Isolated» molecules

🟥 [Shardanand, JQSRT 18, 529 (1977)]

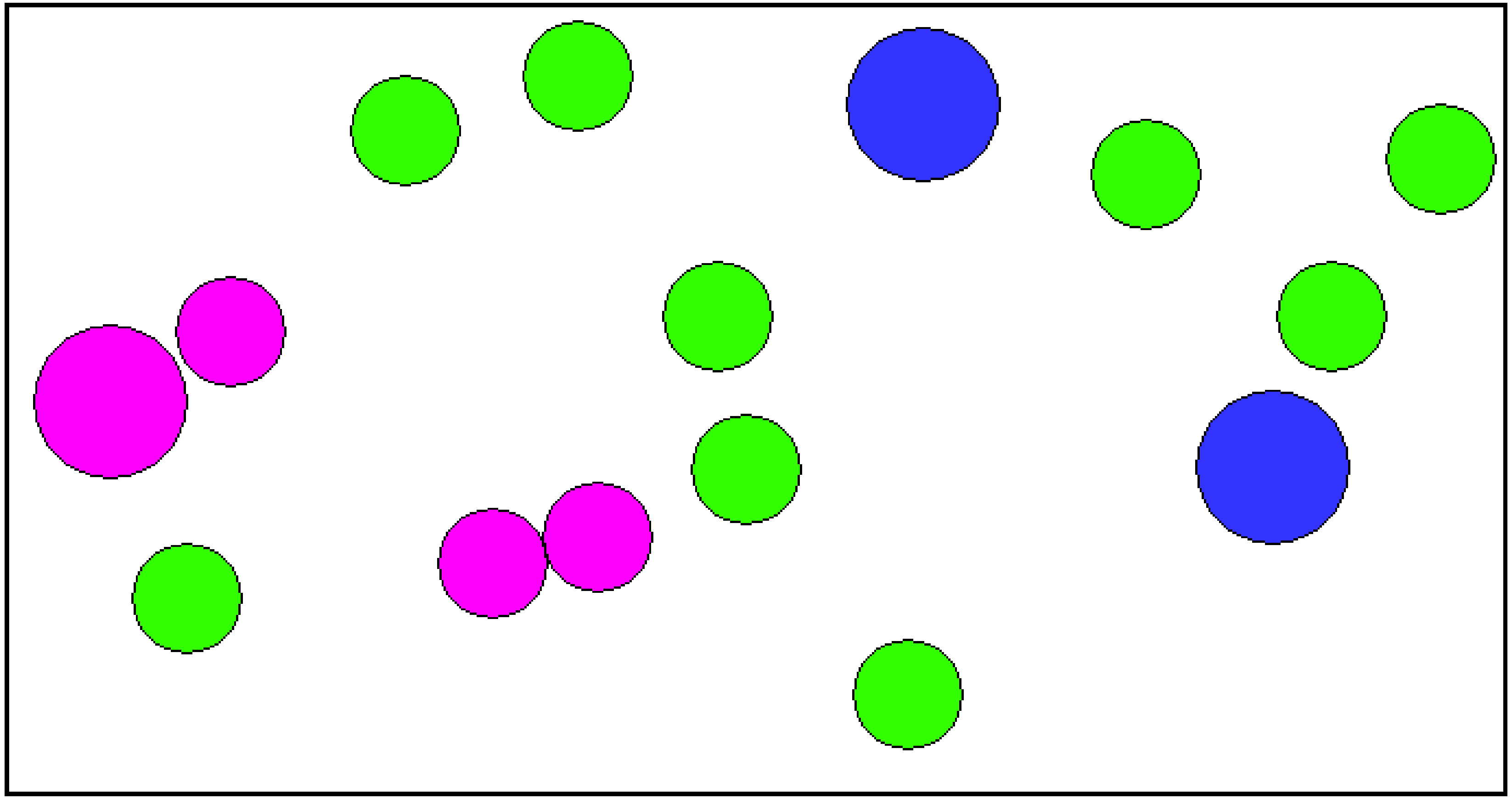
Influence of molecular environment



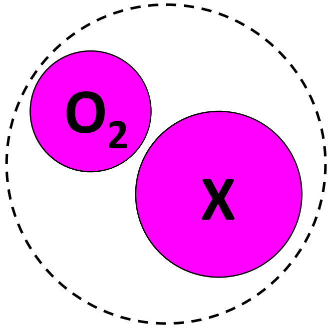
■ [Shardanand, JQSRT 18, 529 (1977)]

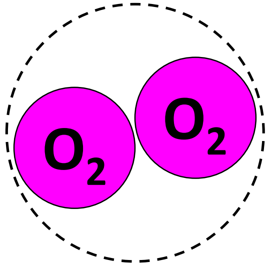


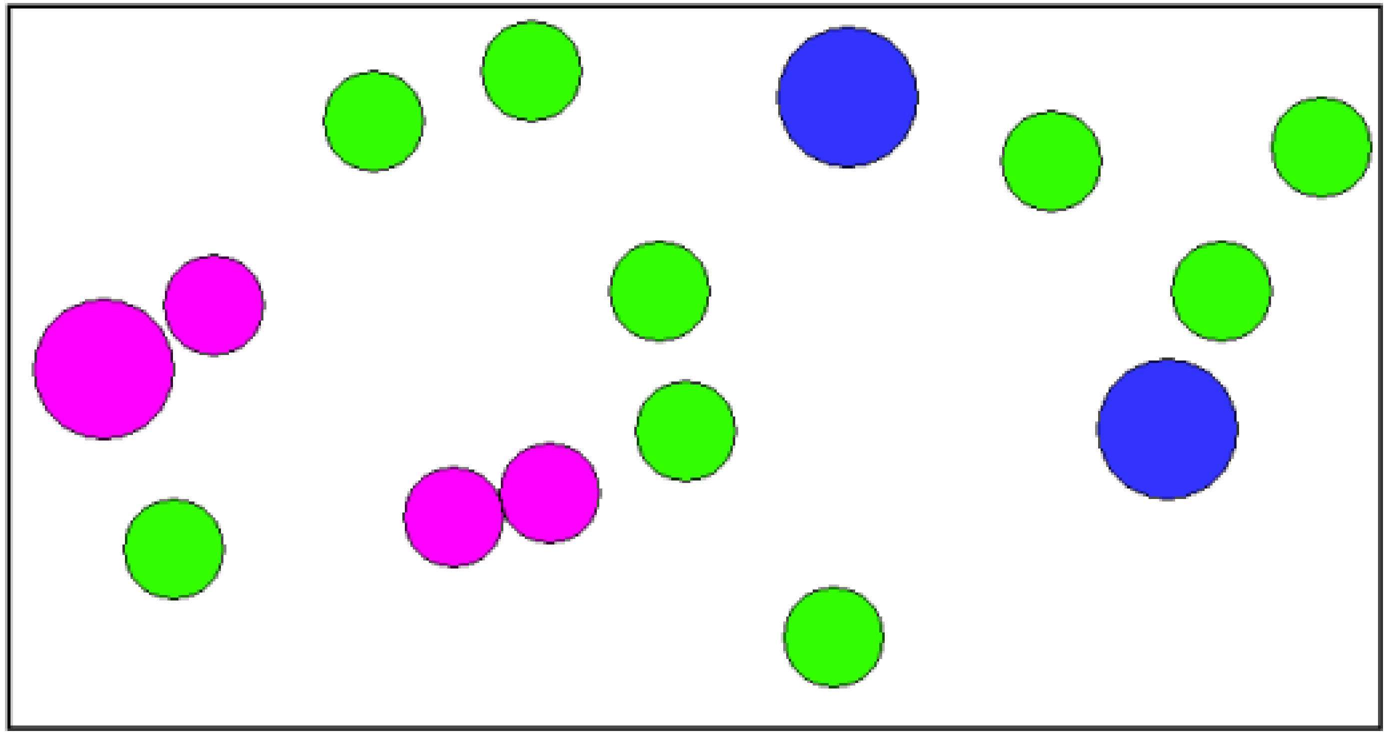
C_5H_8 (516 mbar)-O_2 (81 bar)

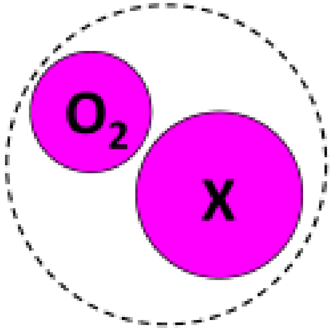


Encounter complexes







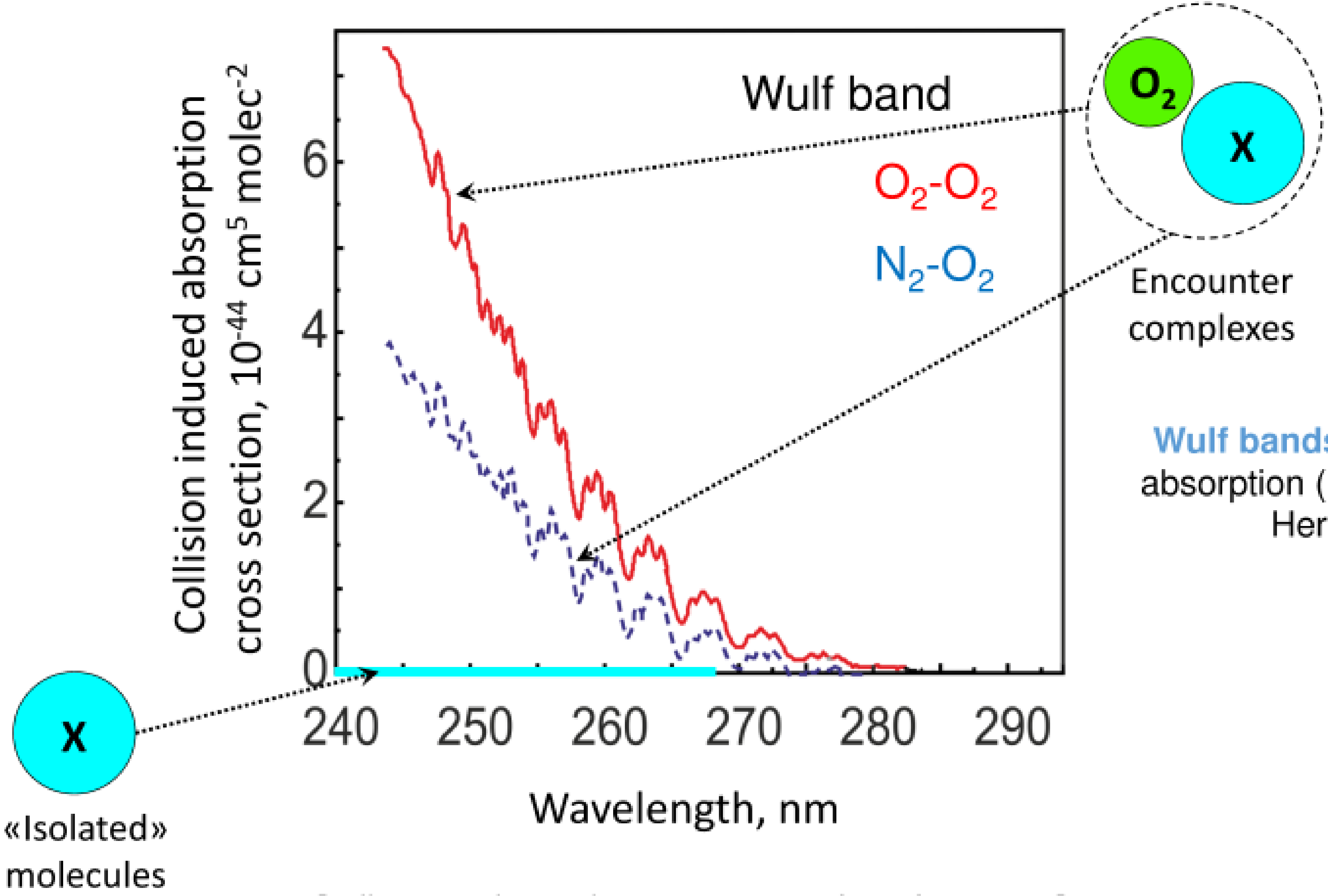


– short lifetime,
but stable concentration

In the atmosphere: $[O_2 - O_2] \sim \frac{1}{2000}[O_2]$

But: $\sigma_{O_2-O_2} \approx 10^3 \cdot \sigma_{O_2}$

Influence of molecular environment



Wulf bands - X-O_2 Collision-induced
absorption (CIA) with O_2 transition into
Herzberg III $O_2(A'_3\Delta_u)$

[Fally S. *et al.* J. Mol. Spectrosc. 204 (2000), 1, p. 10]

CIA provides a crucial influence on the O_2 photophysics and photochemistry

In gas phase

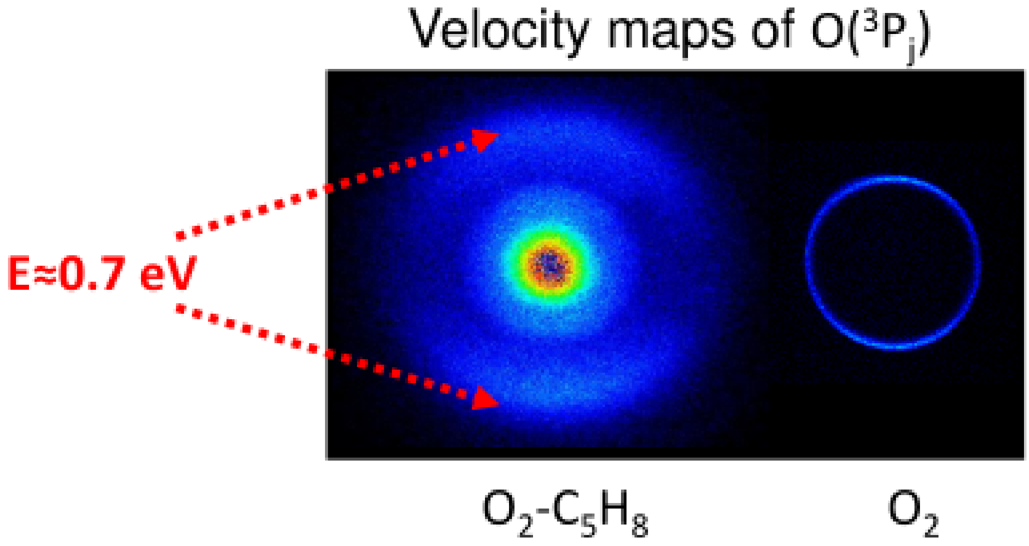
$$X\text{-}O_2 + h\nu\ (\text{UV-C}) \rightarrow O_2(^1\Delta_g) + \ldots$$

[Trushina A. P. *et al.* J. Phys. Chem. A 116 (2012), 6621-6629]

[Trushina A. P. *et al.* Chem. Phys. Lett. (485) 2010, 11–15]

[Pyryaeva A. P. *et al.* Chem. Phys. Lett. 2014, 610-611, 8-13]

In molecular beams



$$O_2(^1\Delta_g) + h\nu \rightarrow O(^3P_2) + O(^3P_2)$$

$$^3(^1X\text{-}^3O_2) + h\nu \rightarrow {}^3(^3X\text{-}^1O_2) \rightarrow$$

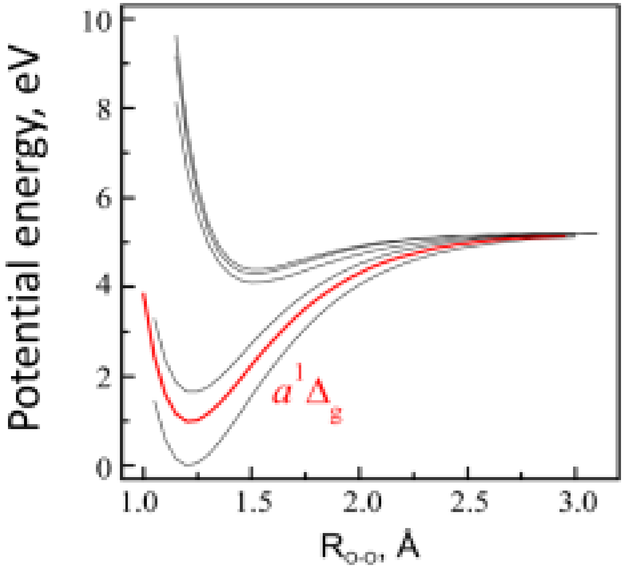
$$\rightarrow {}^3X + O_2(^1\Delta_g)$$

[Vidma K. V. *et al.* J. Chem. Phys. 137 (2012), 5, p.10]

In condensed phase

[Scurlock R. D., Ogilby P. R. J. Am. Chem. Soc. (110) 1988, 640-641]

Singlet oxygen $O_2(^1\Delta_g)$



Singlet oxygen $O_2(^1\Delta_g)$:

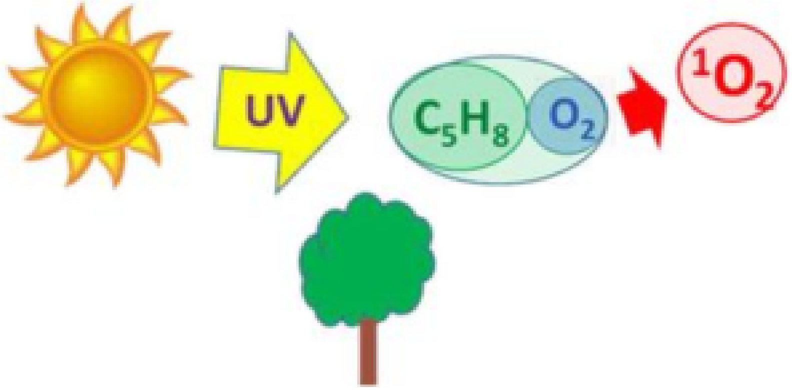
- participate in natural (photo)chemical processes and oxidative stress;
- one of the most prominent reactive oxygen species **causing damage to leaves**.

Isoprene:

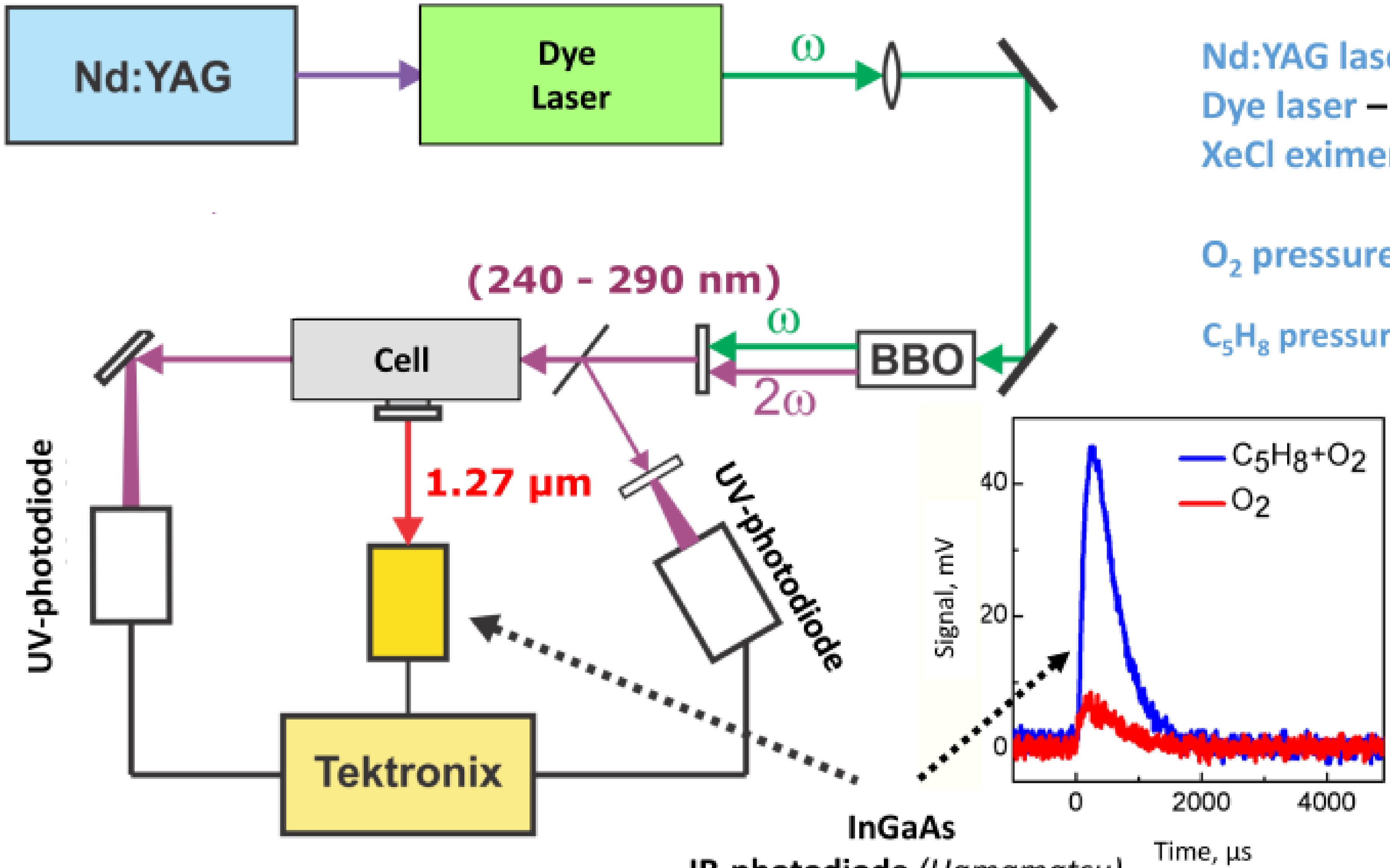
- **protective function** in plants against reactive oxygen species;
- **scavenger** of singlet oxygen.

But!

$$C_5H_8\text{-}O_2 + h\nu\ (\text{UV-A,B,C}) \rightarrow O_2(^1\Delta_g) + \ldots$$



Experimental Setup



InGaAs

IR-photodiode *(Hamamatsu)*

(+ monochromator *(Solar Laser Systems) – luminescence spectra)*

Nd:YAG laser – 266 nm, 355 nm

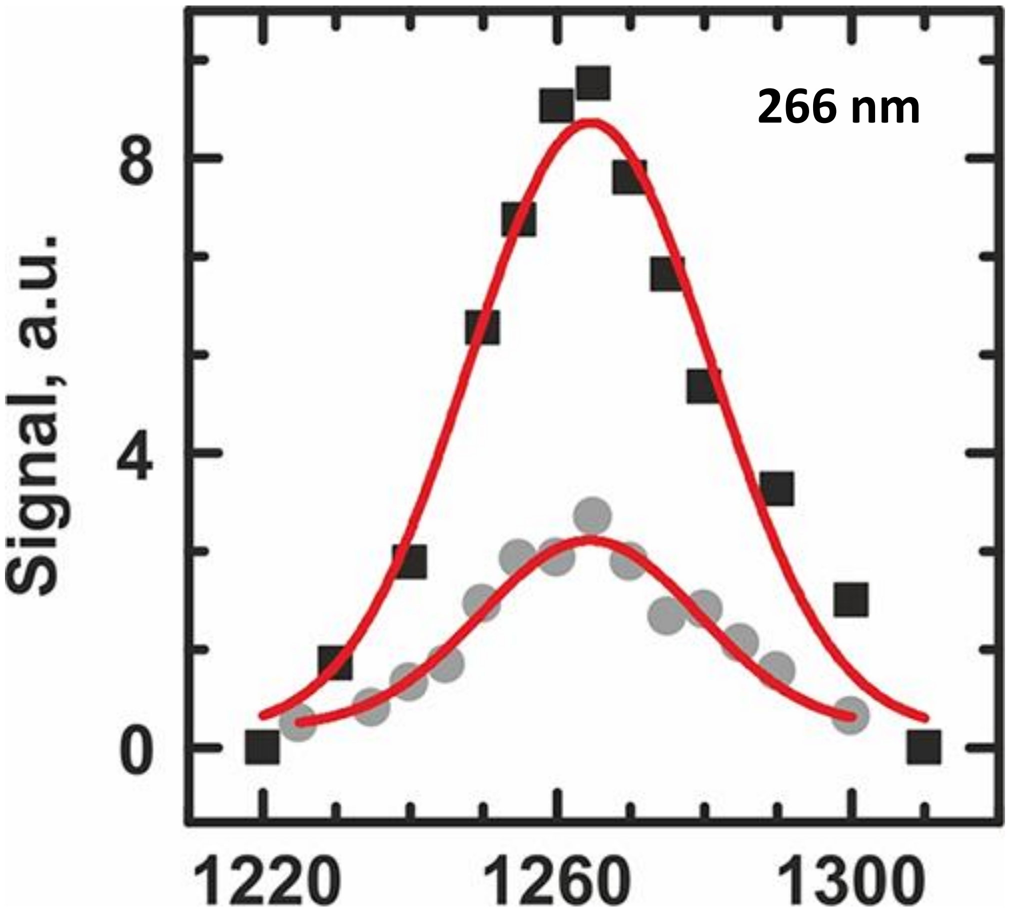
Dye laser – 253 – 278 nm

XeCl eximer laser – 308 nm

O_2 pressure: 3 to 150 bar

C_5H_8 pressure: 70 to 516 mbar

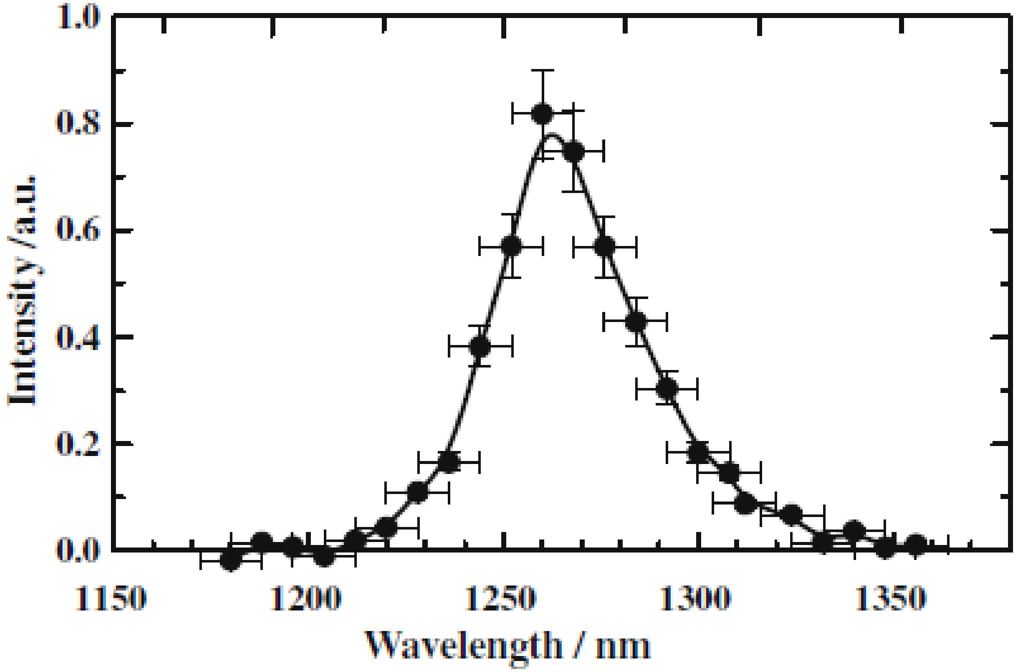
NIR-luminescence spectra



$P(O_2)$=83 bar; $P(C_5H_8)$=147 mbar

$P(O_2)$=83 bar

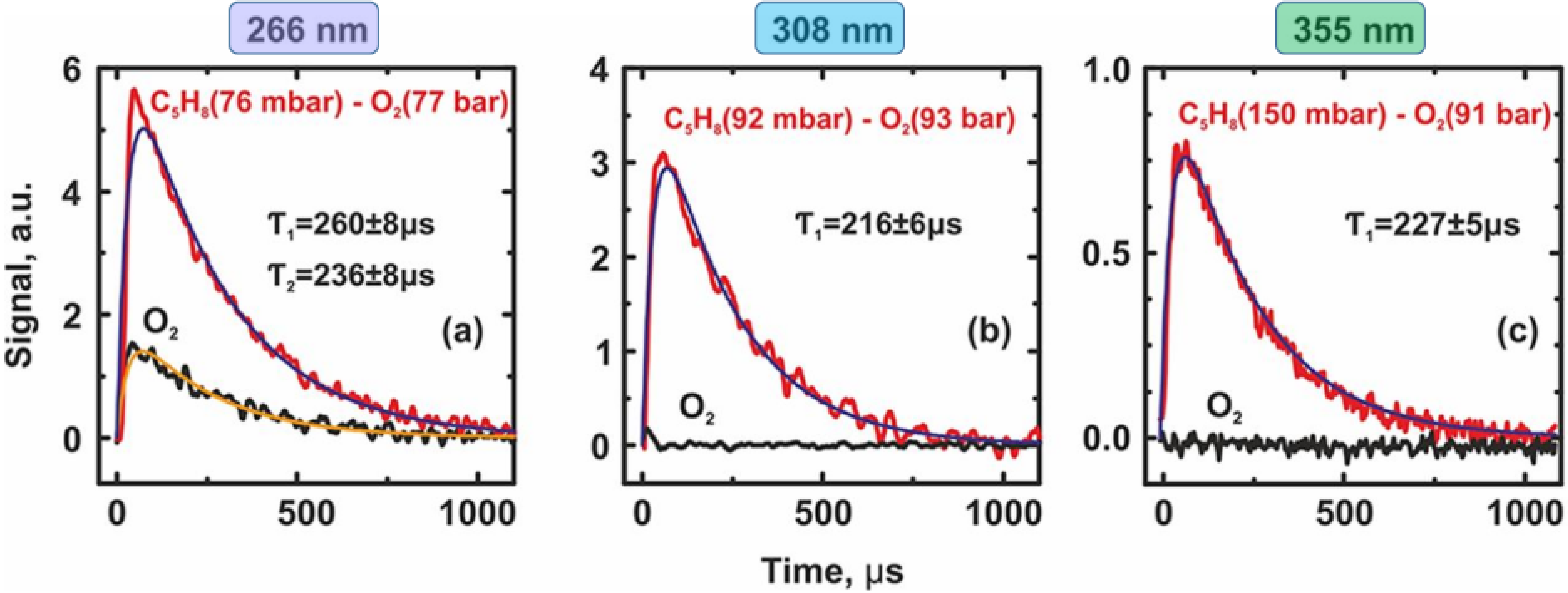
$^1O_2$ luminescence spectrum



[Furui E. *et al.* Chem. Phys. Lett. 471 (2009), p.45]

$P(O_2)$=130 bar

NIR luminescence time profiles



Do not depend on the number of laser pulses

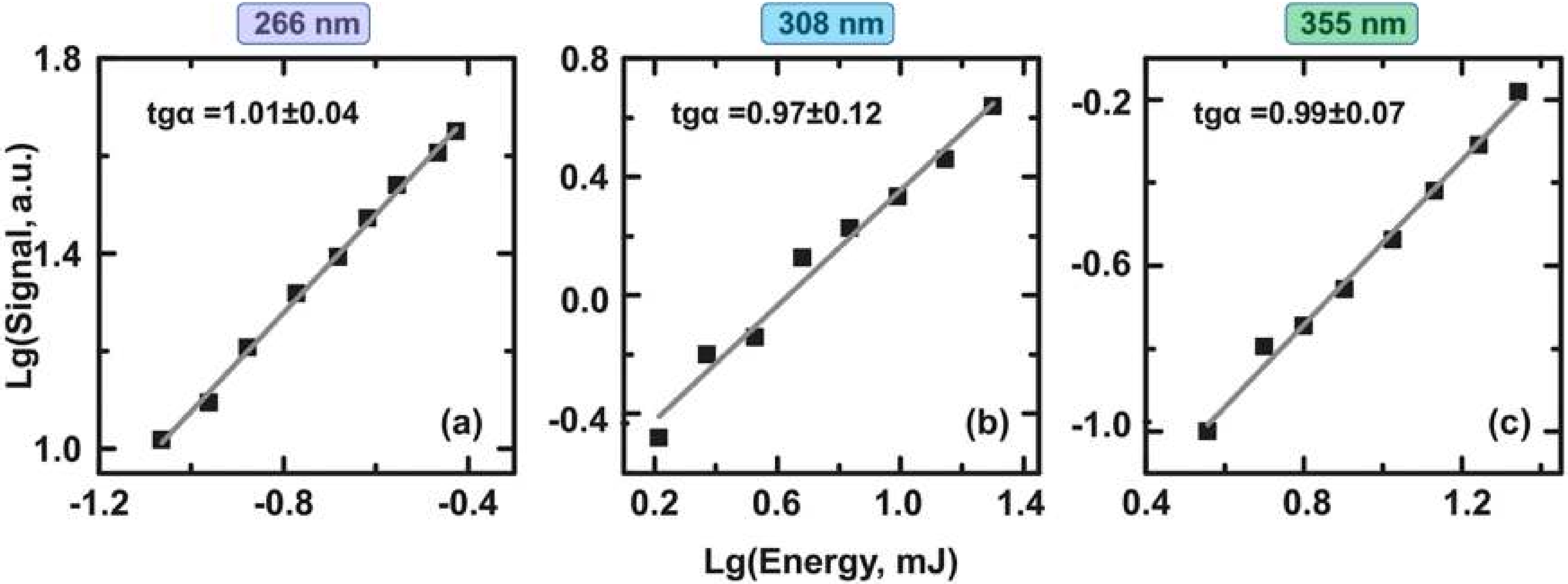
Decay time is governed by the rates of $^1O_2$:

O_2 quenching and **C_5H_8 quenching and C_5H_8 reaction**

$(1.93 \pm 0.02) \times 10^{-18}$ cm^3·molecule^{-1}·s^{-1}

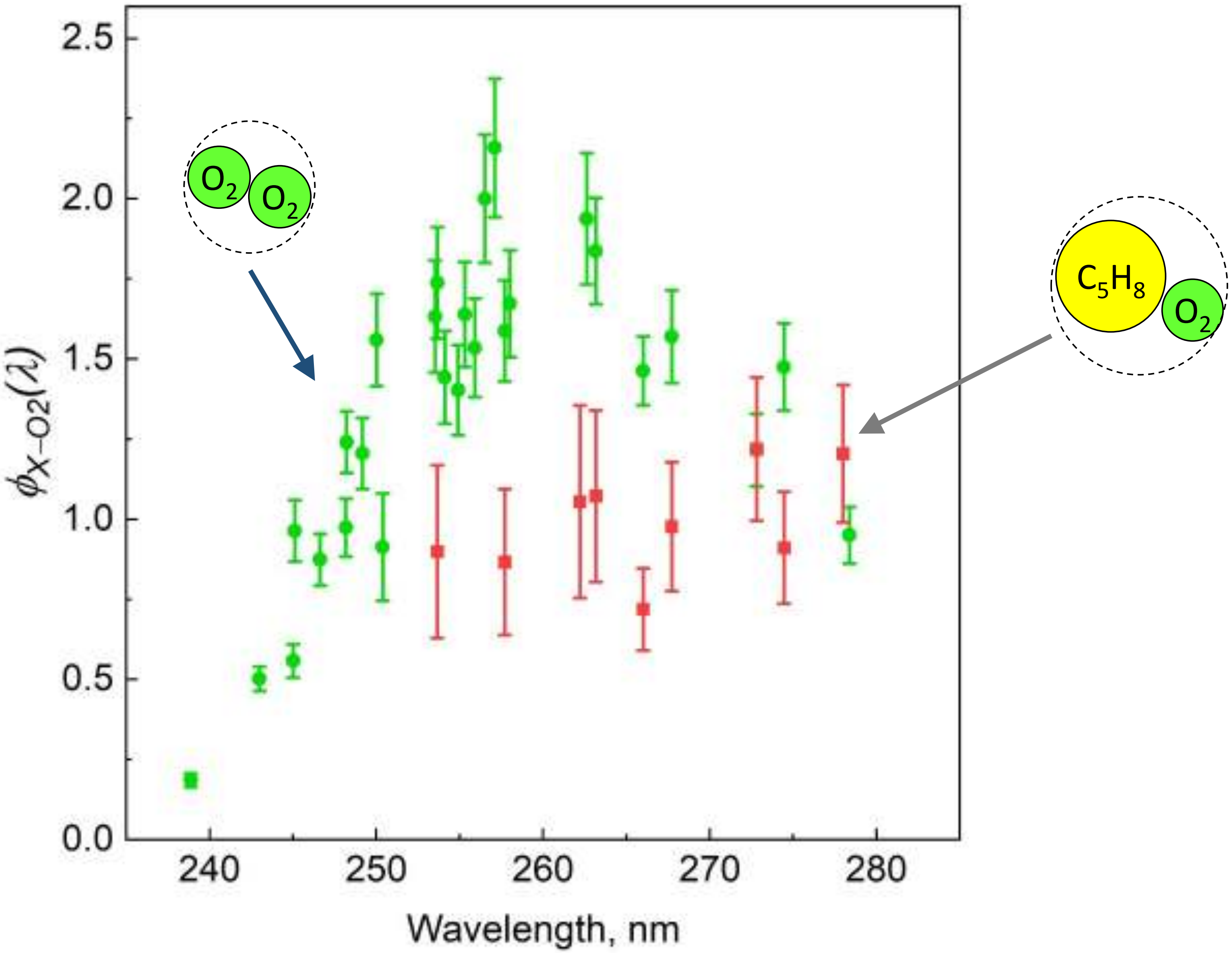
$(2 \pm 1) \times 10^{-16}$ cm^3·molecule^{-1}·s^{-1}

$^1O_2$ luminescence signal via laser pulse energy

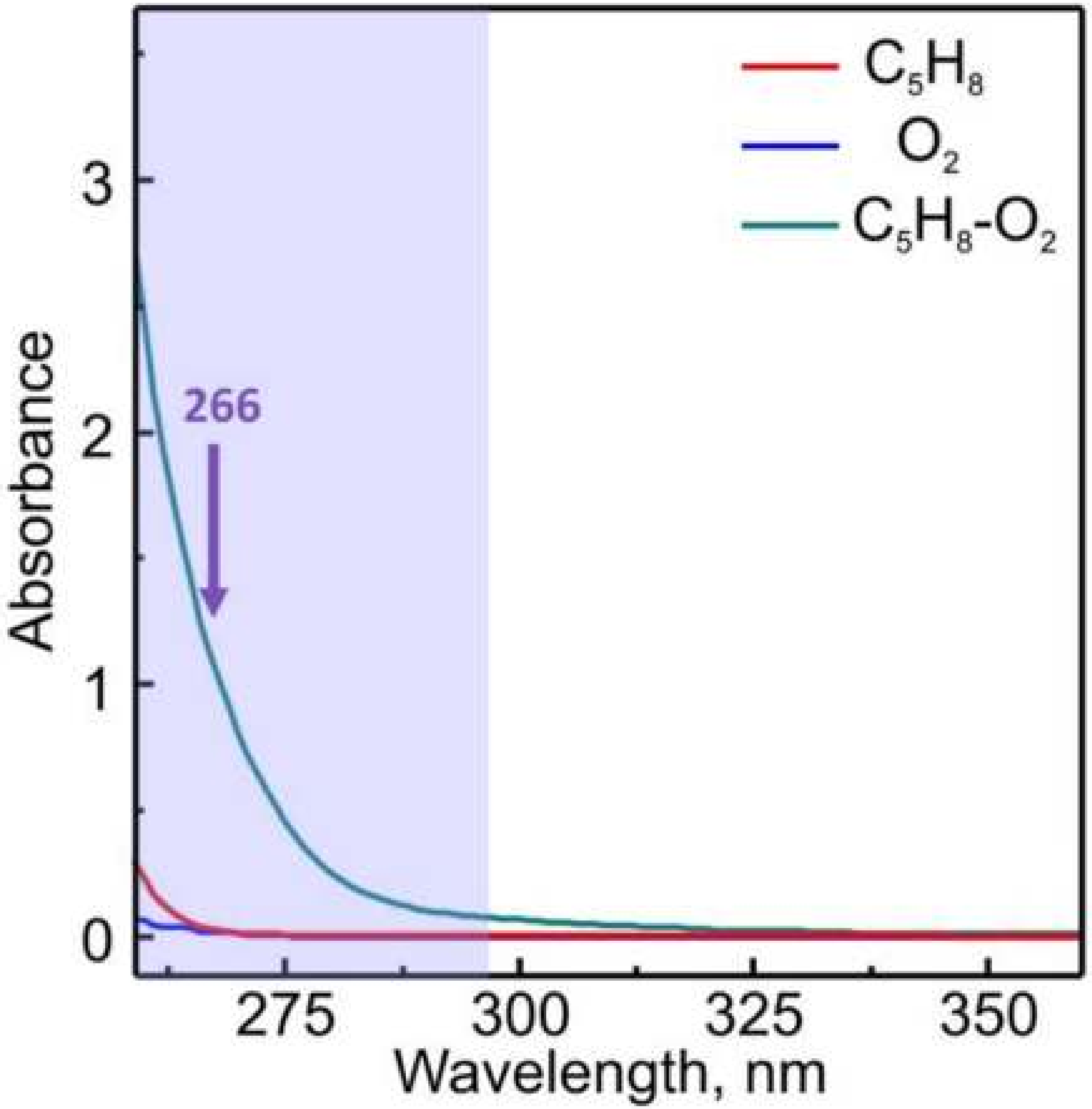


One-photon process

Quantum yield of $O_2(^1\Delta_g)$ generation via encounter complexes

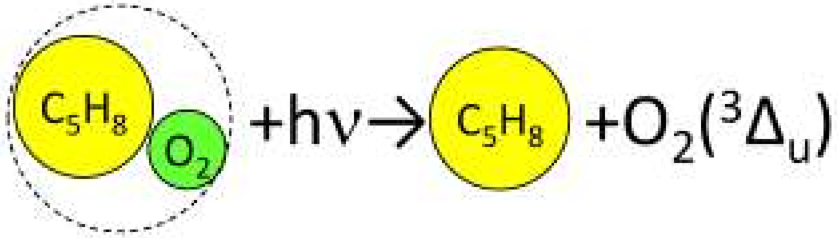


$O_2(^1\Delta_g)$ formation mechanism



$\lambda<290$ nm – collisional induced absorption (the Wulf band)

$^1O_2$ formation via Hezberg III state $O_2(^3\Delta_u)$ (for X-O_2, where X is O_2, N_2, C_5H_8, …)

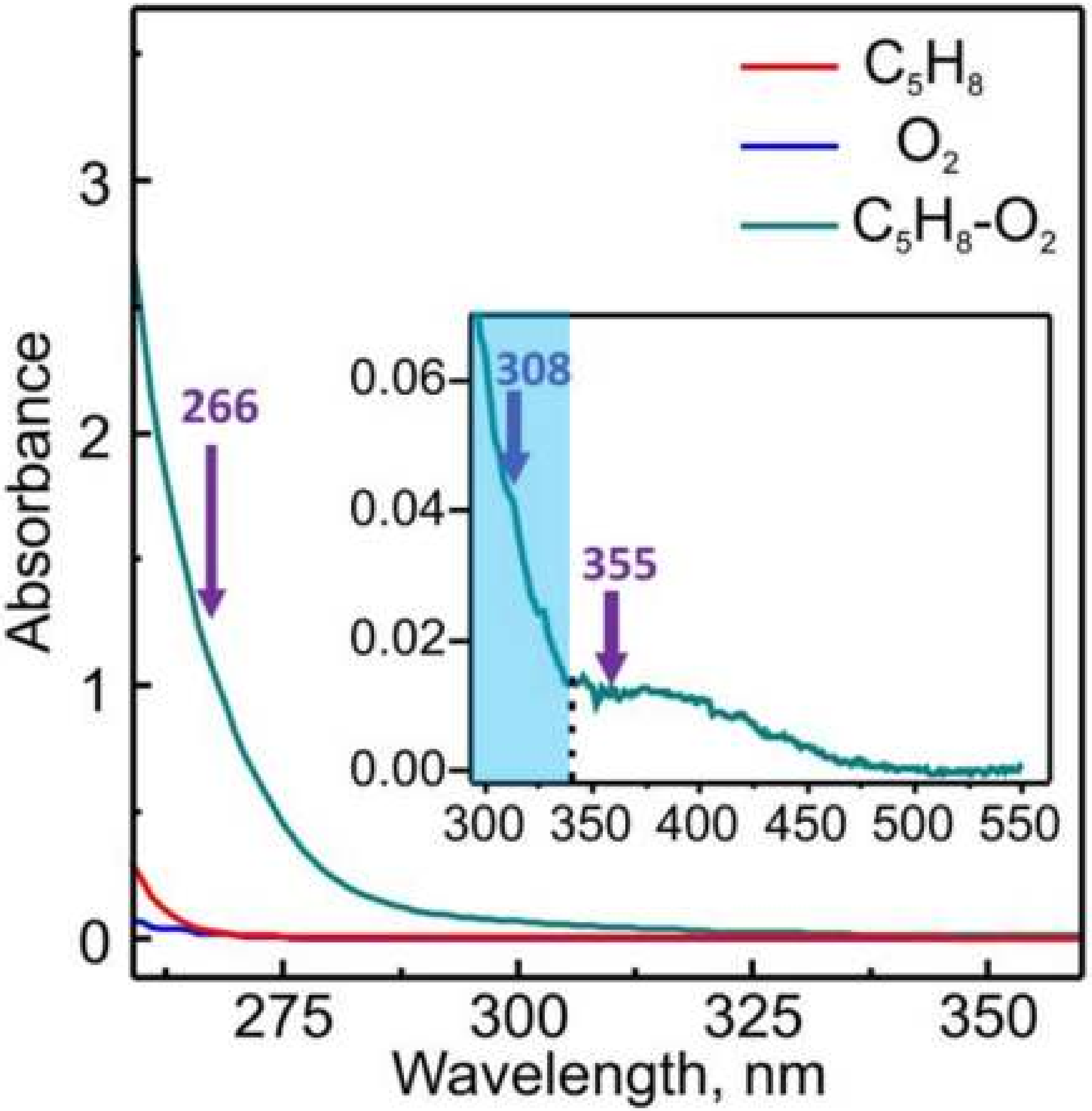


$$C_5H_8\,O_2 + h\nu \rightarrow C_5H_8 + O_2(^3\Delta_u)$$

$$O_2(^3\Delta_u) + O_2(^3\Sigma_g^-) \rightarrow \mathbf{O_2(^1\Delta_g) + O_2(^1\Delta_g, {}^1\Sigma_g^+)}$$

The enhancement in $^1C_5H_8$ $^3O_2$ comparing $^3O_2$ is 10^6 times higher!

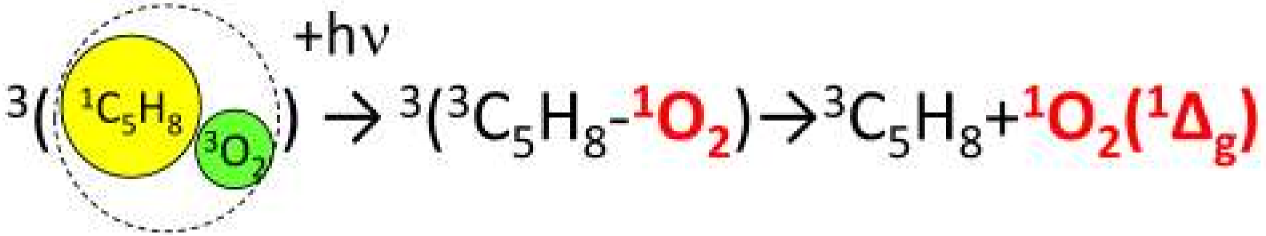
$O_2(^1\Delta_g)$ formation mechanism



290 nm < λ < 340 nm – DSF Band

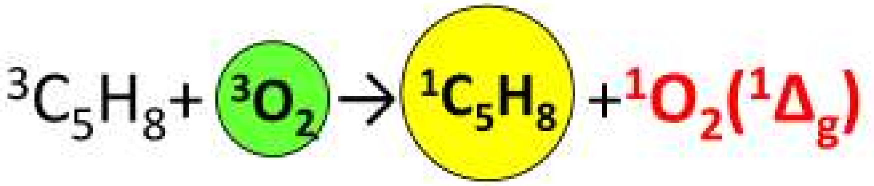
(Cooperative Double spin flip transition)

$^1O_2$ formation only in C_5H_8-O_2 mixture



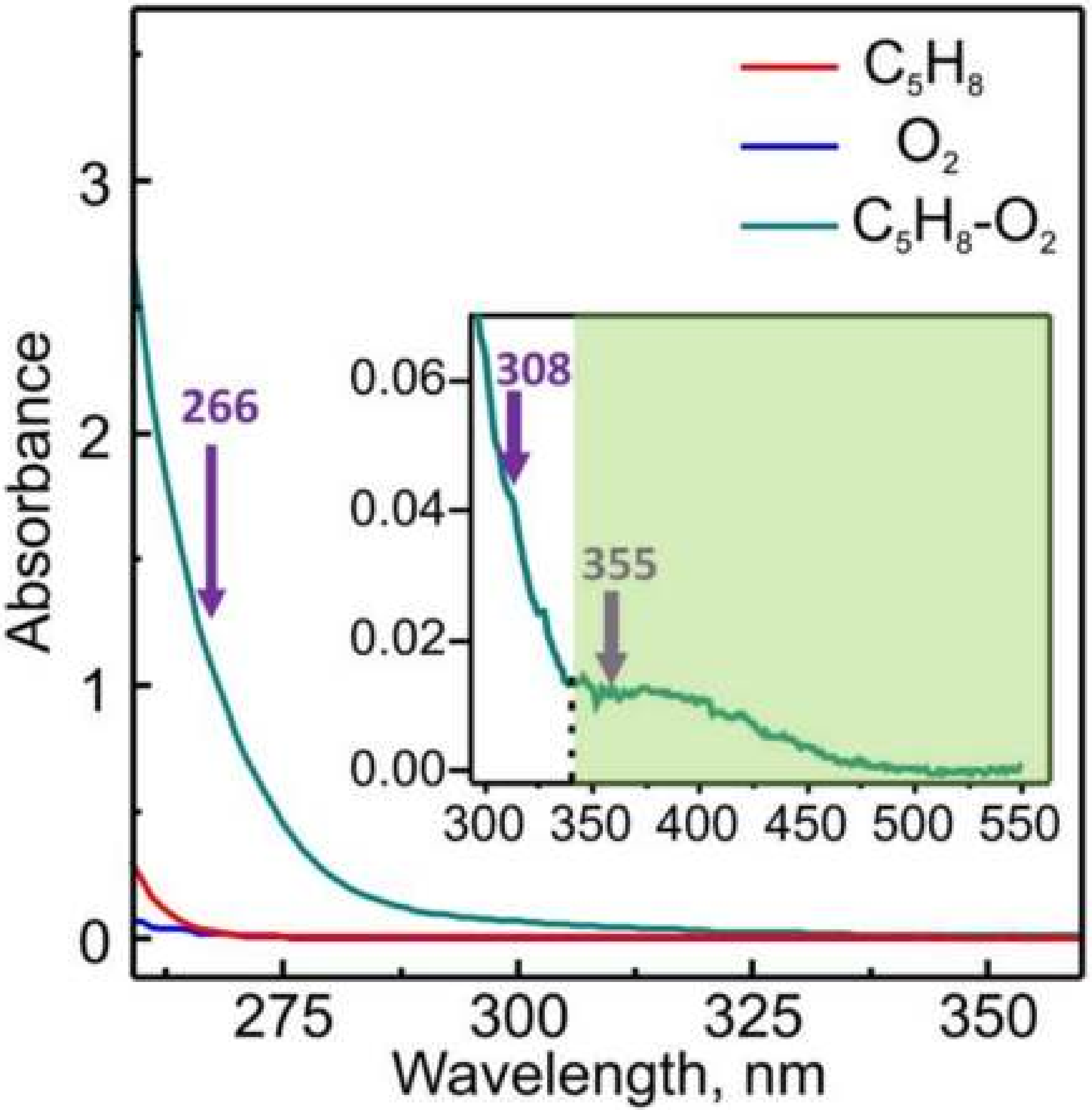
$$^3({}^1C_5H_8\ {}^3O_2) \xrightarrow{+h\nu} {}^3({}^3C_5H_8\text{-}{}^1\mathbf{O_2}) \rightarrow {}^3C_5H_8 + {}^1\mathbf{O_2(^1\Delta_g)}$$

As $\Delta E_{T\text{-}S}(C_5H_8) \approx 2.6$ eV and $\Delta E(^1O_2) = 0.977$ eV



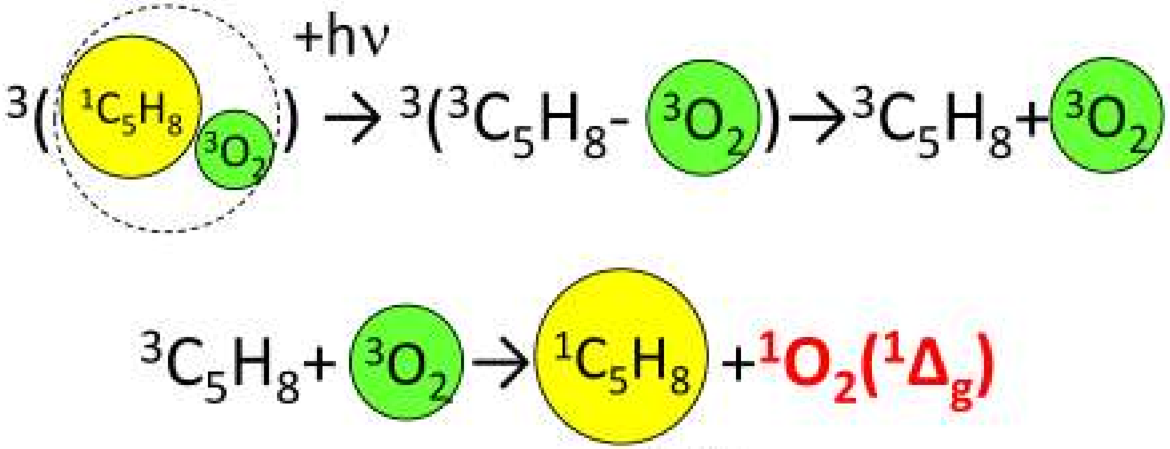
$$^3C_5H_8 + {}^3\mathbf{O_2} \rightarrow {}^1\mathbf{C_5H_8} + {}^1\mathbf{O_2(^1\Delta_g)}$$

$O_2(^1\Delta_g)$ formation mechanism



$\lambda > 340$ nm – Enhanced T←S Absorption Band

$^1O_2$ formation only in C_5H_8-O_2 mixture



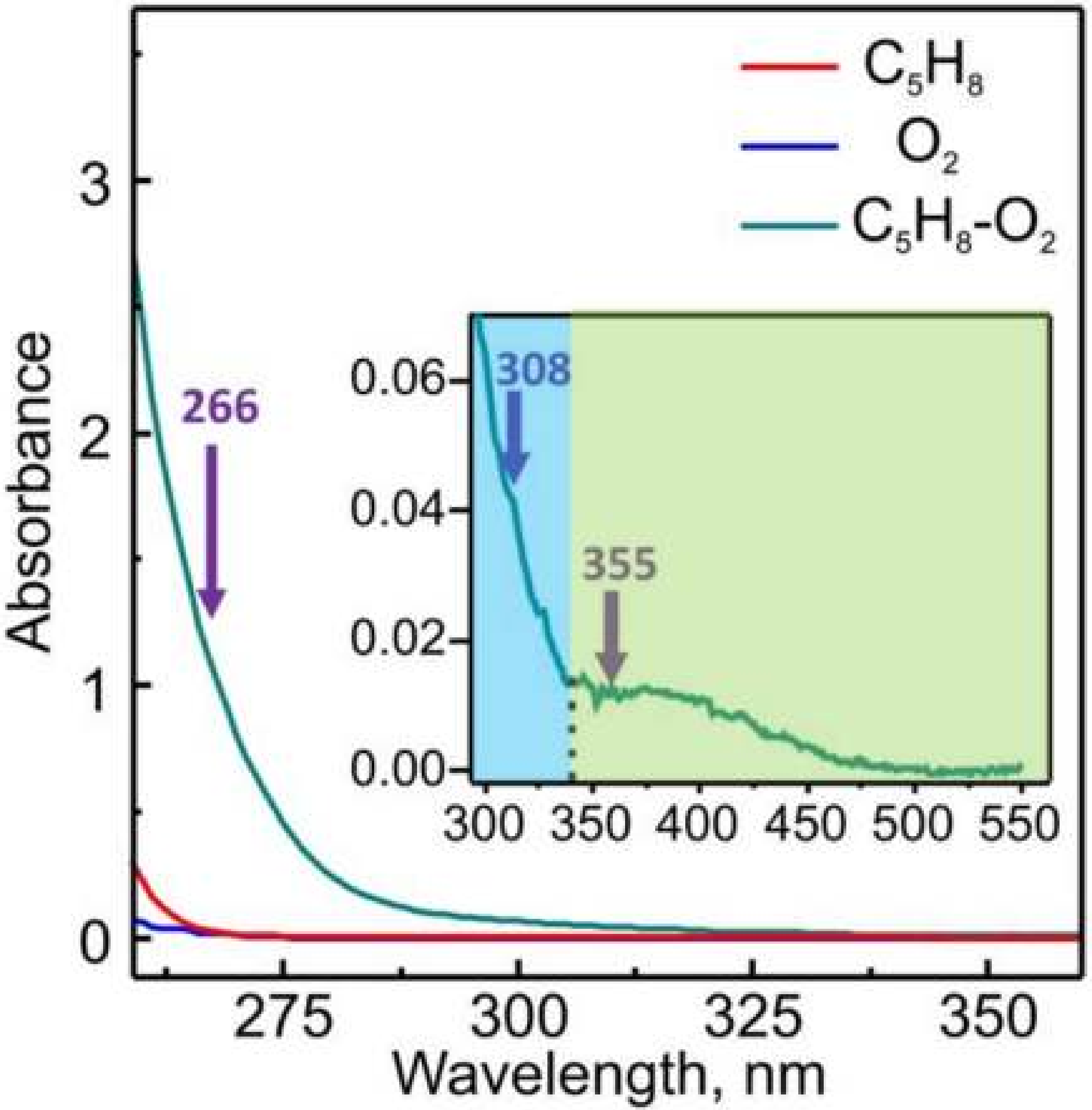
$$^3(^1C_5H_8\,^3O_2) \xrightarrow{+h\nu} {}^3(^3C_5H_8\text{-}\,^3O_2) \rightarrow {}^3C_5H_8 + {}^3O_2$$

$$^3C_5H_8 + {}^3O_2 \rightarrow {}^1C_5H_8 + {}^1O_2(^1\Delta_g)$$

The enhancement in $^1C_5H_8\,^3O_2$ comparing $^1C_5H_8$

is 10^4 times higher!

Is there a competition with troposheric processes?



Solar radiation in troposphere λ > 290 nm

$^1O_2$ formation via:

290 nm < λ < 340 nm – DSF Band
(Cooperative Double spin flip transition)

λ > 340 nm – Enhanced T←S Absorption Band

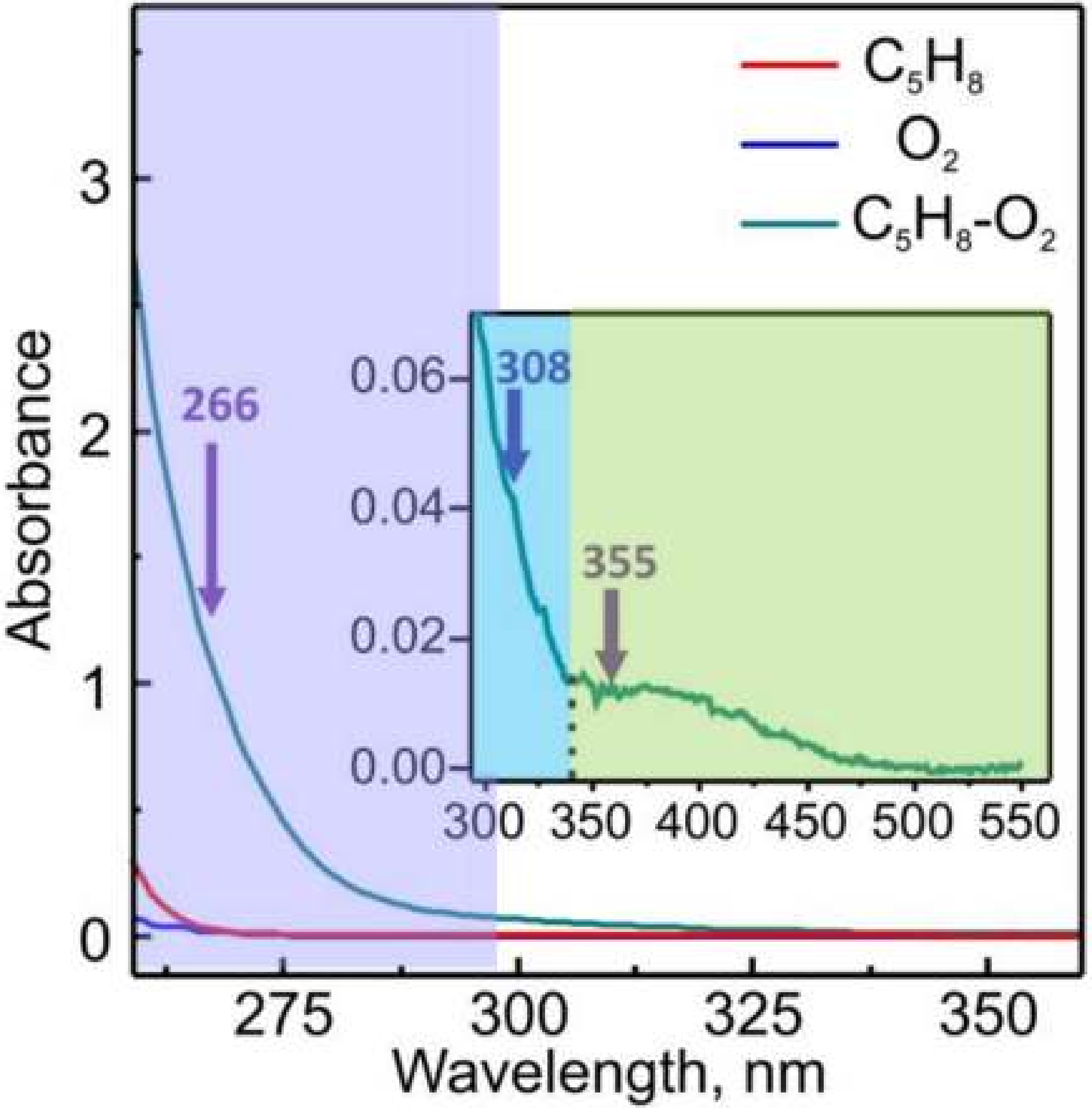
C_5H_8-O_2 complexes can provide a contribution to the $^1O_2$ production at a level of about 10^{-5} relative to the sum of other known sources in the troposphere

$^3C_5H_8 + O_2 \rightarrow$ reaction τ ≈ 1 year

$C_5H_8 \xrightarrow[+O_3]{+OH^\bullet}$ **Ozone** **Aerosols** τ ≈ 2 hours – 2 days

C_5H_8-O_2 photoexcitation may shorten the C_5H_8 lifetime in the troposphere by no more than 0.02%

Summary



$^1O_2$ formation after C5H8-O2 photoexcitation passes via:

Wulf band

DSF Band

Enhanced T←S Absorption Band

X-O_2 general case

Depending on the X lower triplet energy DSF process may exist in visible region

$$^3(^1X\text{-}^3O_2) \xrightarrow{+h\nu} {}^3(^3X\text{-}^1O_2) \rightarrow {}^3X + {}^1O_2(^1\Delta_g)$$

Molecular
photodynamics group

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The Russian Foundation for
Basic Research Grants №16-13-10024

Tank you for your attention!