Velocity map imaging at icy surfaces

An oxygen story

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Motivation: Why oxygen?

a) the extensive knowledge of its gas-phase photochemistry achieved in Nijmegen

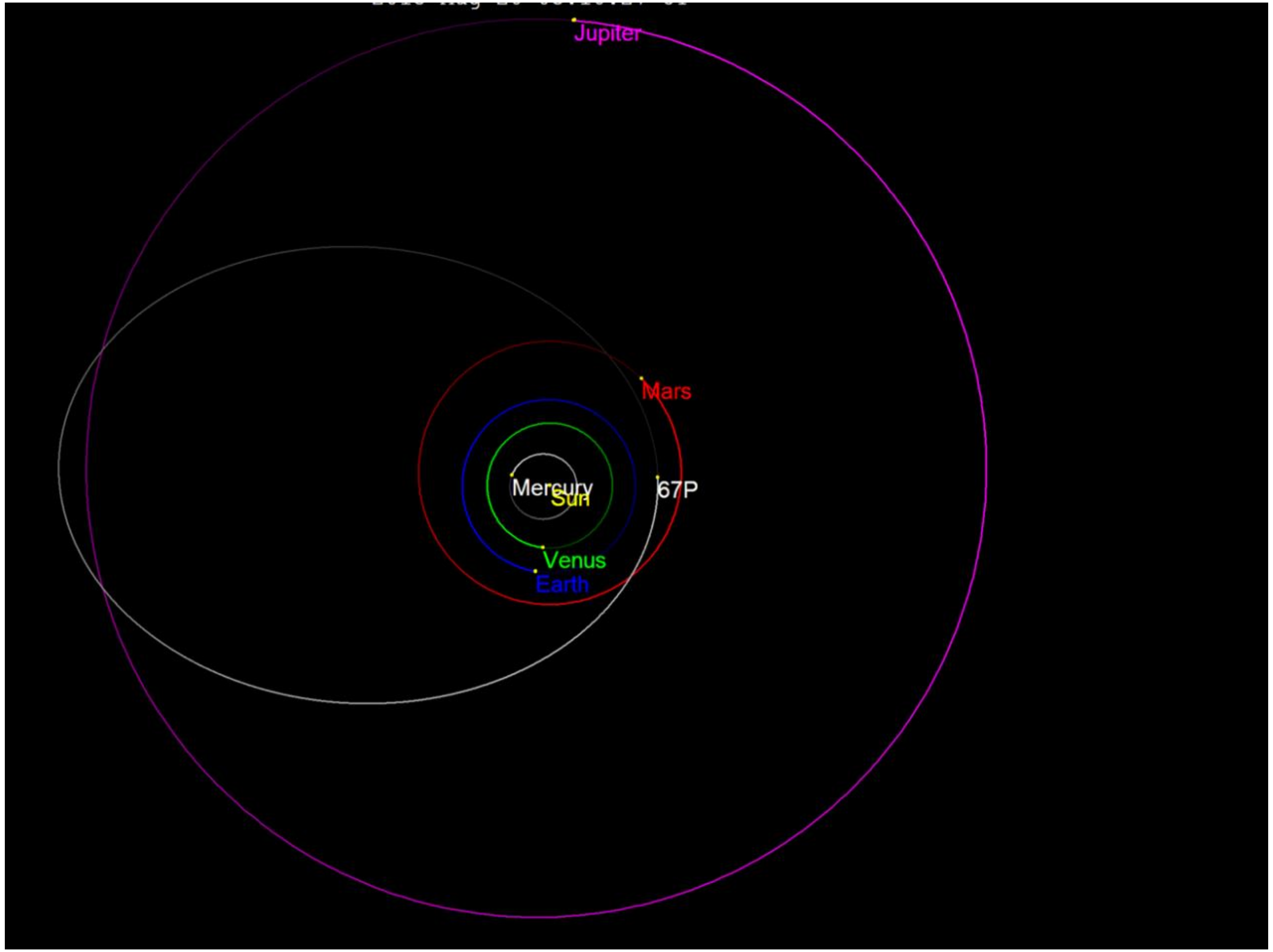
b) Rich photochemistry possible in an all O-atom system

c) The discovery of significant amounts of O_2-ice in two recent direct studies of comets:

67P/Churyumov–Gerasimenko and 1P/Halley

Both of these comets are well known of containing primordial ice, the H_2O and O_2 is fixed

Motivation: *67P/Churyumov–Gerasimenko*



Jupiter-family comet
Originally Kuiper belt

Rosetta finds oxygen on comet 67P in 'most surprising discovery to date'

Oxygen revealed to be fourth most abundant gas in the comet's atmosphere, contradicting long-held theories of comet formation

680 | NATURE | VOL 526 | 29 OCTOBER 2015

LETTER

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Abundant molecular oxygen in the coma of comet 67P/Churyumov–Gerasimenko

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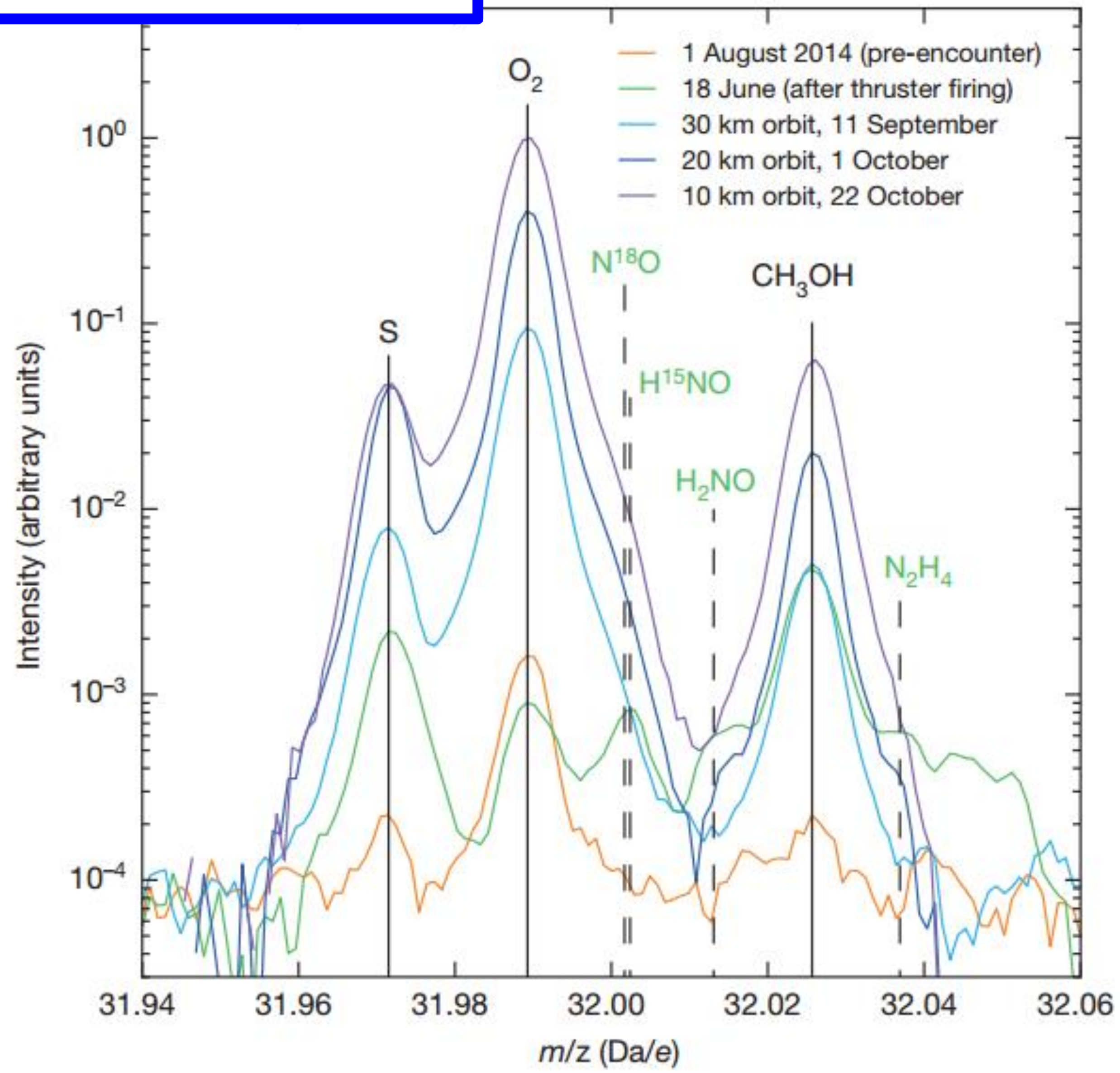


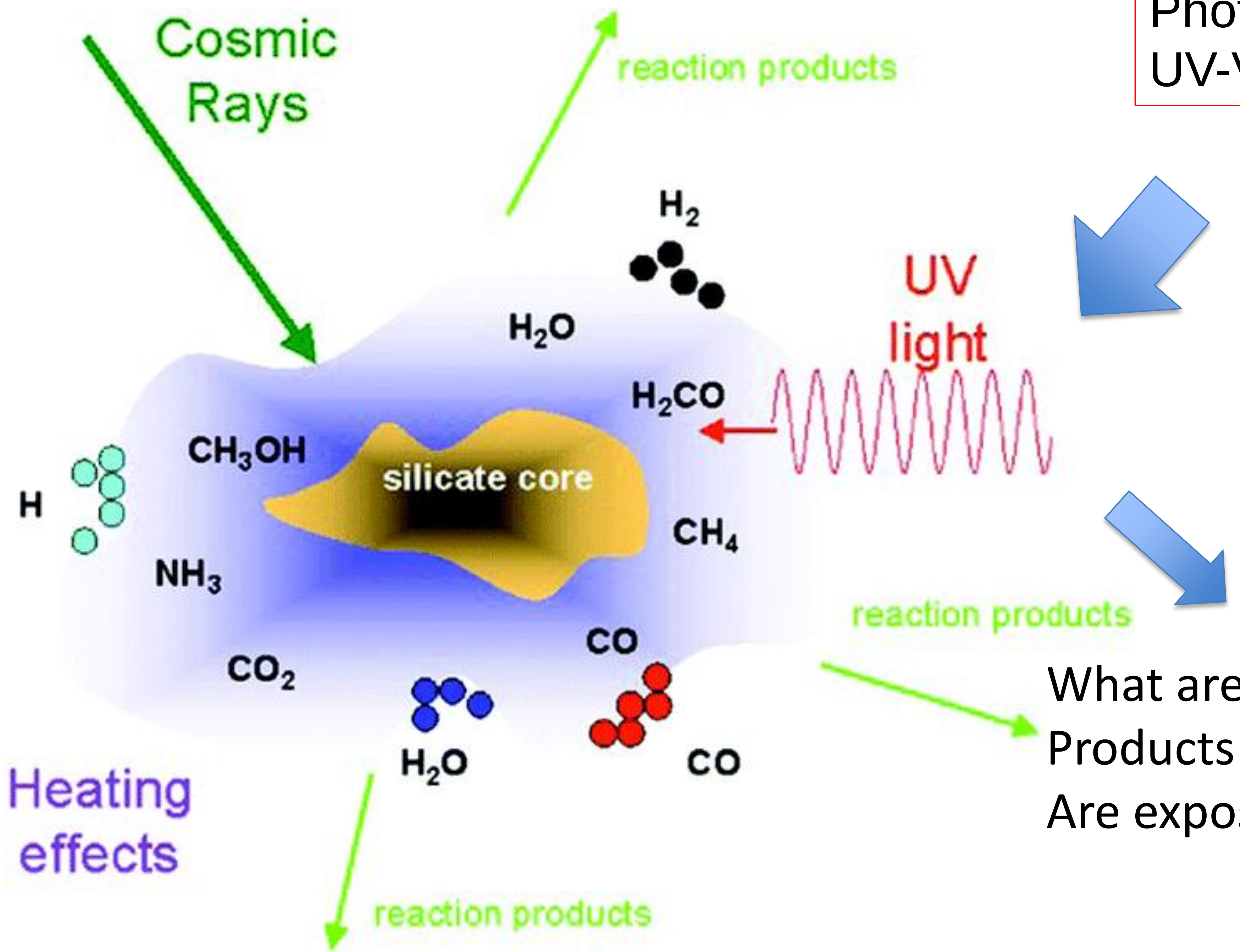
Mass spectrometer data

67P/Churyumov–Gerasimenko observed by Rosetta

O_2 is relevant in the ISM!

Photodesorption from ice-covered grains

T = 10-100K
too much gas!

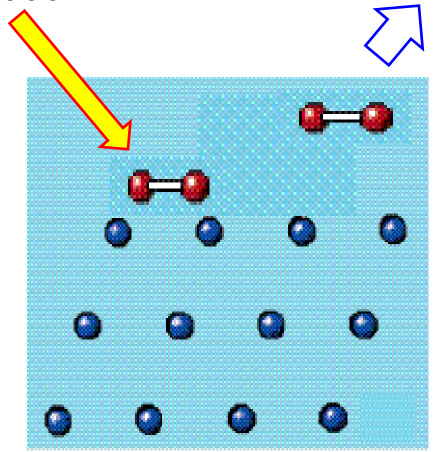


Photodesorption by UV-VUV light

What are the reaction
Products when cold ice surfaces
Are exposed to UV/VUV light

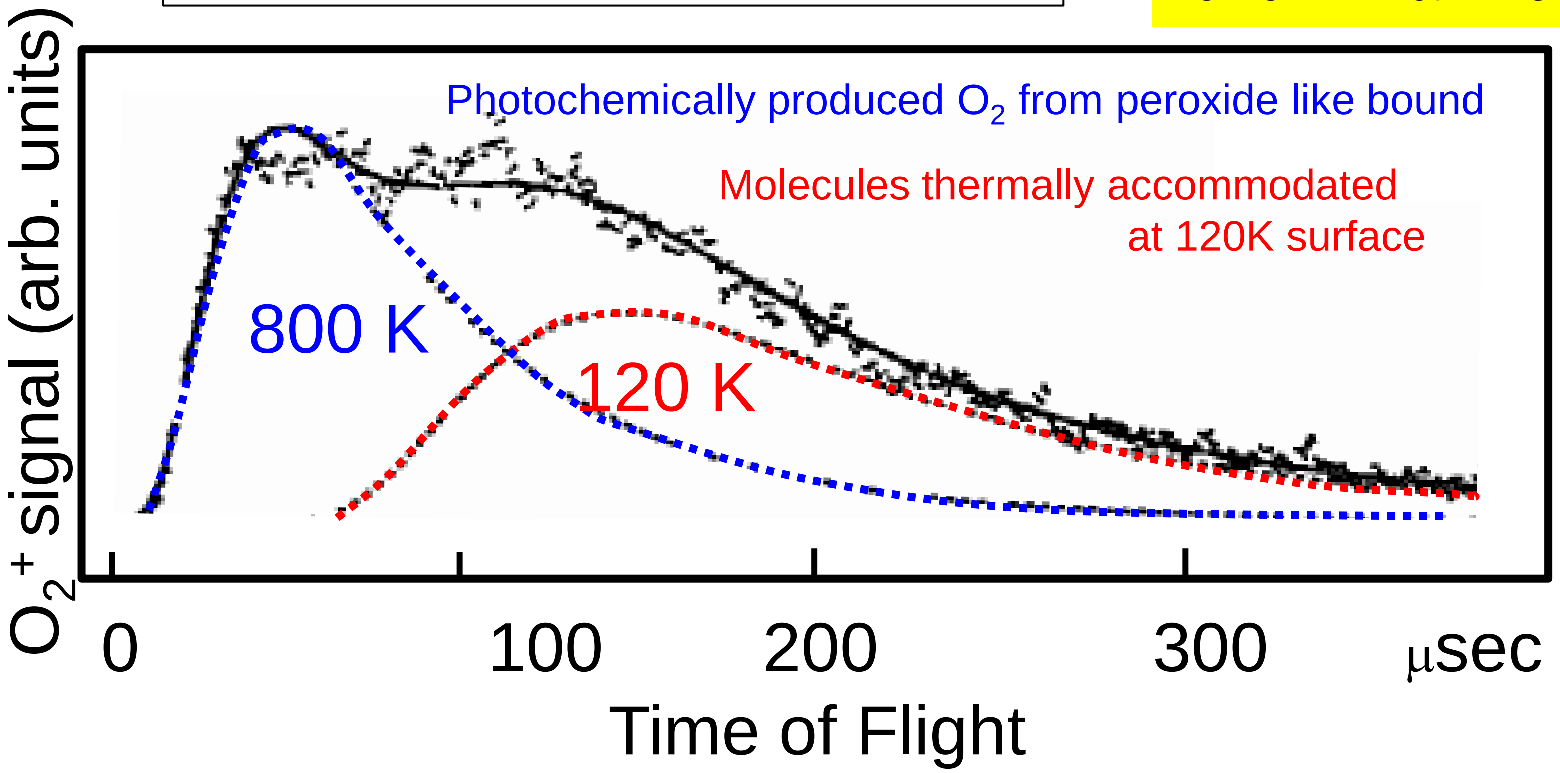
Previous work: Time-of-Flight Mass spectroscopy work

Desorption of O_2 from a Pt crystal at 320 nm



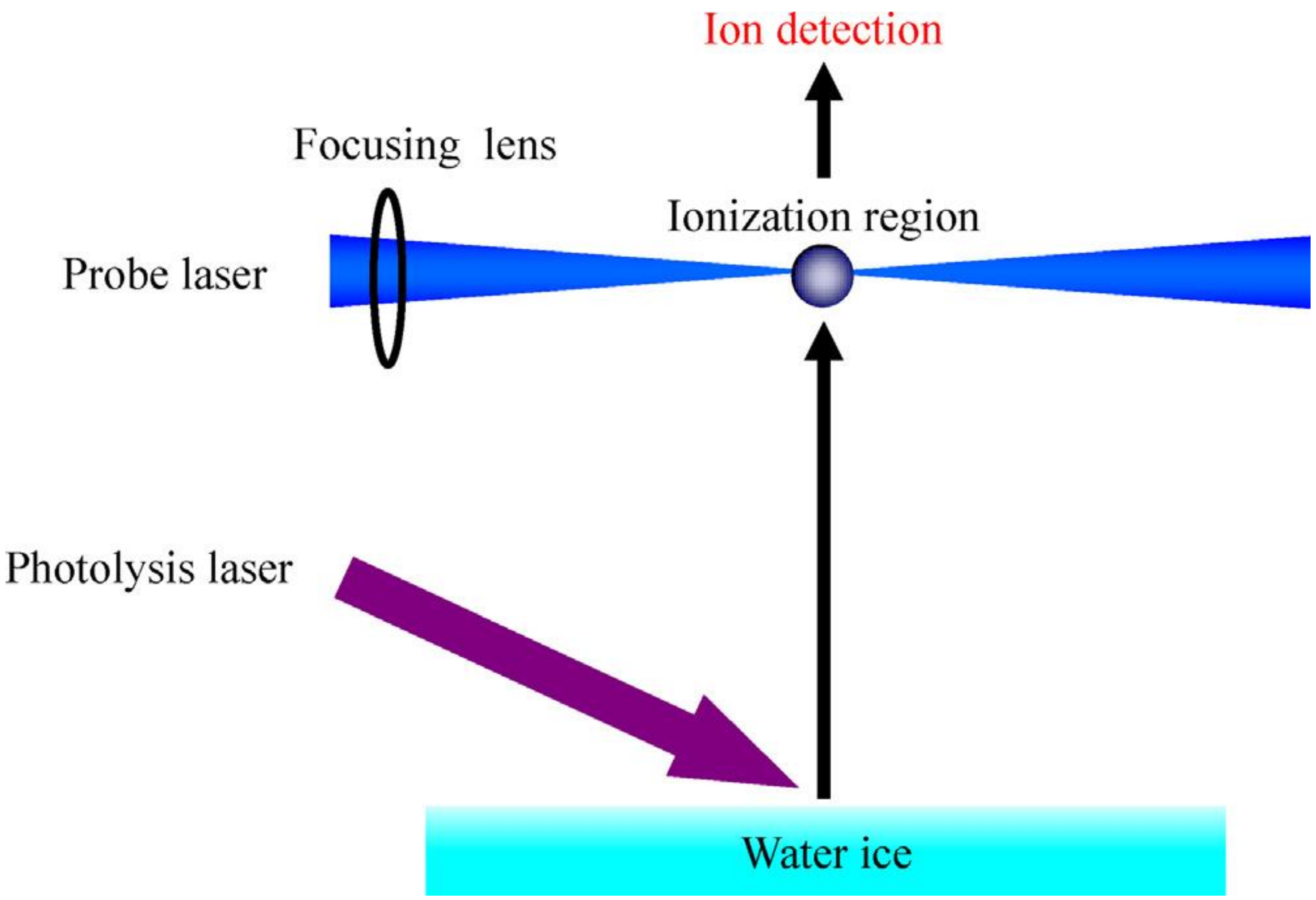
Ertl *Surf Sci* **269** 235 (1992)

When electronic relaxation of a solid sample is fast (< 1 fs) compared to nuclear motion, the speed distributions of photo-ejected products follow Maxwell-Boltzmann statistics.



Previous work II: Time-of-Flight Mass spectroscopy combined with state-selective ionization

REMPI-TOF-MS with H, O(^{3}P), OH, H_2O detection



Kawasaki, Watanabe, and coworkers

O_2 formation after irradiation of water ice with 157 nm

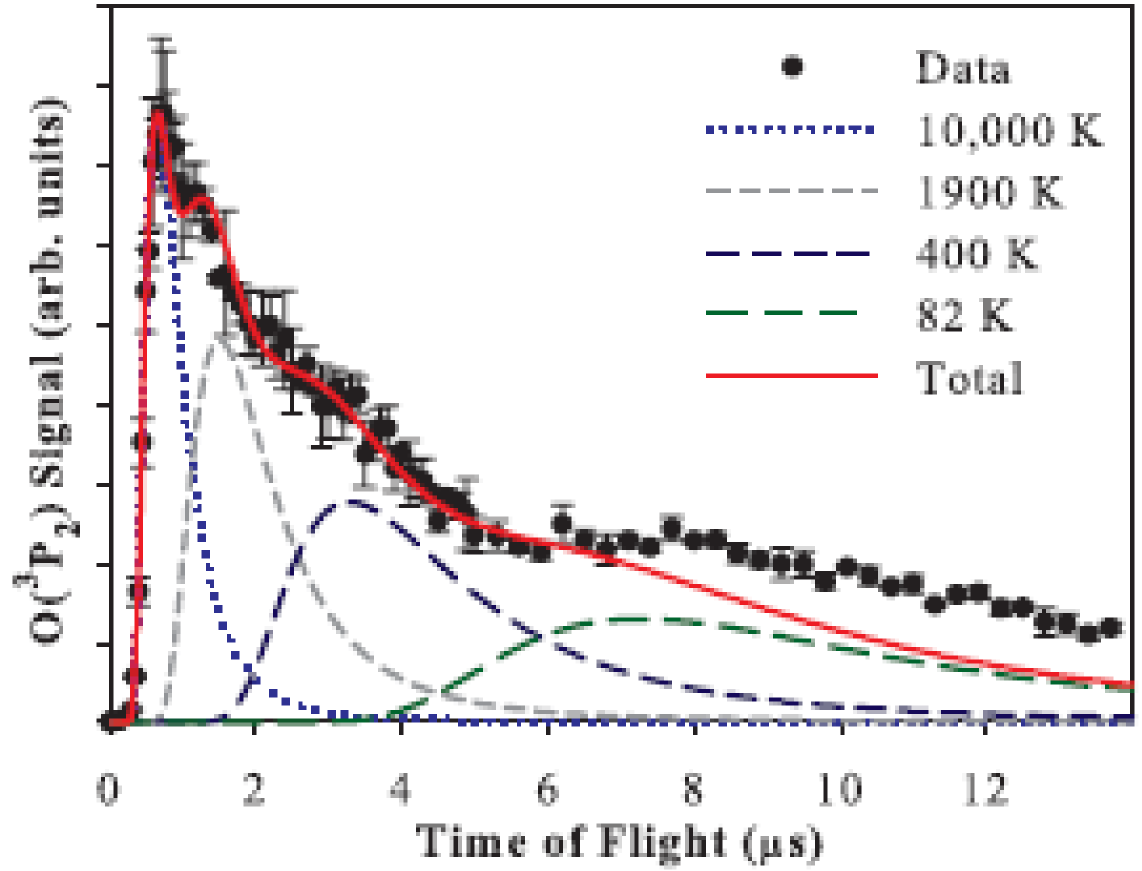
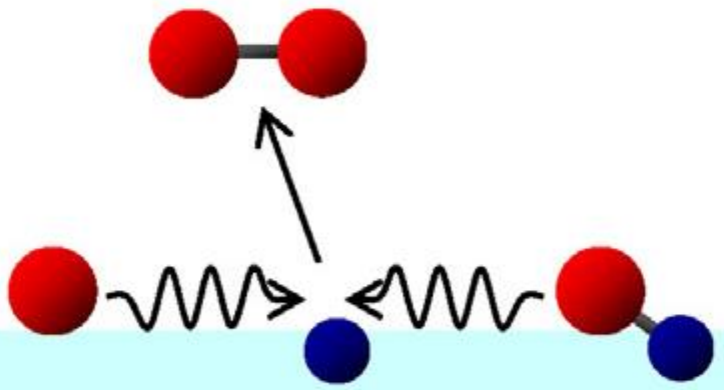


FIG. 4. TOF spectrum of $O(^3P_2)$ desorbing from 600 L ASW at 82 K due to 157-nm irradiation.

from OH (after 10K shots)

Photochemically produced O, O_2

Molecules thermally accommodated at 82K surface



$H_2O + h\nu(157\text{ nm}) \rightarrow H + OH$

$OH + OH \rightarrow H_2O + O(^3P_J)$

$OH + O(^3P_J) \rightarrow O_2(X^3\Sigma_g^-, v{=}0) + H$

THE JOURNAL OF CHEMICAL PHYSICS **140**, 094702 (2014)

$O(^3P_J)$ formation and desorption by 157-nm photoirradiation of amorphous solid water

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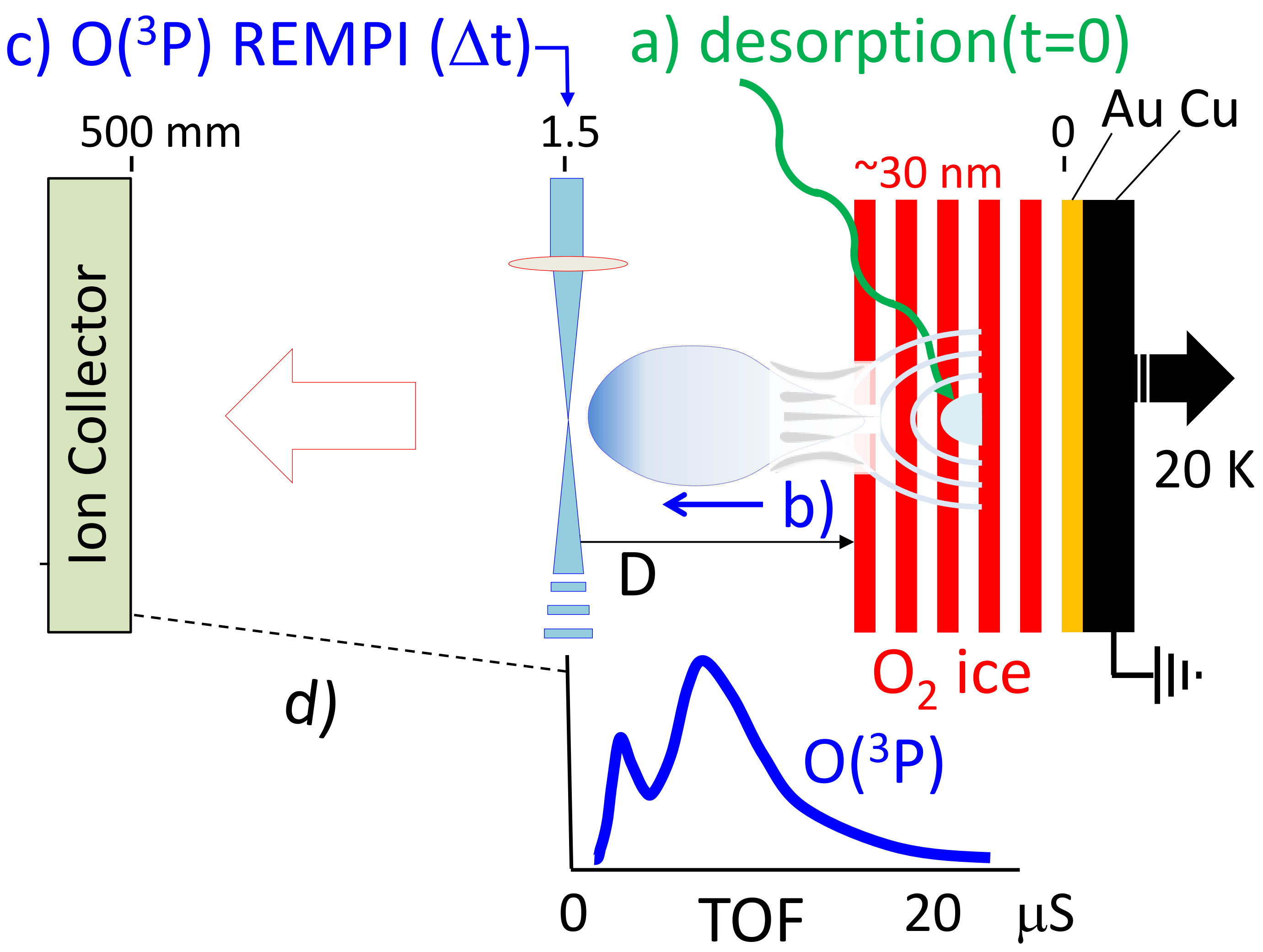
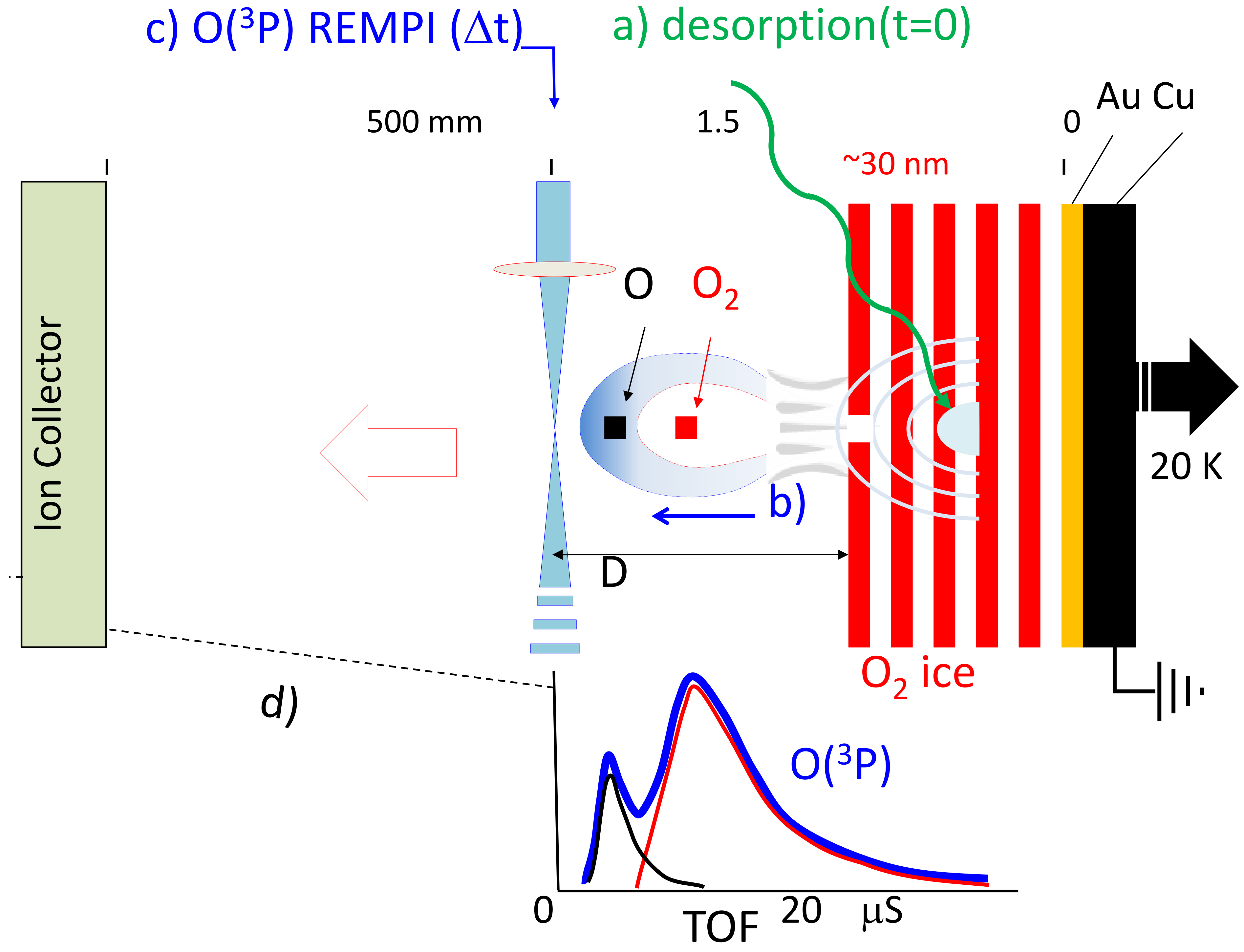
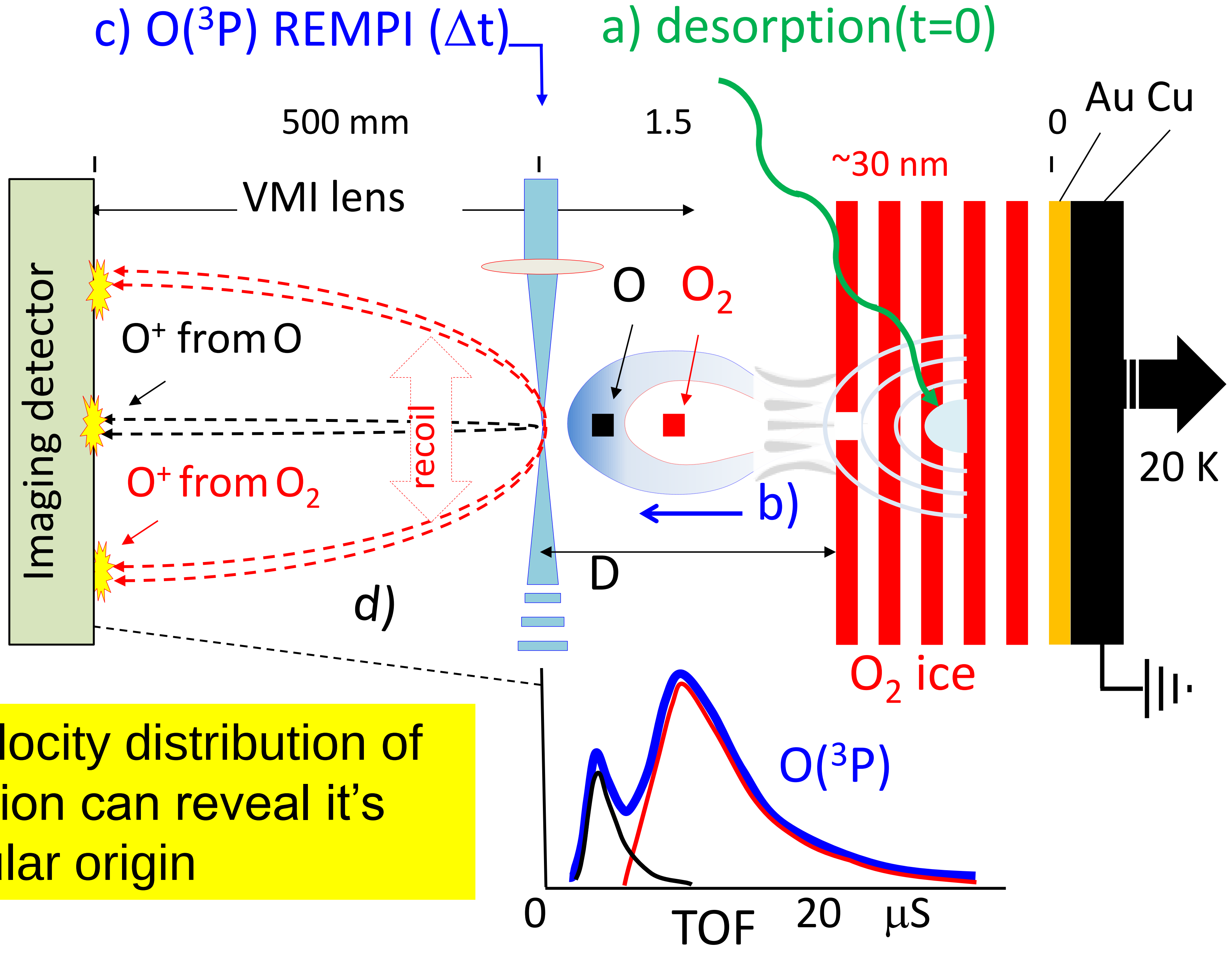
Overview of a Time-of-Flight experiment (one axial information)



It is well known that O-atom REMPI at 226 nm also dissociates O_2



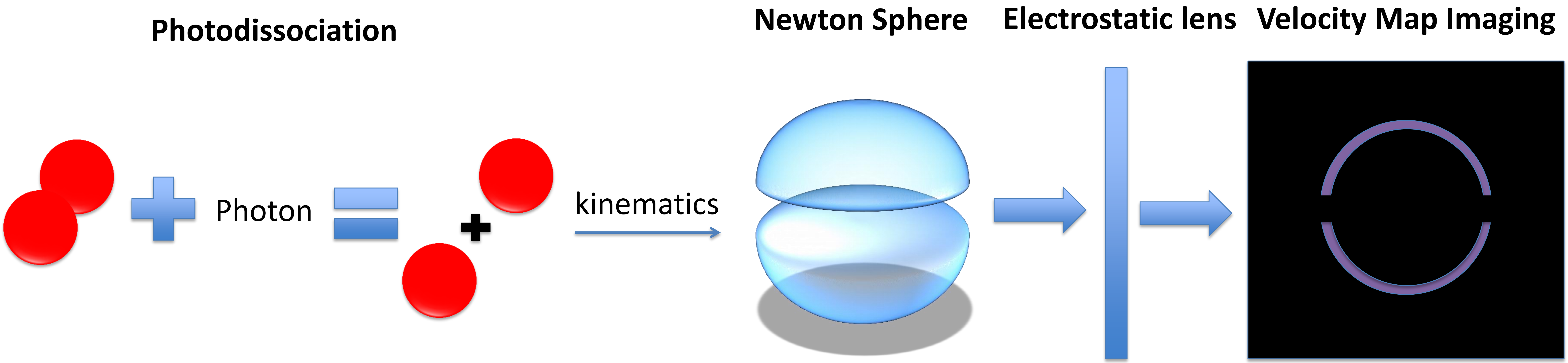
Photodissociation → recoil of the O-atom fragments



The velocity distribution of the O⁺ ion can reveal it’s molecular origin

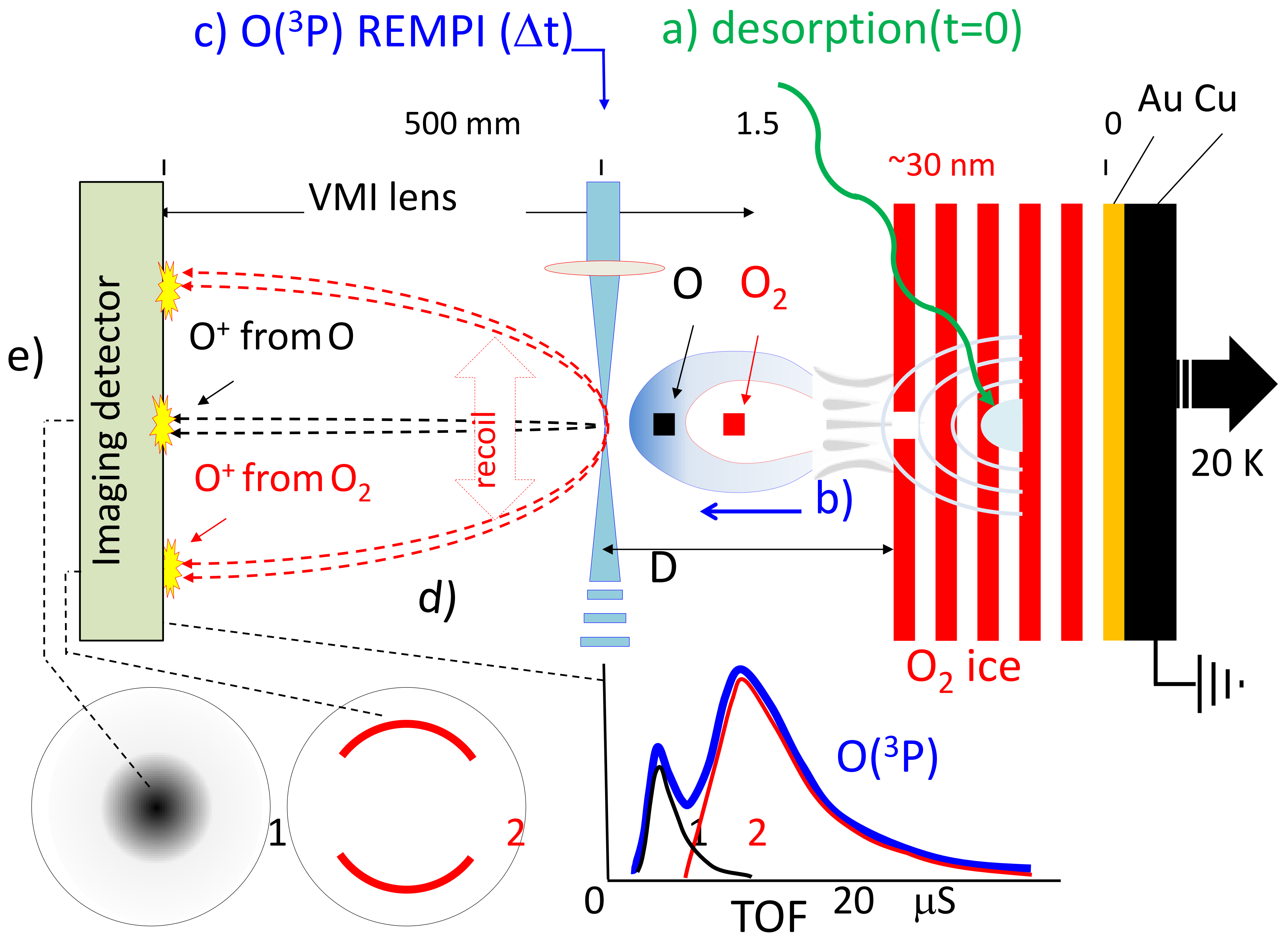
Principle of VMI

Principle of VMI:
Each charged particle with the same direction and velocity will be mapped at the samepoint of a 2D detector

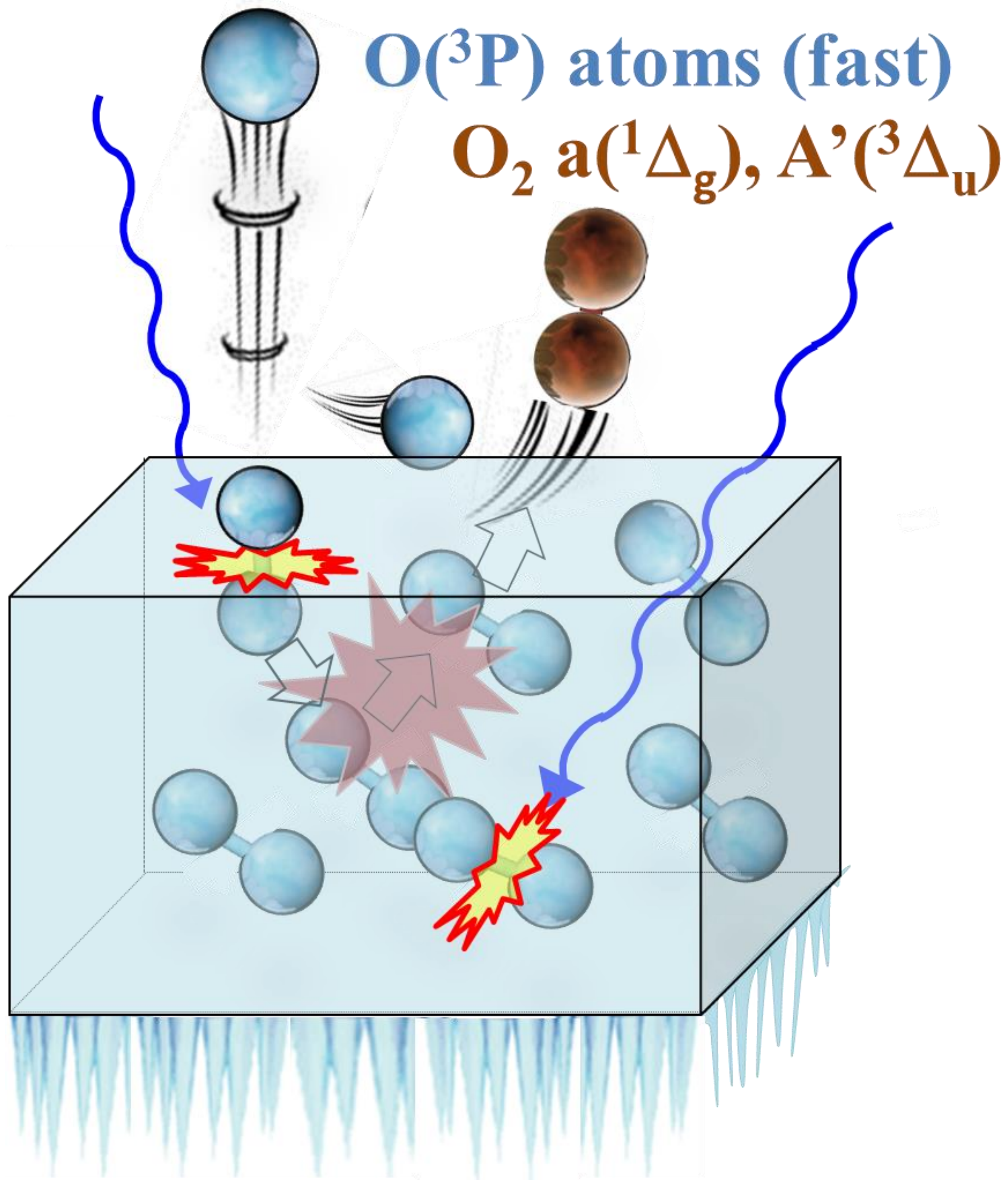


Angular distribution: $F(\Theta) = [1+\beta P_2(\cos \Theta)]/4\pi$

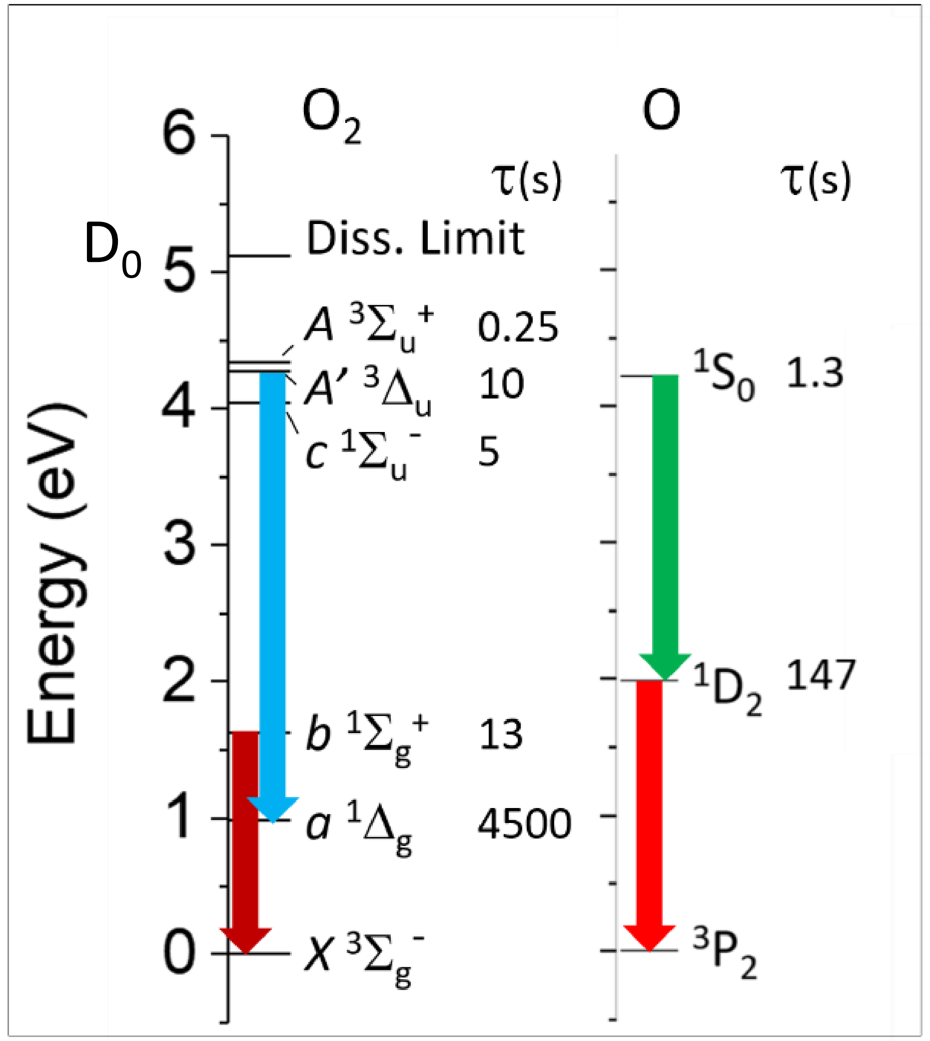
Velocity Map Imaging records the recoil pattern for any Δt, showing different origins of O(^{3}P) atoms



What to expect? Photolysis of oxygen ice



- O atom leaving the surface
- O_2 molecule leaving the surface → Thermal / Kick-out: O or O_2^*
- O atom recombination to O_2^*, O_3



D_0 5.117 eV (<242 nm) → O(^{3}P) + O (^{3}P)
D_1 7.084 eV (<175 nm) → O(^{3}P) + O (^{1}D)
D_2 9.051 eV (<137 nm) → O(^{1}D) + O (^{1}D)

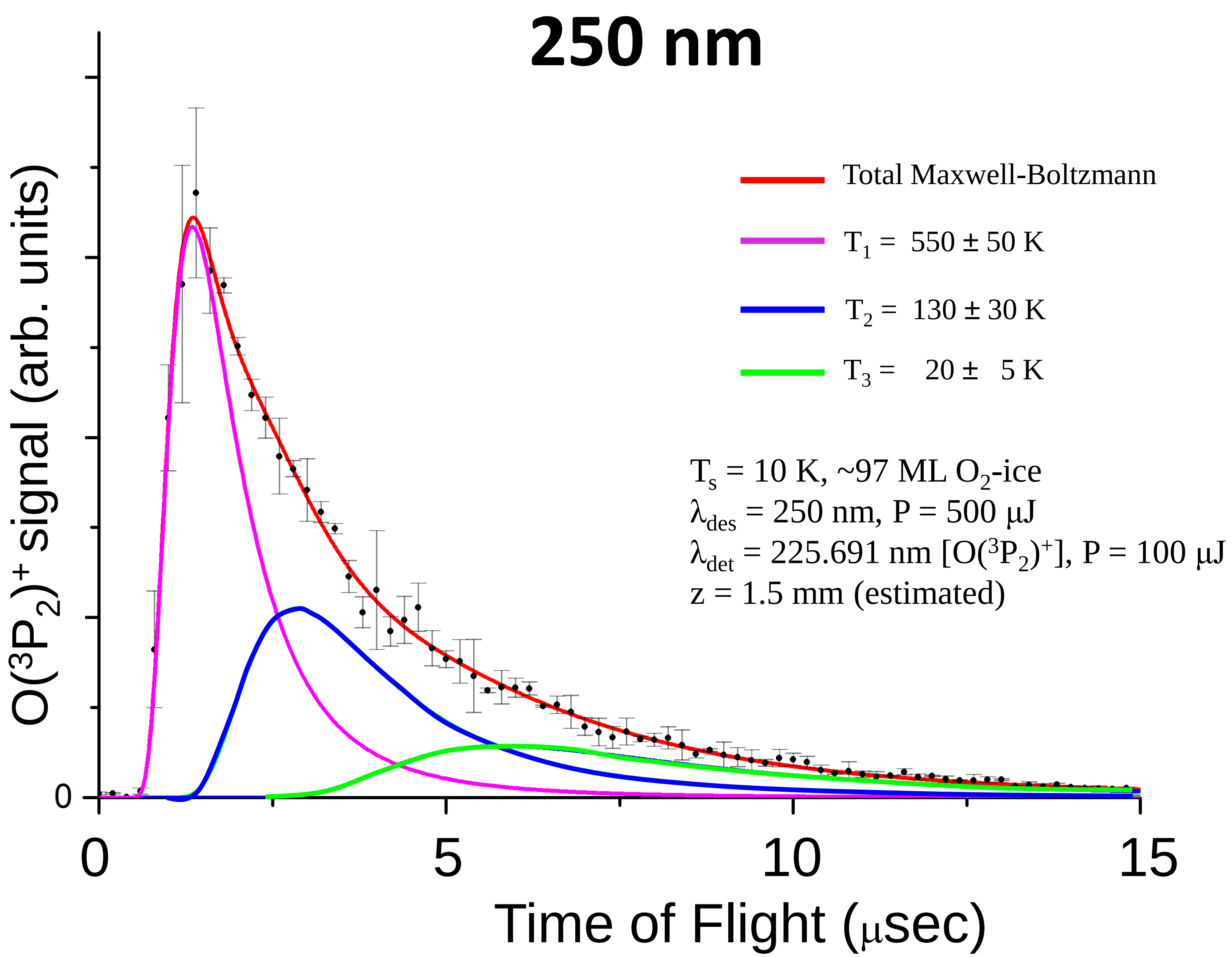
Imaging results

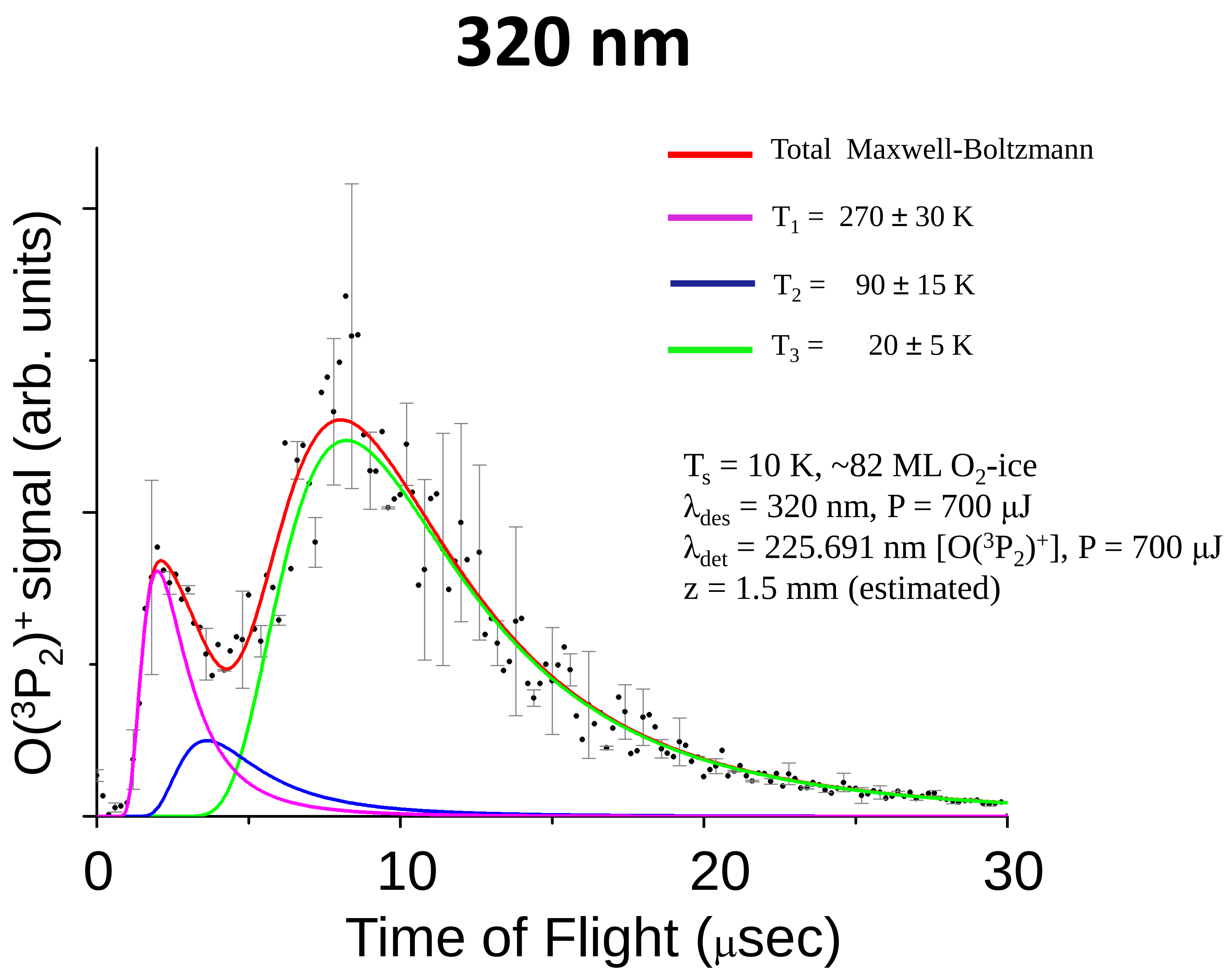
- Photodesorption at 250 and 320 nm (respectively 4.96 eV and 3.87 eV)

- Detection of O_2 X by 2+1 REMPI at 225 nm
- Detection of O_2 a by 2+1 REMPI at 315 nm

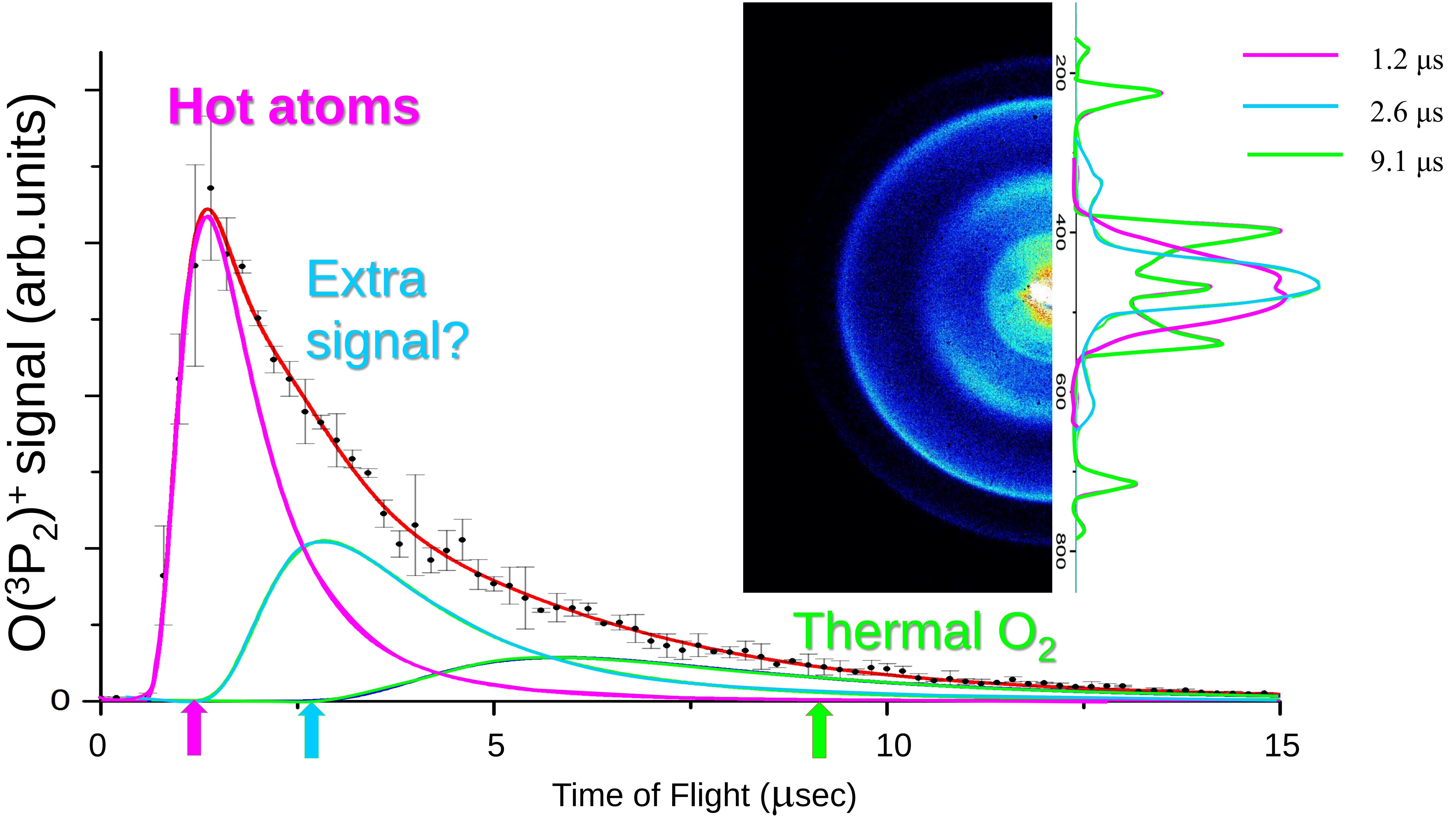
- Detection of $O(^3P)$ by 2+1 REMPI at 225.6 nm
- Detection of $O(^1D)$ by 2+1 REMPI at 203.5 nm

Desorption of $O(^3P_2)$ from 15 Kelvin O_2-ice at 250 and 320 nm

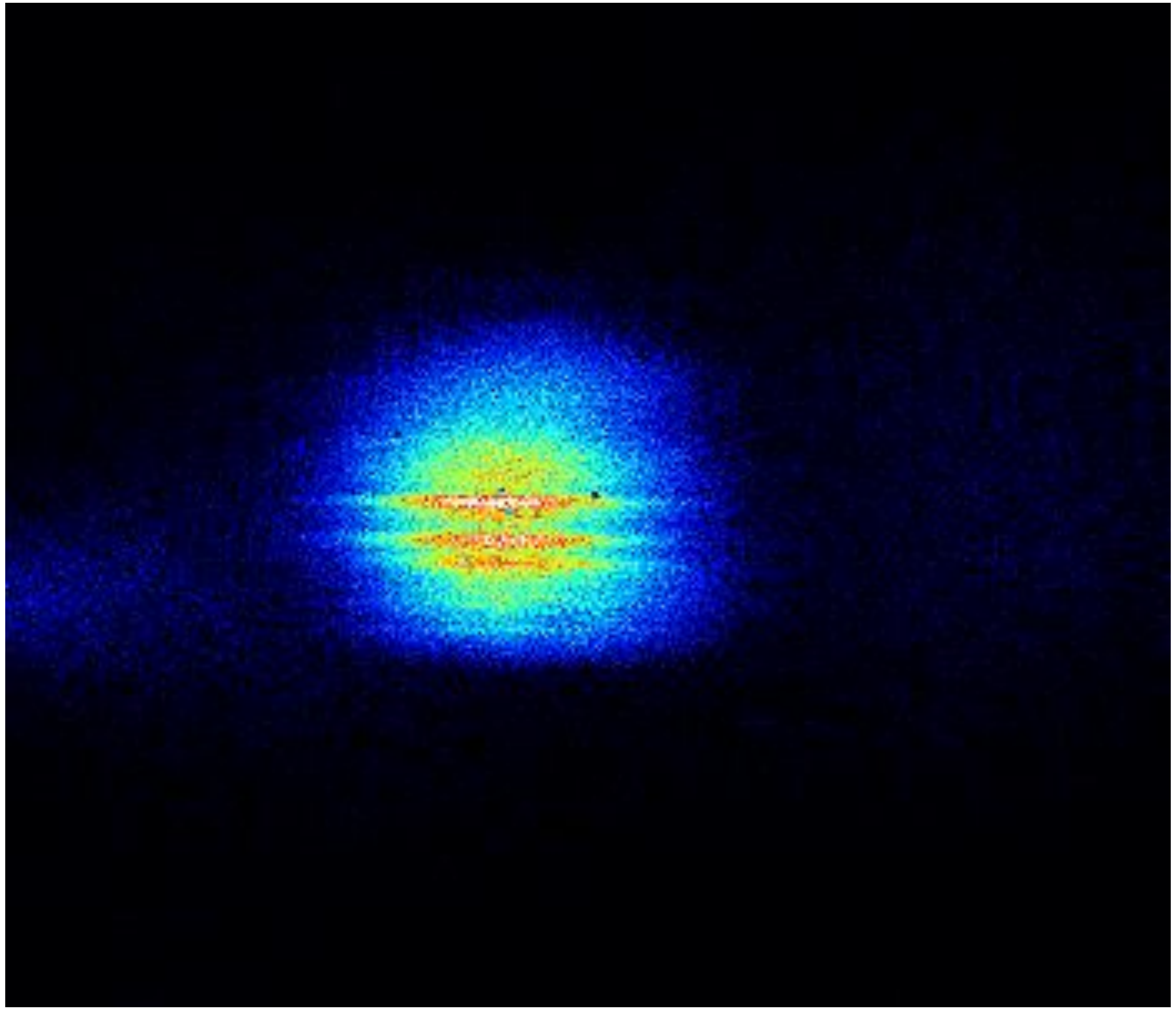




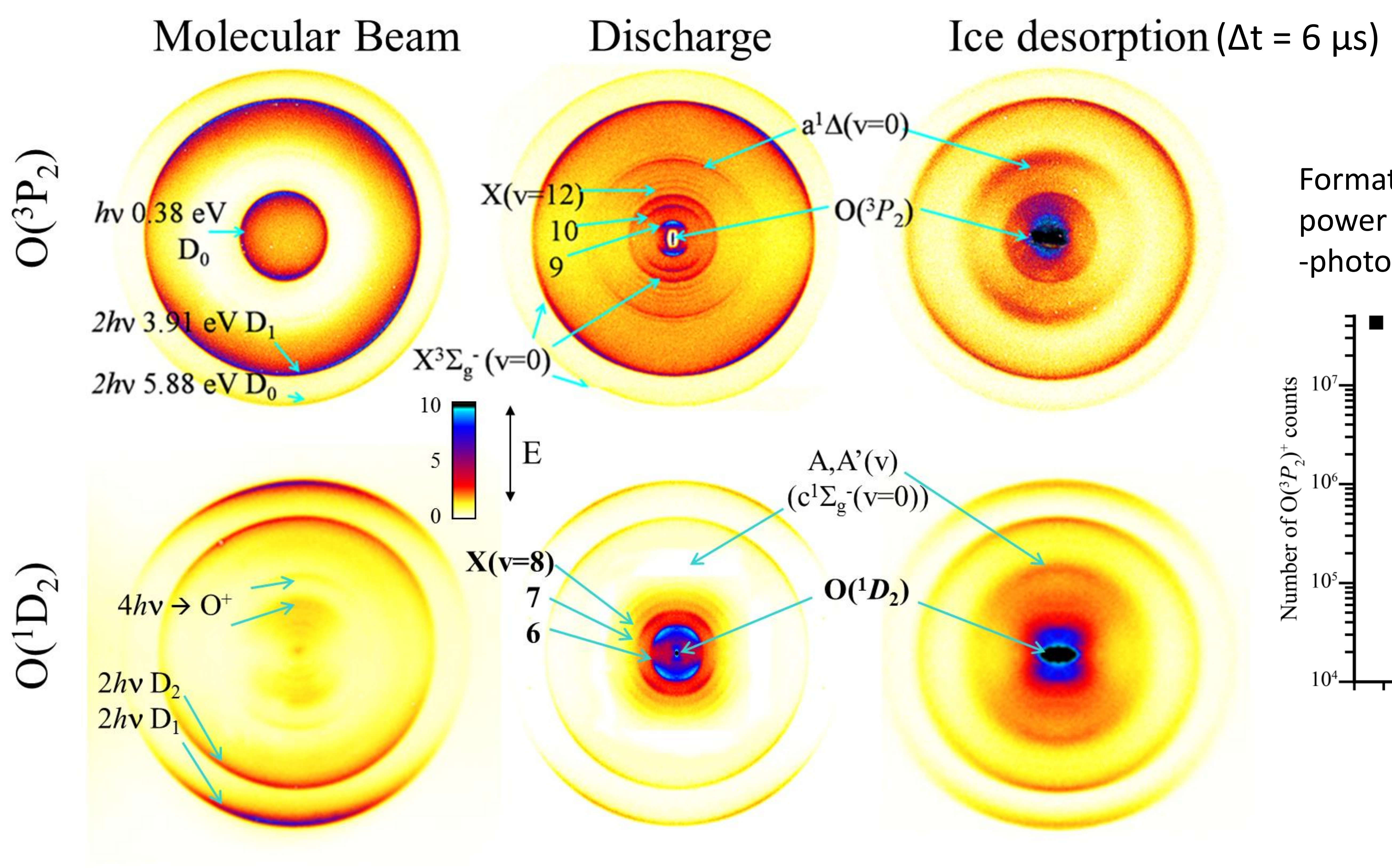
Desorption of $O(^3P_2)$ from 15K O_2-ice at 250 nm



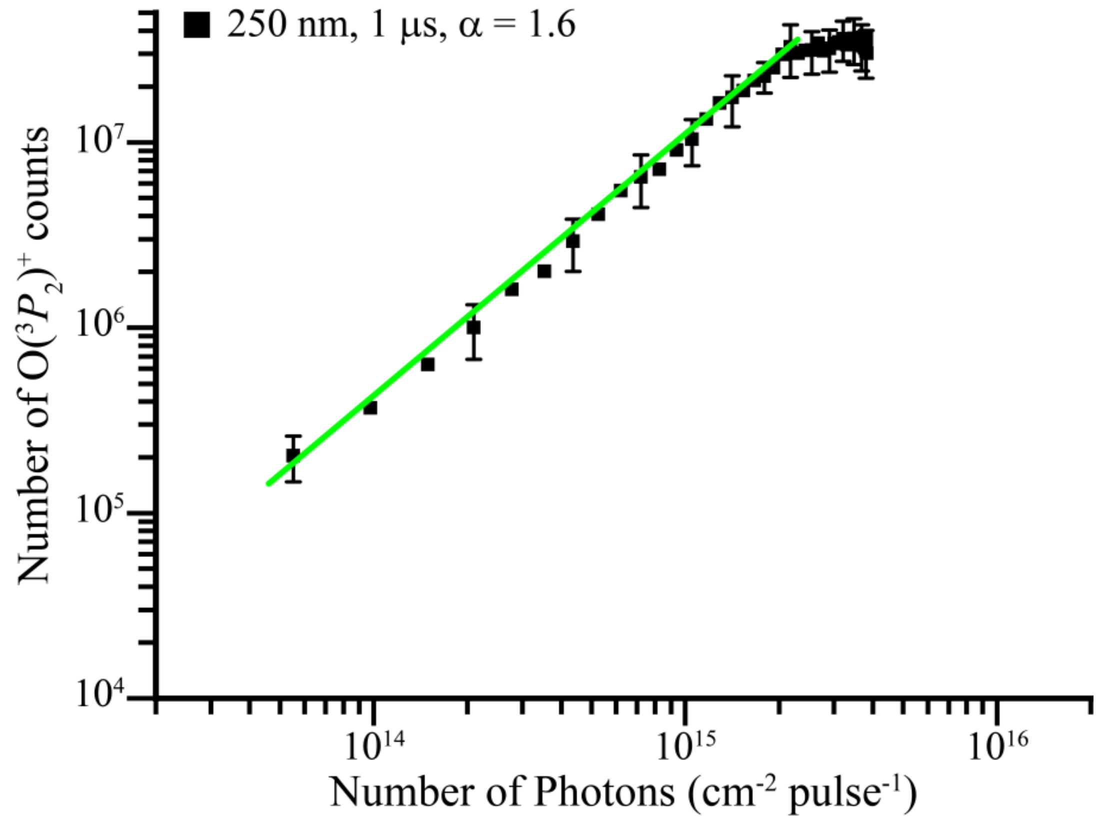
MOVIE of Desorption of $O(^3P_2)$ from 15 Kelvin O_2-ice at 250



Photodesorption of pure O_2 ice at 20 K using 250 nm

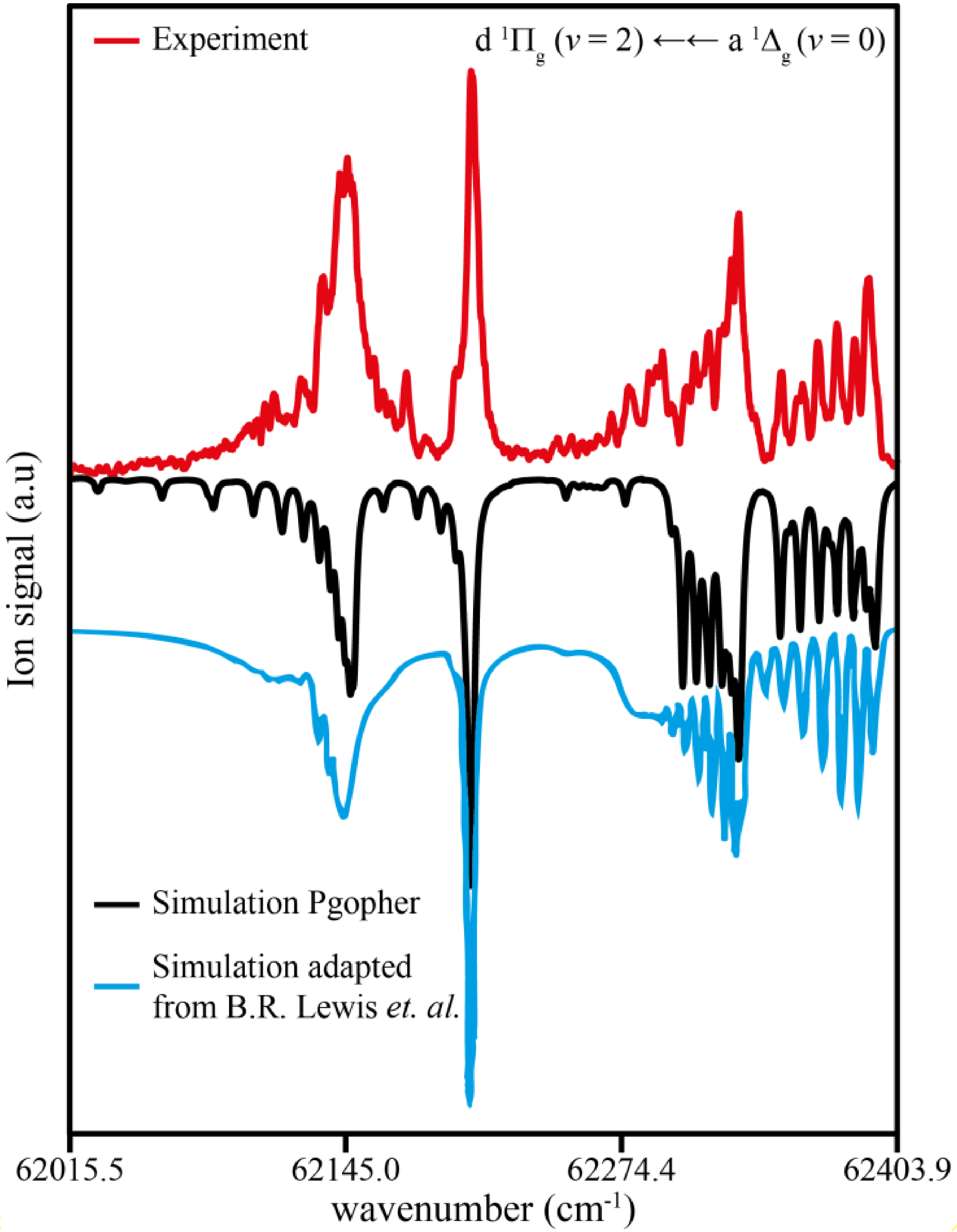


Formation of O(¹D) and power scan confirms two -photon absorption (TPA) event

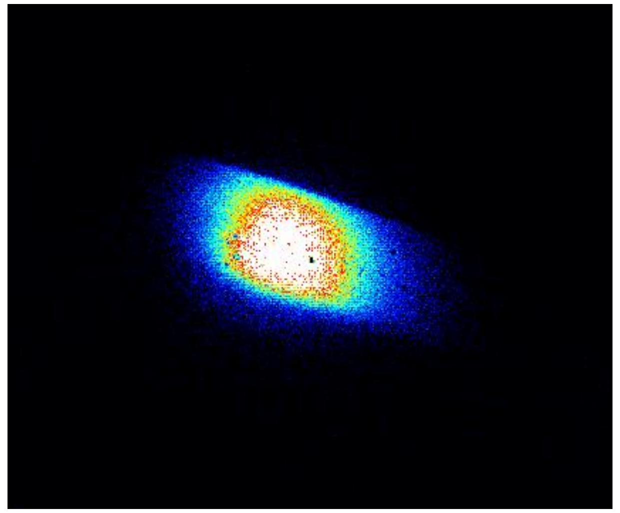


REMPI spectrum: Confirmation of O_2 (a $^1\Delta$)

T_s = 10 K, ~80 ML O_2-ice
λ_{des} = 250 nm, P = 600 μJ
λ_{det} = REMPI 641 – 645 nm[O_2^+],
P_{det} = 1500 μJ
z = 1.5 mm

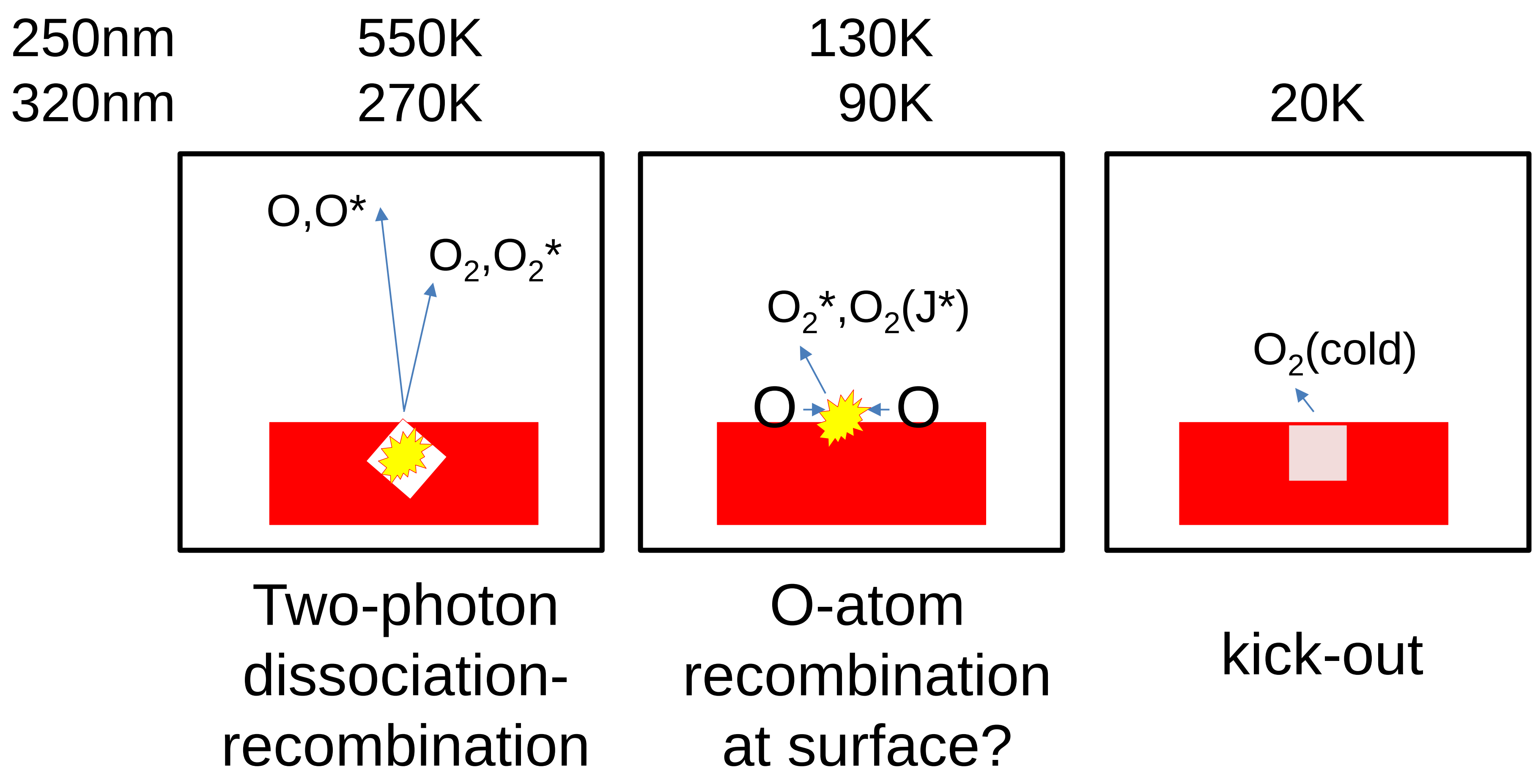


Shape of image: molecules are from surface, not from photodissociation of O_3 in probe beam



Slanger, Lewis, Journal of Molecular Spectroscopy 219 (2003) 200–216

Temperature to mechanism



Discussion

- O_2* *(a,b)* is known to rapidly destroy O_3 in the gas phase
- O_2* *(a)* is produced while photodesorbing water ice
- Could VUV irradiation of water ice in the ISM cause build-up of O_2 in primordial ice with little O_3 formation?

Conclusion

- Combination of VMI with ice is good and results in not too bad images
- VMI greatly enhance ToF-MS by identifying molecular origin of O-atom signals
- Primary process is the TPA of the oxygen ice resulting in O_2 photodissociation and recombination to produce energetic O atoms and metastable oxygen molecules.

Acknowledgements

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EXTRA: Time-of-Flight of different origins at 250 nm and 15 Kelvin