Singlet Oxygen
production, photodissociation, and detection
in discharges, clusters and ice surfaces using velocity map imaging

Radboud Universiteit Nijmegen

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Molecular and Laser Physics
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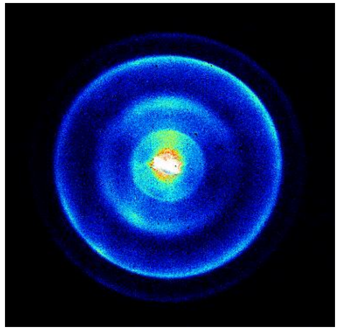
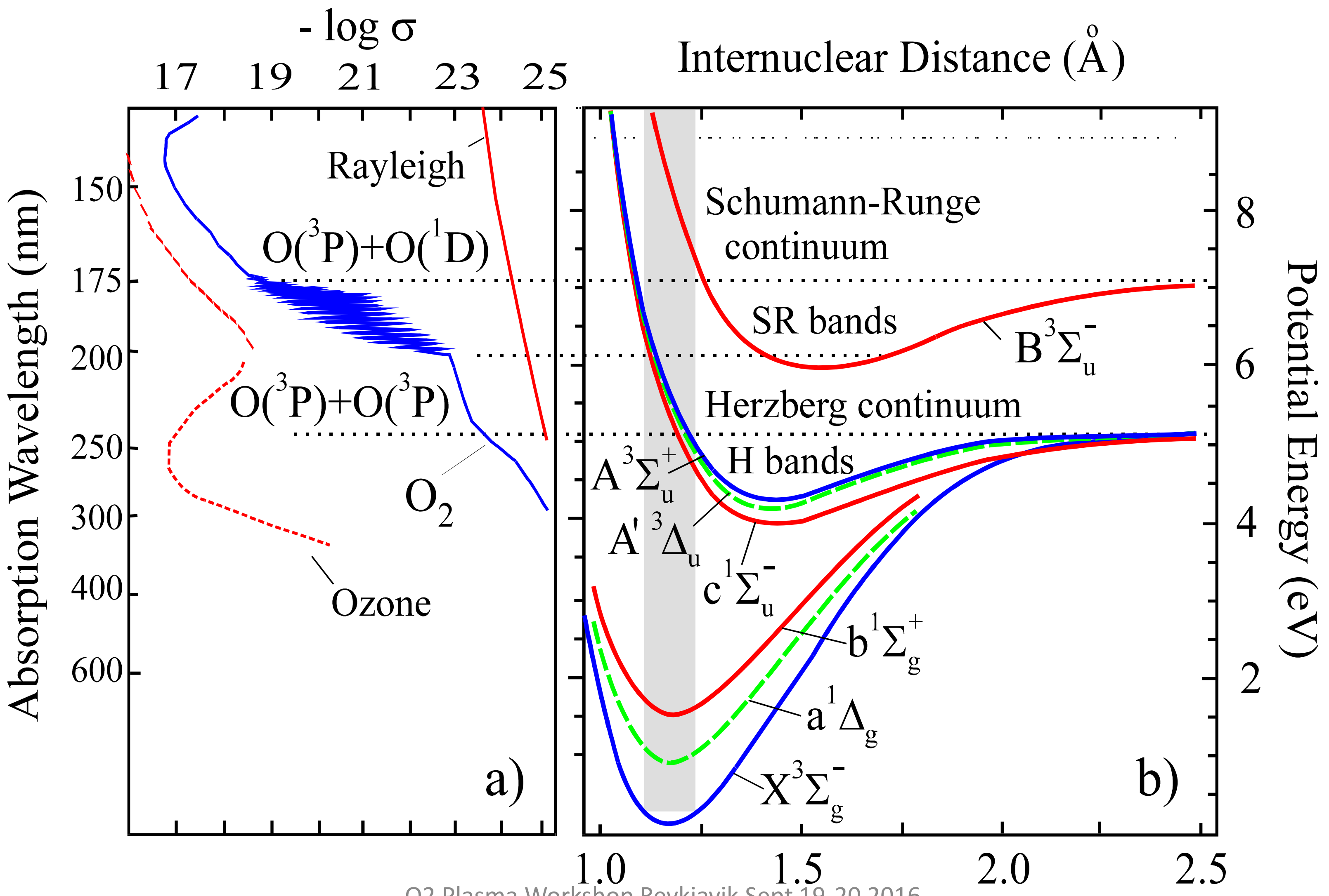


Molecular Oxygen

- Photodissociation (W. vd Zande, X.M. Yang,…)
- REMPI (C. Western)
- O_2-X Clusters (A. Baklanov) and CIA
- Inelastic Scattering with H_2, He, Ar (F. Lique)
- Photodesorption of O_2-ice at 10K (H. Linnartz)

Electronic structure and spectrum of O_2

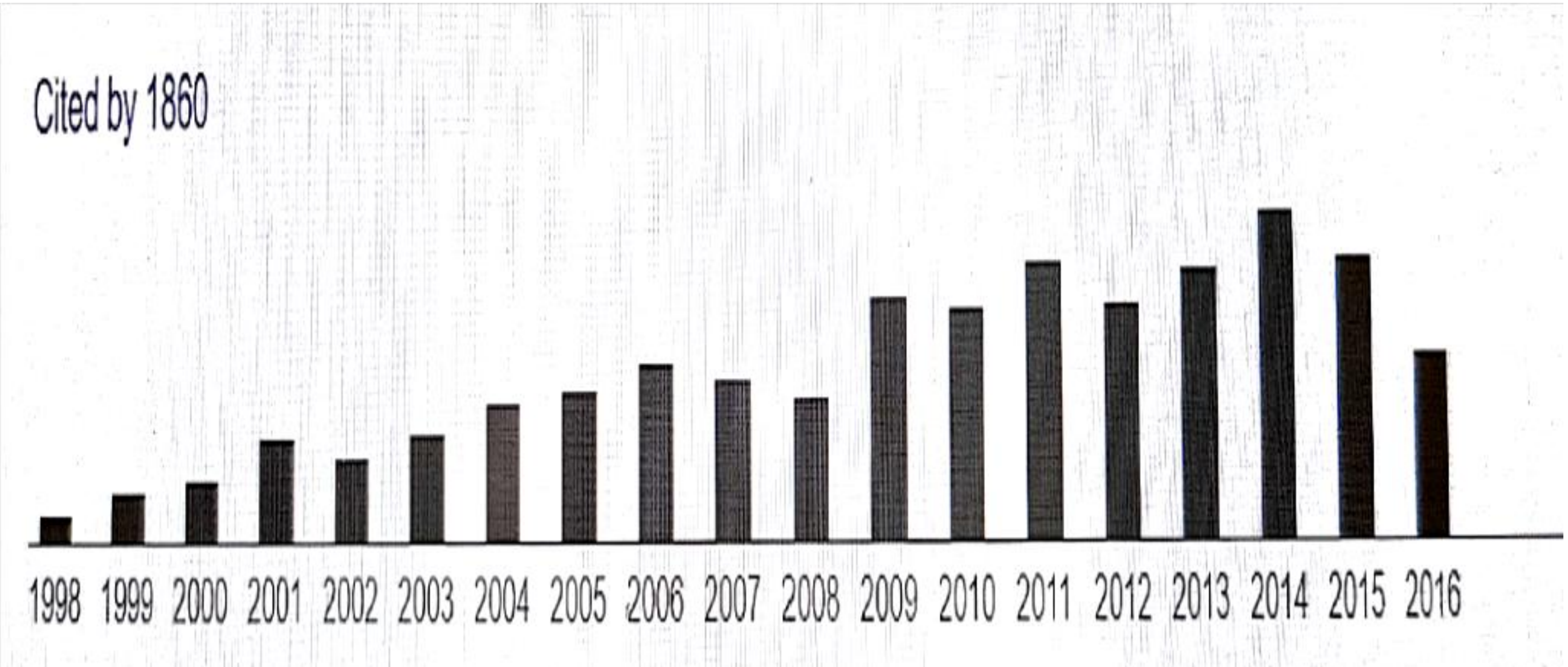


David H. Parker

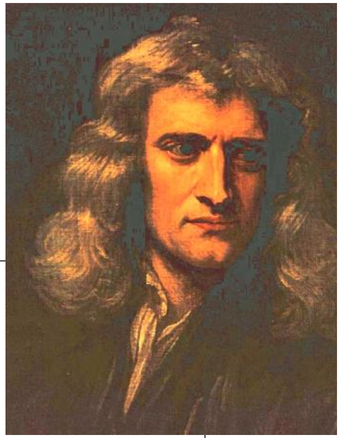
Velocity map imaging of ions and electrons using electrostatic lenses: Application in photoelectron and photofragment ion imaging of molecular oxygen

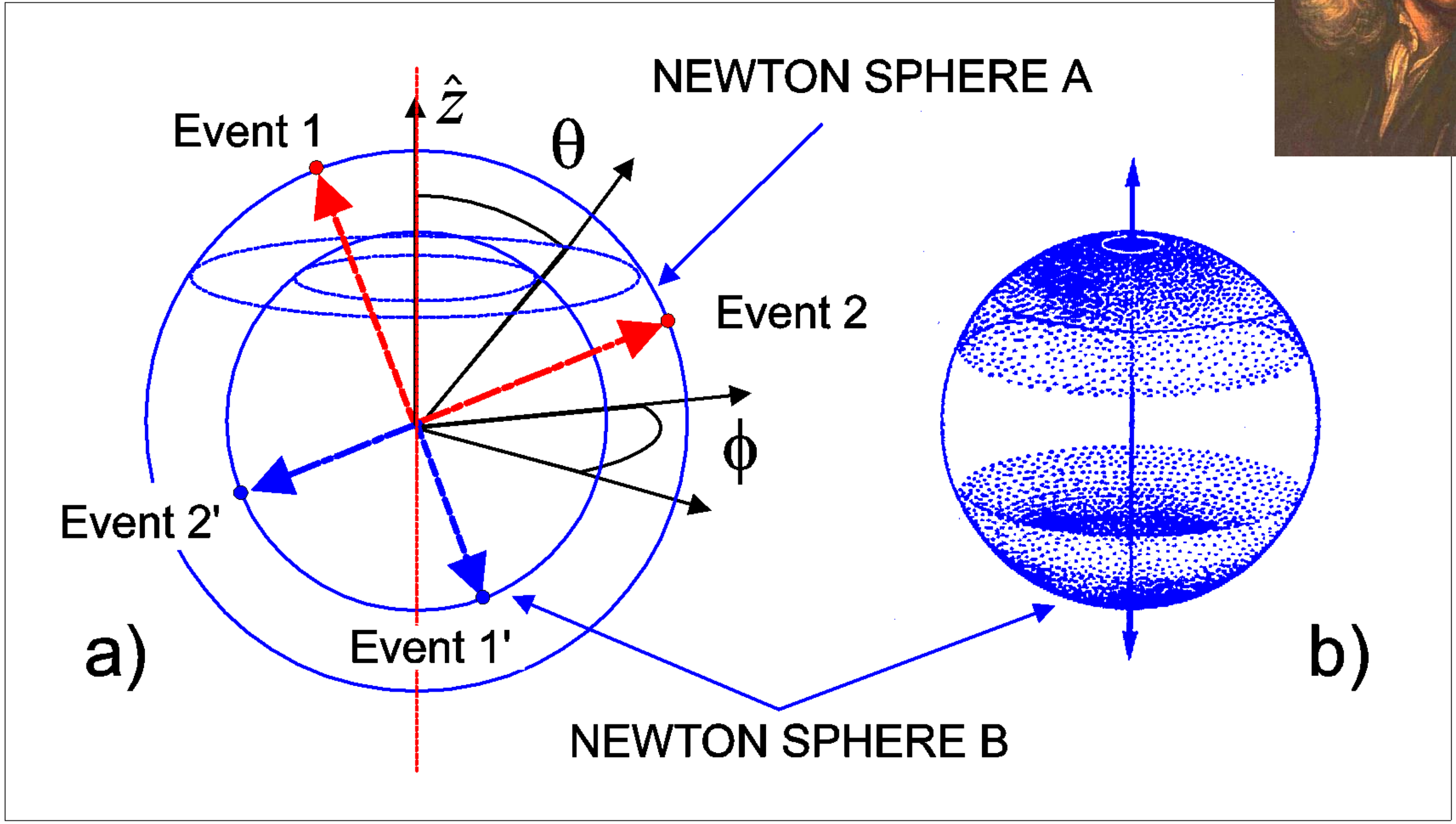
Authors	André TJB Eppink, David H Parker
Publication date	1997/9/1
Journal	Review of Scientific Instruments
Volume	68
Issue	9
Pages	3477-3484
Publisher	AIP Publishing

Description: The application of electrostatic lenses is demonstrated to give a substantial improvement of the two-dimensional (2D) ion/electron imaging technique. This combination of ion lens optics and 2D detection makes “velocity map imaging” possible, ie, all particles with the same initial velocity vector are mapped onto the same point on the detector. Whereas the more common application of grid electrodes leads to transmission reduction, severe trajectory deflections and blurring due to the non-point source geometry, these problems ...

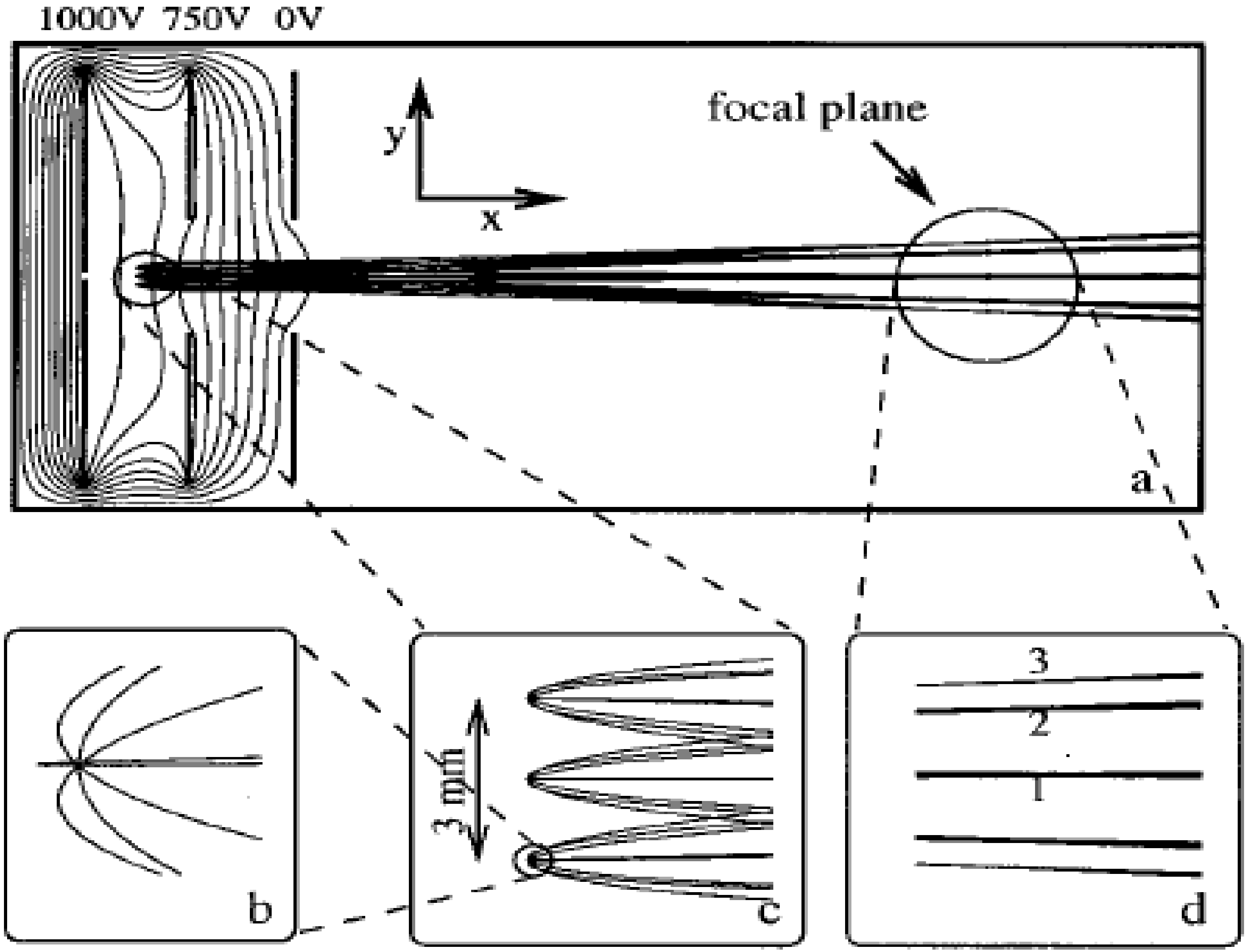


$AB^* \longrightarrow A + B$

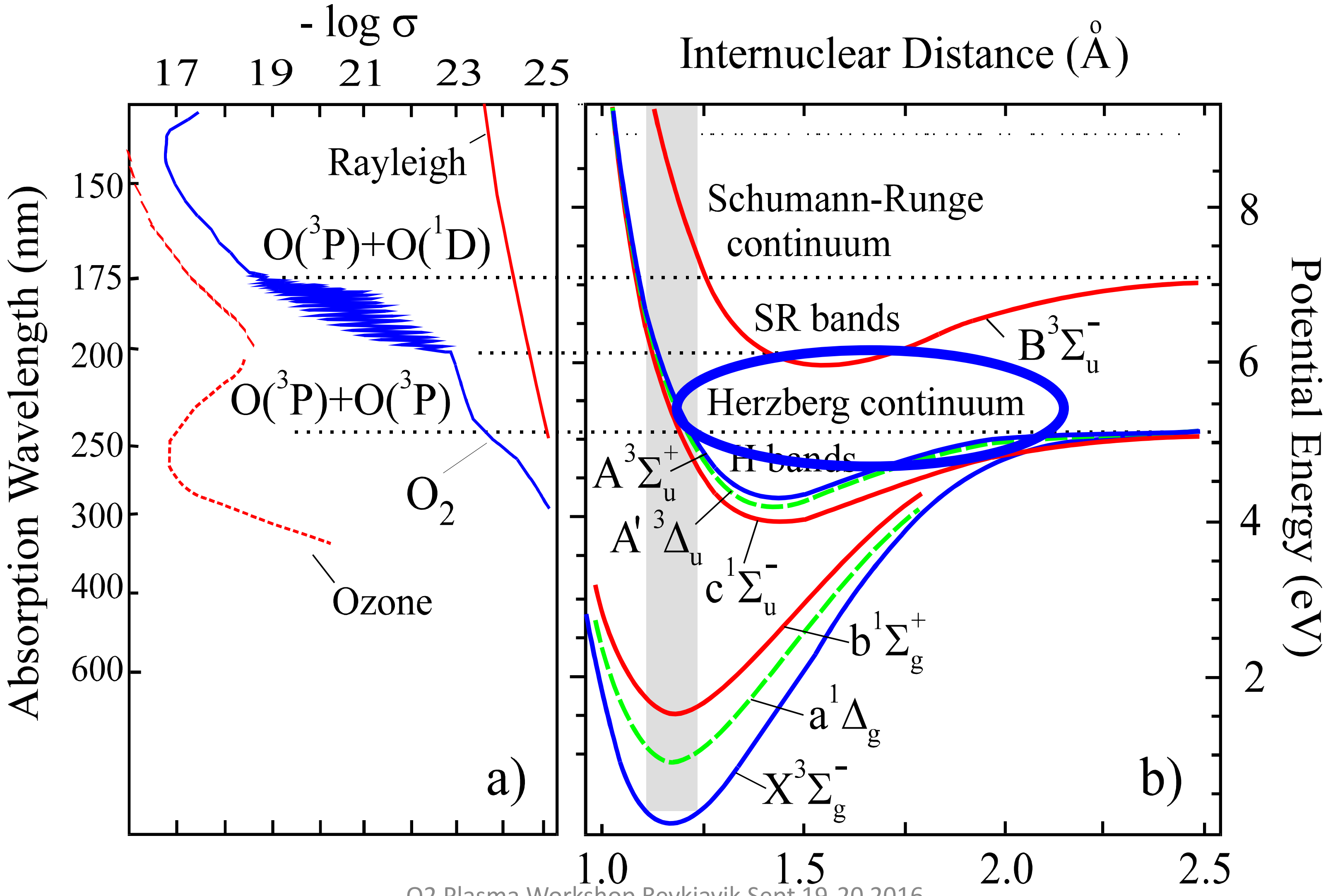




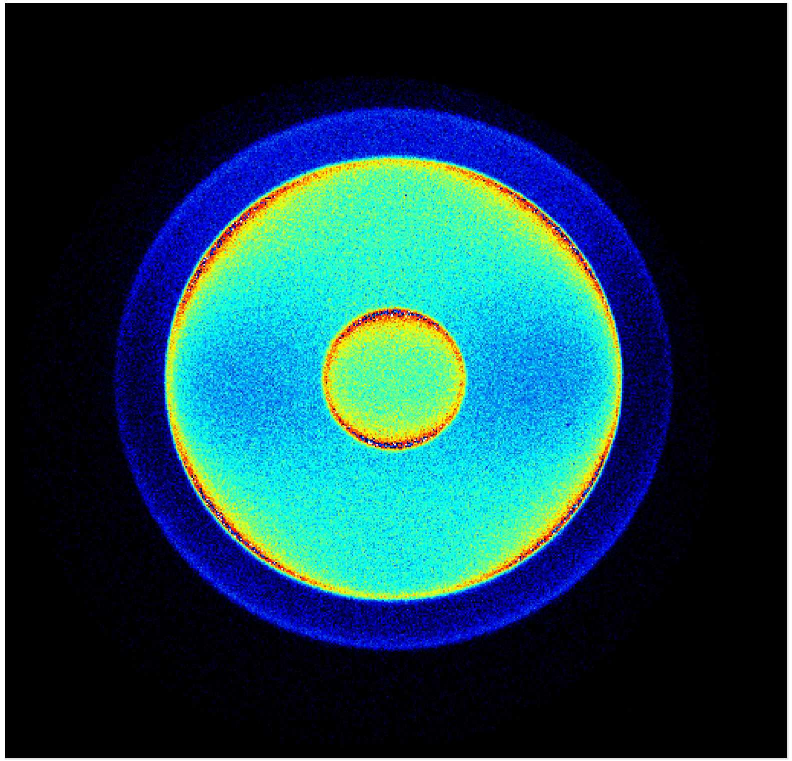
parallel transition ($\sin^2\theta$) β = 2


1000V 750V 0V
y
x
focal plane
a
b
3 mm
c
3
2
1
d

Electronic structure and spectrum of O_2

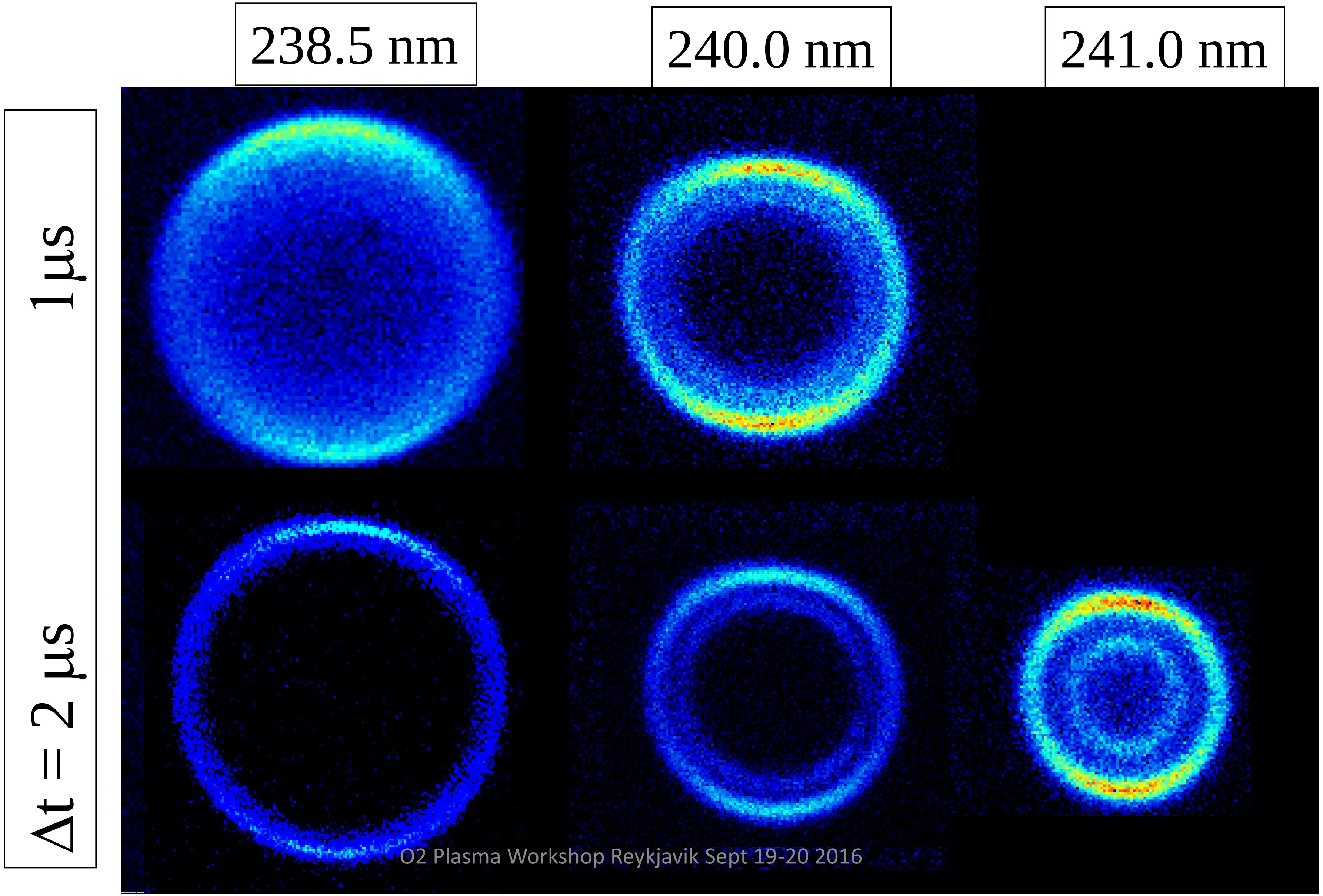


Detection of cold O_2 X-state by the $O(^3P_2)$ image

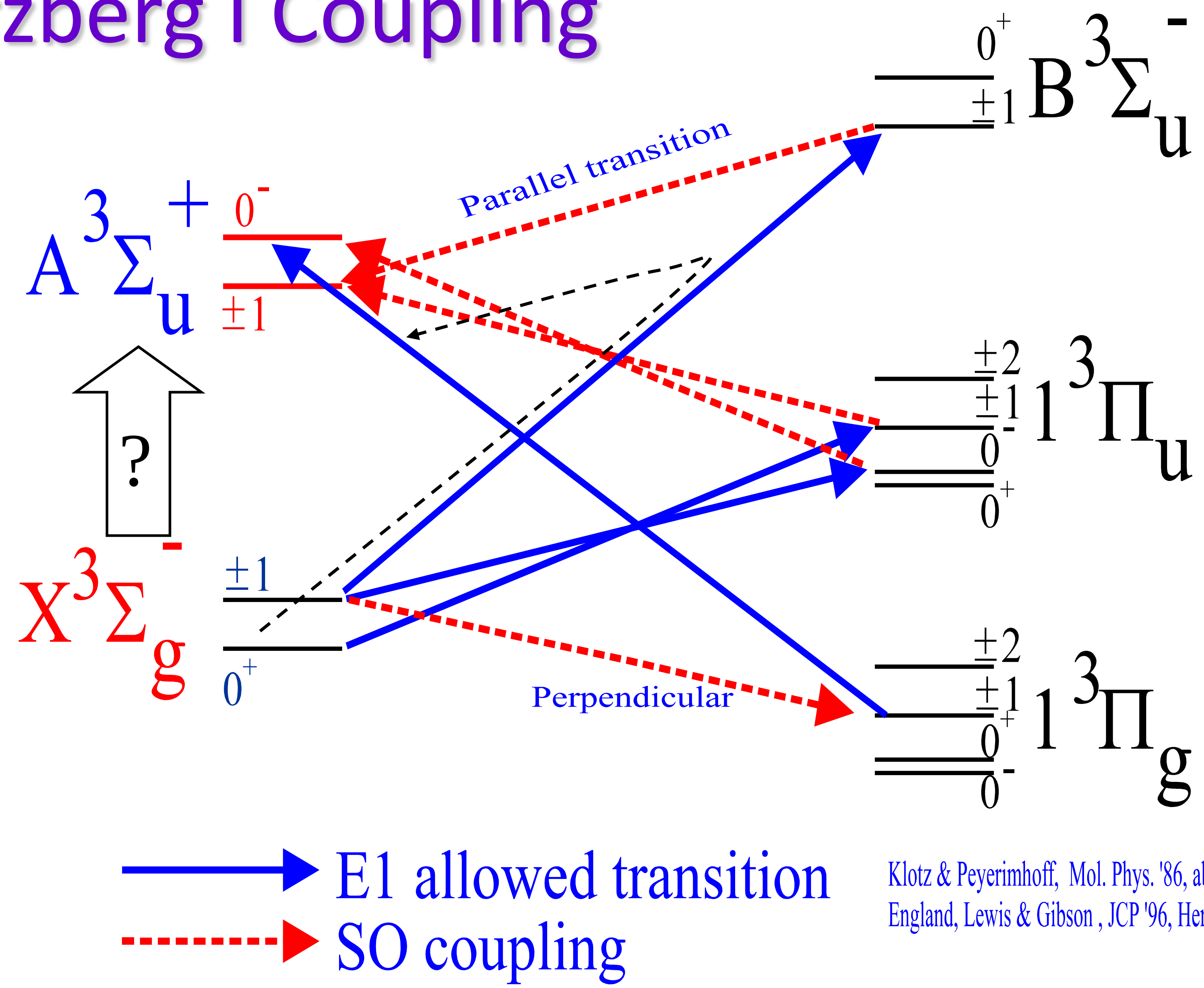


$O(^3P_2)$ (2+1) REMPI at 225.6 nm

Photodissociation of cold X-state O_2 via the HC

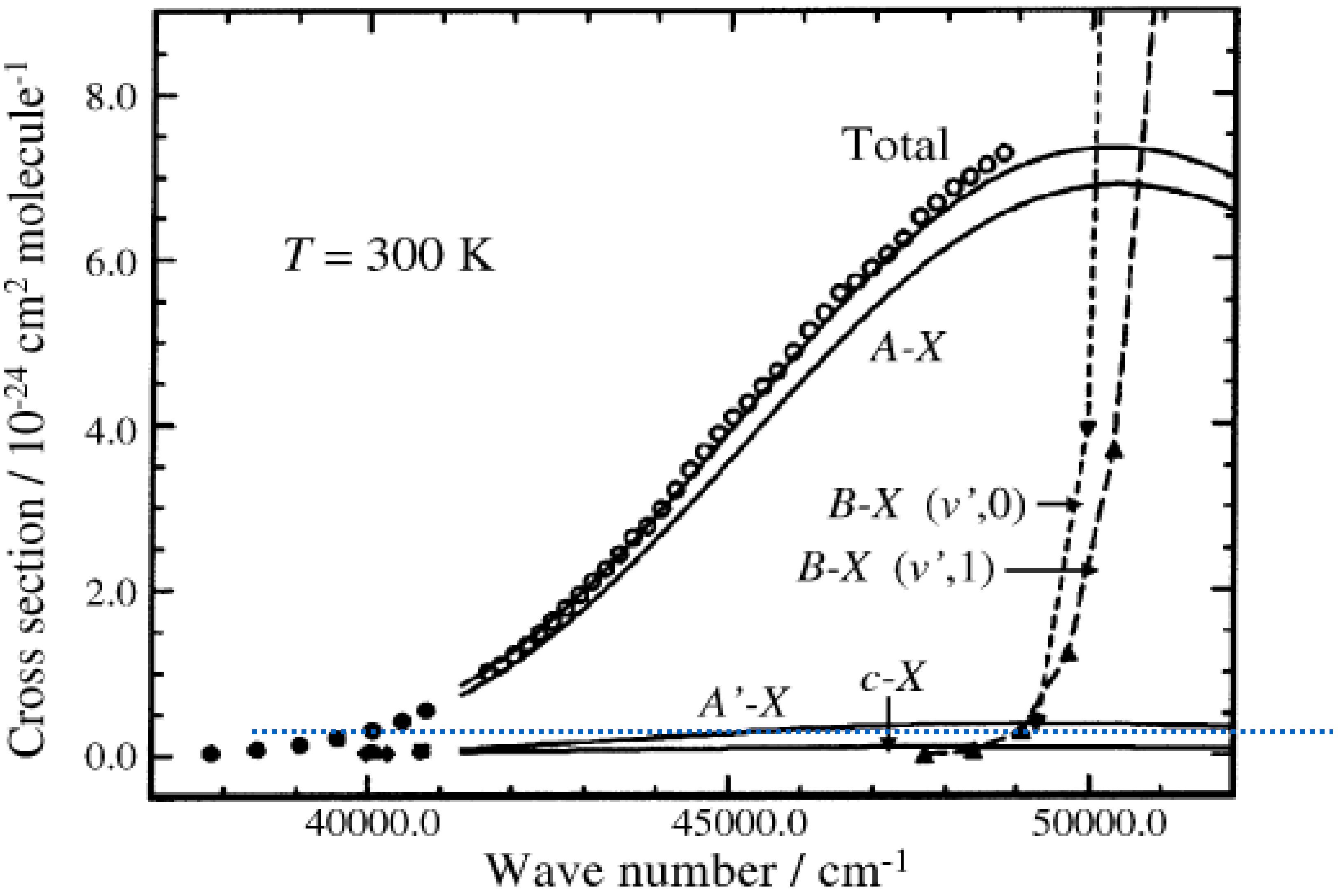


Herzberg I Coupling

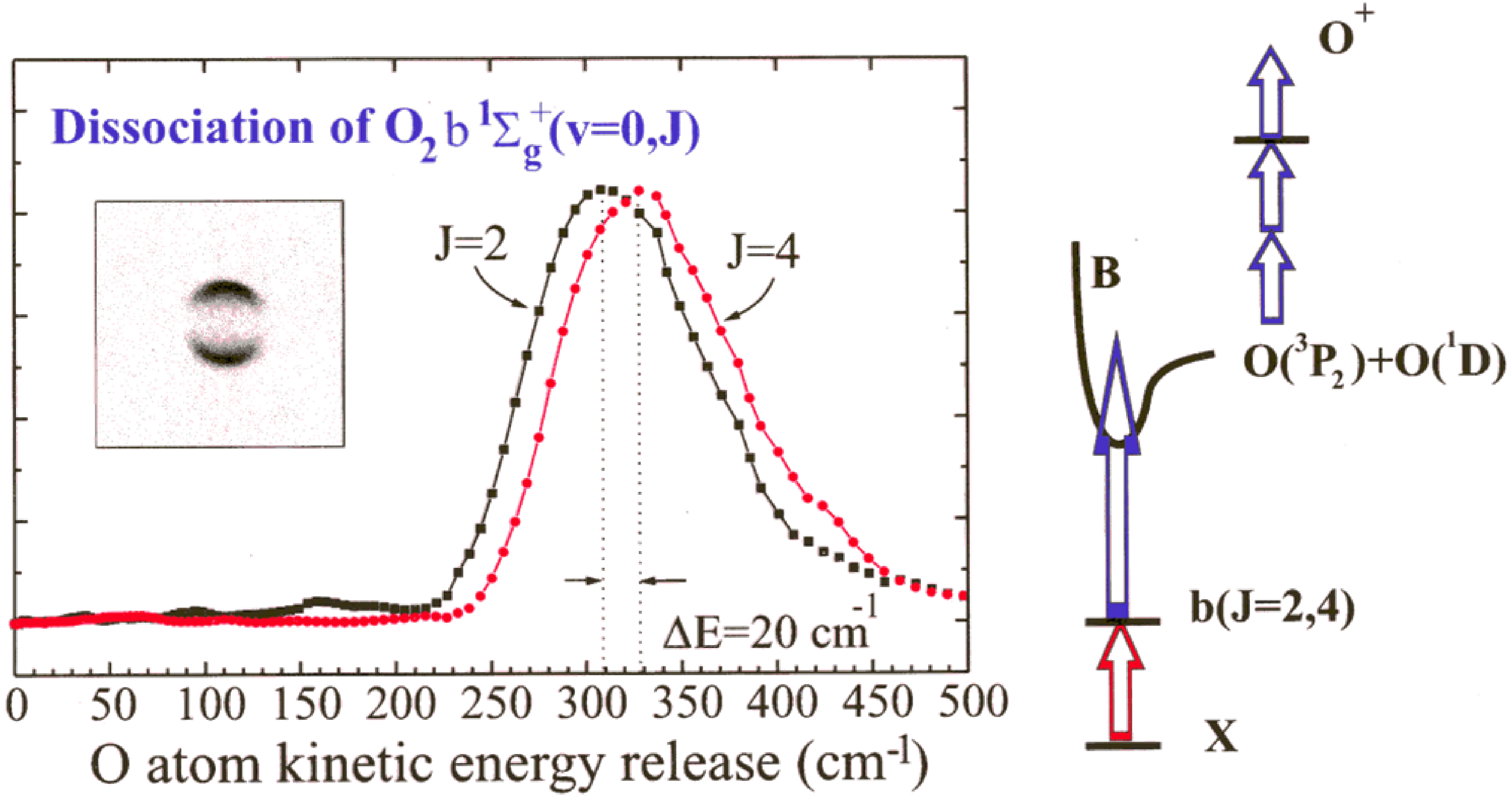


Klotz & Peyerimhoff, Mol. Phys. '86, ab initio
England, Lewis & Gibson , JCP '96, Herzberg I exp.

Deconvolution of the Herzberg Continuum

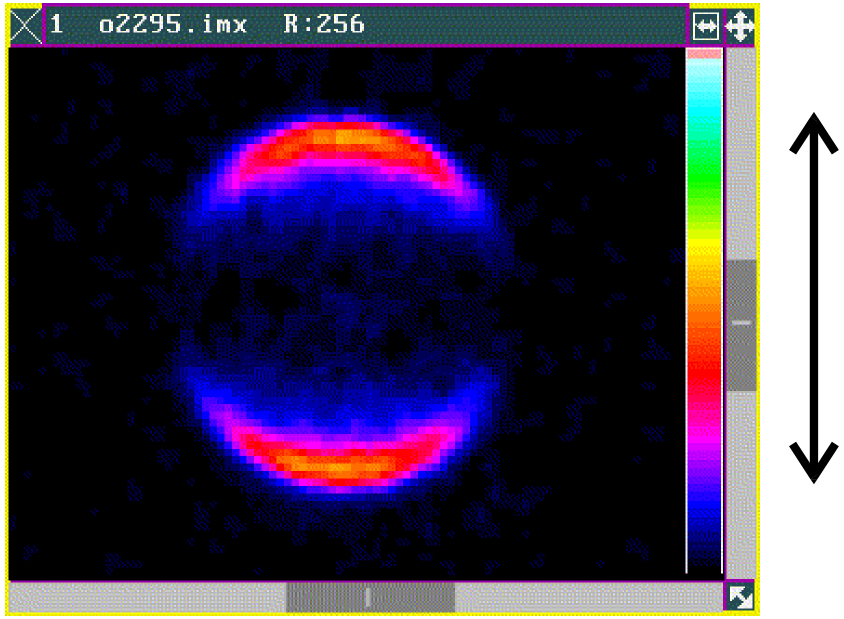


Detection of O_2 b-state by the O($^3P_2$) image

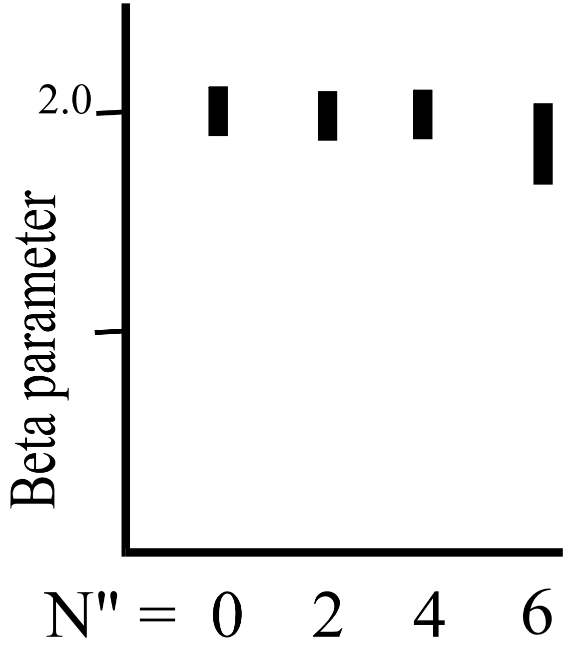


good test of aparatus resolution (limited by electron recoil)

Detection of O_2 b-state by the $O(^3P_2)$ image



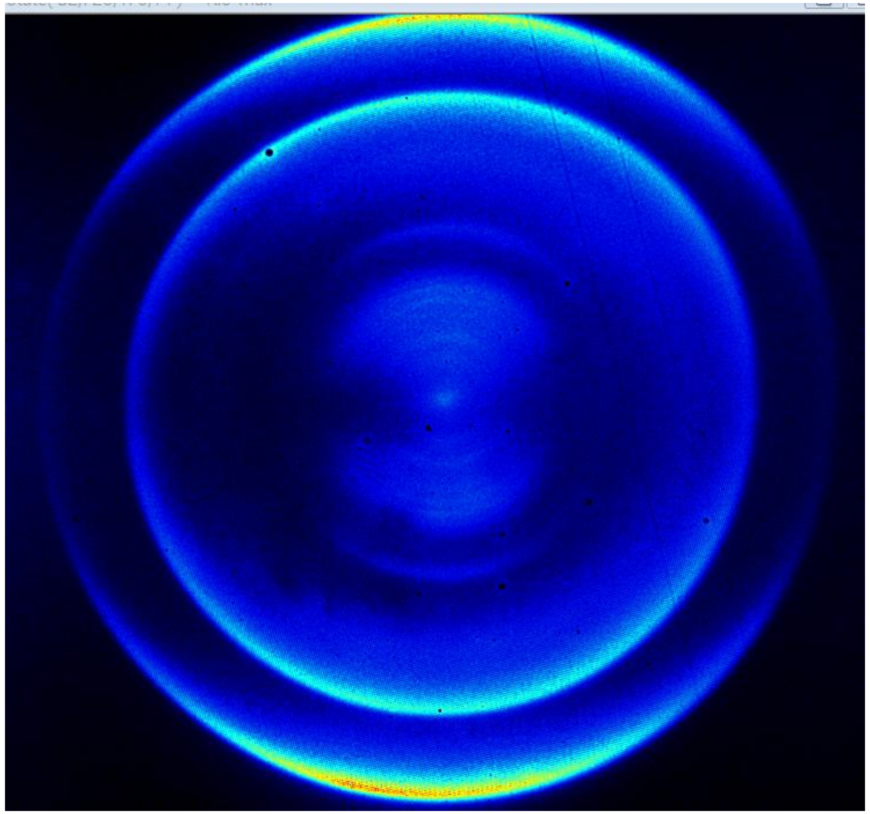
Energy Release =0.04 eV



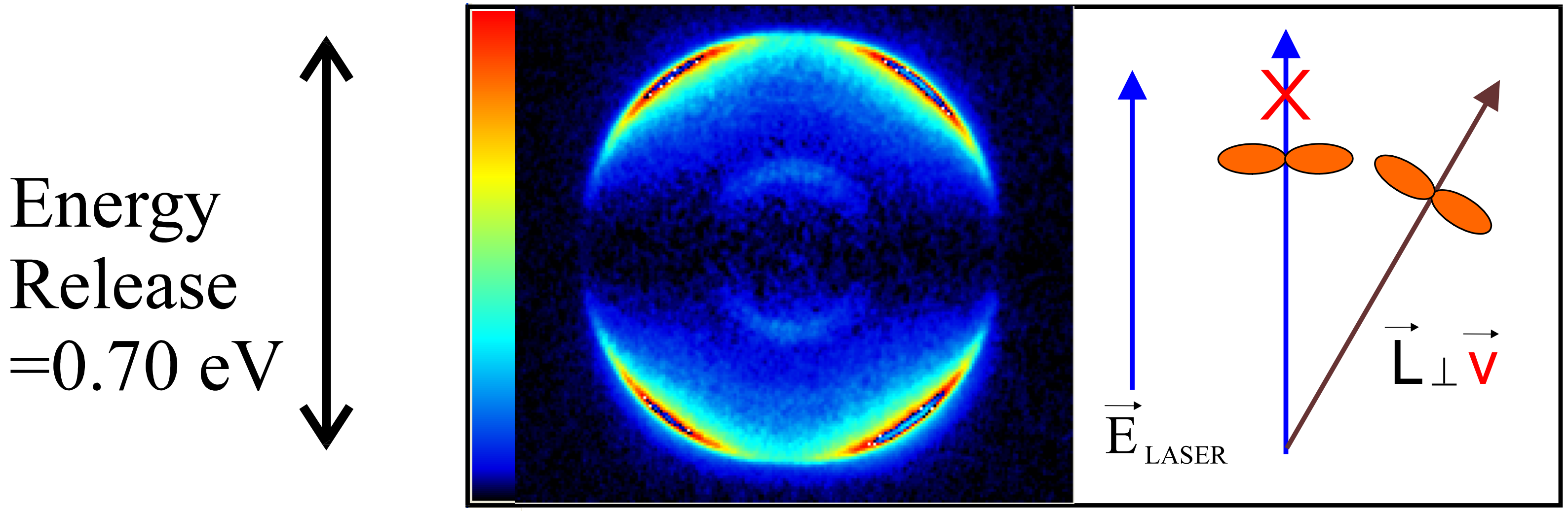
Fine Structure Ratios: $O(^3P_J)$ J=2:1:0 are 1.00 (+/-0.05) : 0 : 0

At threshold β = 2.0, no evidence of alignment effects

Detection of O_2 X-state by the $O(^1D_2)$ image



Detection of O_2 b-state by the $O(^1D_2)$ image



Extra rings are due to (2+1) rempi of b state, dissociation of O_2^+

Maximal M_J=0 production is seen via the b-state

Cluster photodissociation

$$O_2\text{-}X + UV \rightarrow O_2\ (X, a, b) + X$$

$$O_2^- + X^+$$

$$O + O\text{-}X$$

Detection: Absorption, Emission, REMPI ?

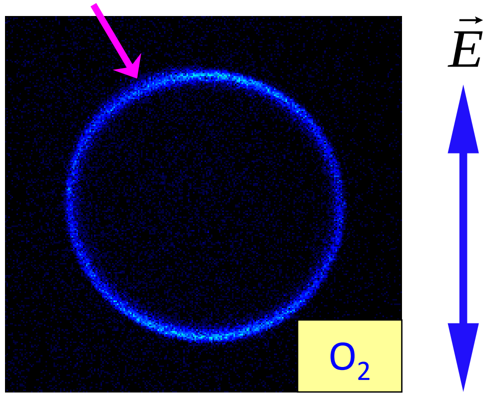
We use: 2+1 REMPI of $O(^3P_{2,1,0})$ at 226 nm

THE $O(^3P)$ IMAGE IS A SIGNATURE OF MANY POSSIBLE FORMS OF O_2

Formation of O_2 a($^1\Delta$) from O_2-X 1:1 van der Waals clusters

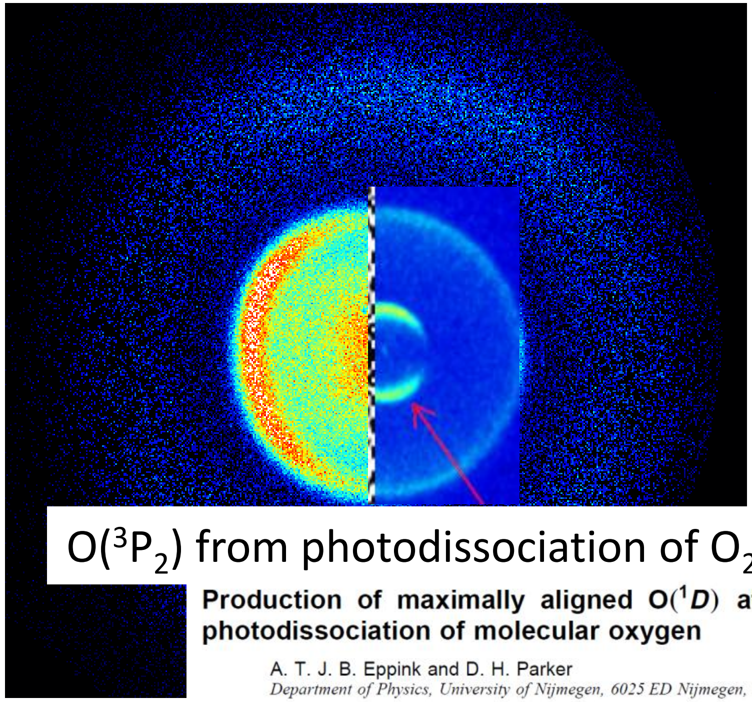
$O_2 + h\nu \rightarrow O + O$

T_{kin}= 0.183 eV



Photodissociation of van der Waals clusters of isoprene with oxygen, C_5H_8–O_2, in the wavelength range 213–277 nm
Konstantin V. Vidma, Pim W. J. M. Frederix, David H. Parker, and Alexey V. Baklanov
J. Chem. Phys. **137**, 054305 (2012)

>330 enhancement in the O($^3P_2$) yield !!!



O($^3P_2$) from photodissociation of O_2 b$^1\Sigma_g$

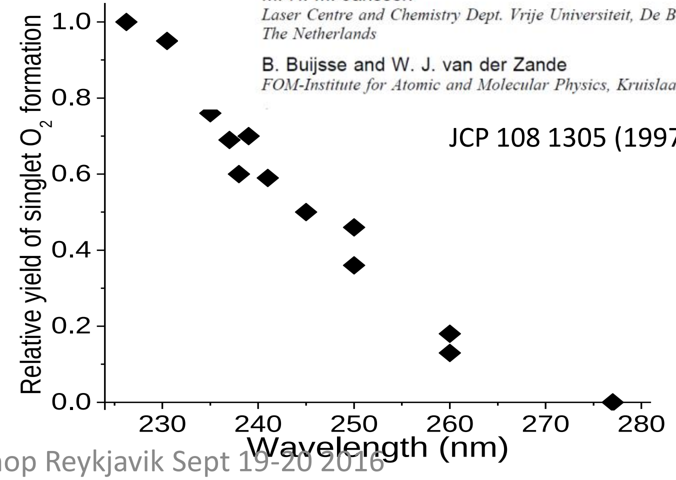
Production of maximally aligned O(^1D) atoms from two-step photodissociation of molecular oxygen

A. T. J. B. Eppink and D. H. Parker
Department of Physics, University of Nijmegen, 6025 ED Nijmegen, The Netherlands

M. H. M. Janssen
Laser Centre and Chemistry Dept. Vrije Universiteit, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

B. Buijsse and W. J. van der Zande
FOM-Institute for Atomic and Molecular Physics, Kruislaan 407, 1098 SJ Amsterdam, The Netherlands

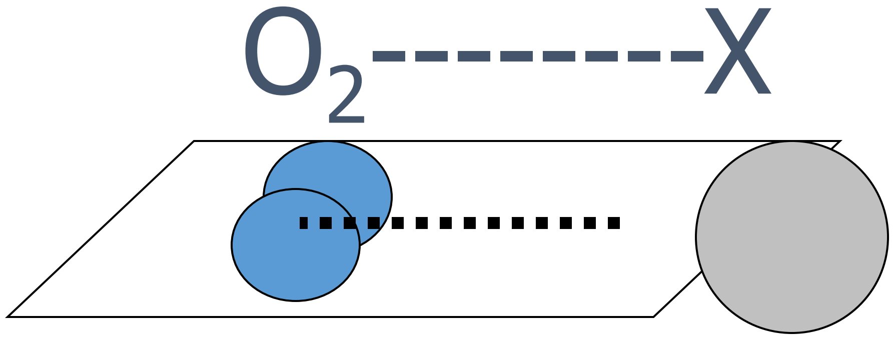
JCP 108 1305 (1997)



Clusters X-O_2

Symmetry breaking

	Herzberg transition	⊥ / ll	forbidden by:
I	$X^3\Sigma_g^- \rightarrow A^3\Sigma_u^+$	mixed	parity ($\sigma_{mol\ plane}$)
II	$X^3\Sigma_g^- \rightarrow c^1\Sigma_u^-$	⊥	spin
III	$X^3\Sigma_g^- \rightarrow A'^3\Delta_u$	⊥	$\Delta L=2$ (press. dep.)

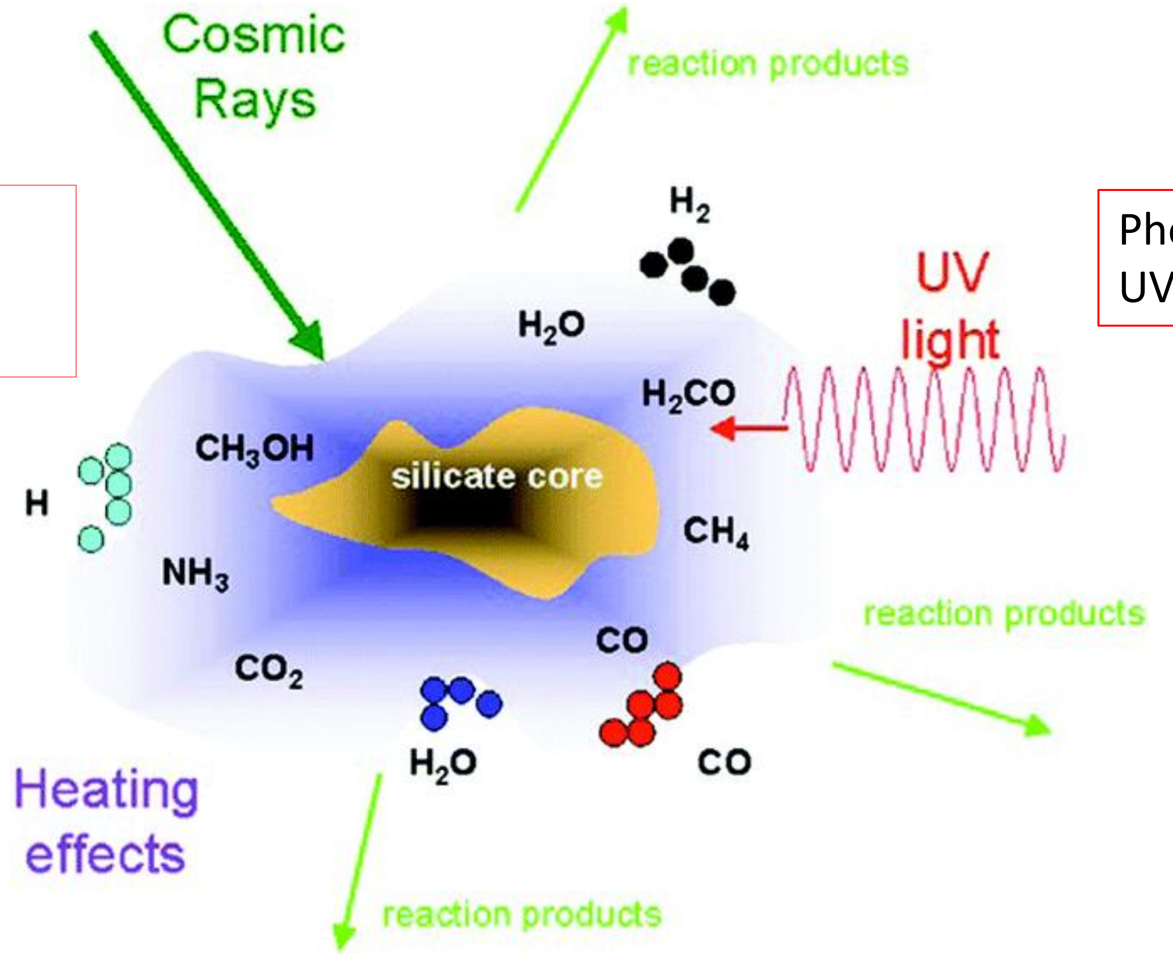


The Herzberg III band is enhanced by collisions (x50 at 1 bar)

Ice surfaces and astrochemistry

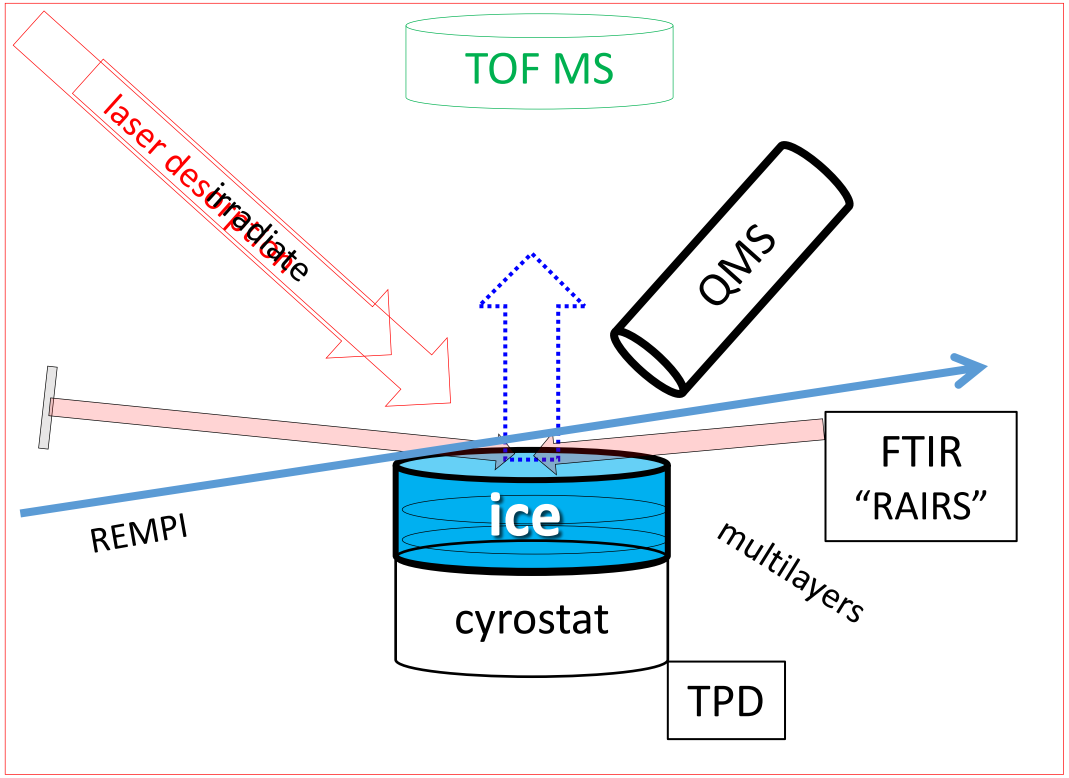
T = 10-100K

too much gas!



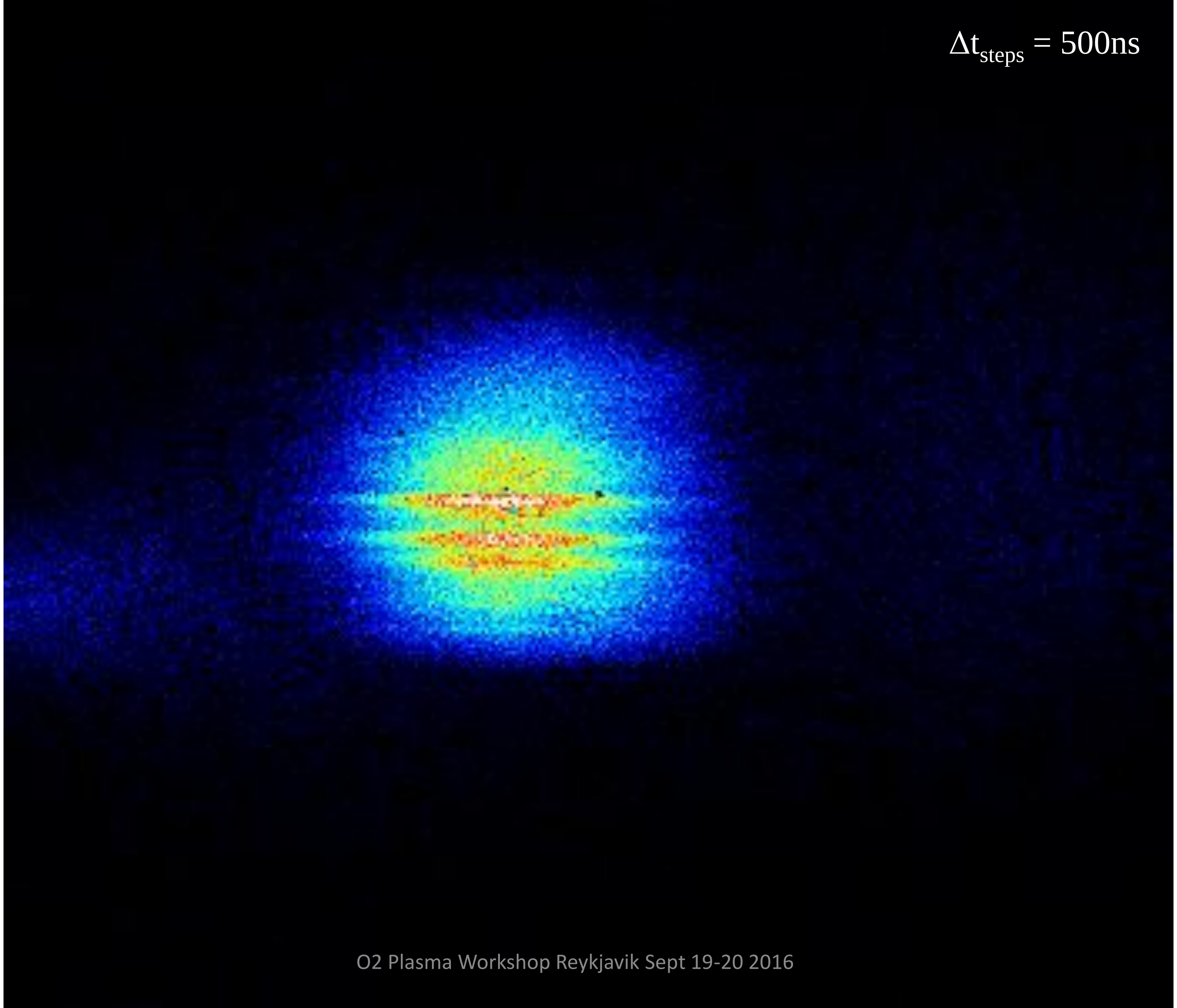
Photodesorption by UV-VUV light

Studying ice surface photochemistry

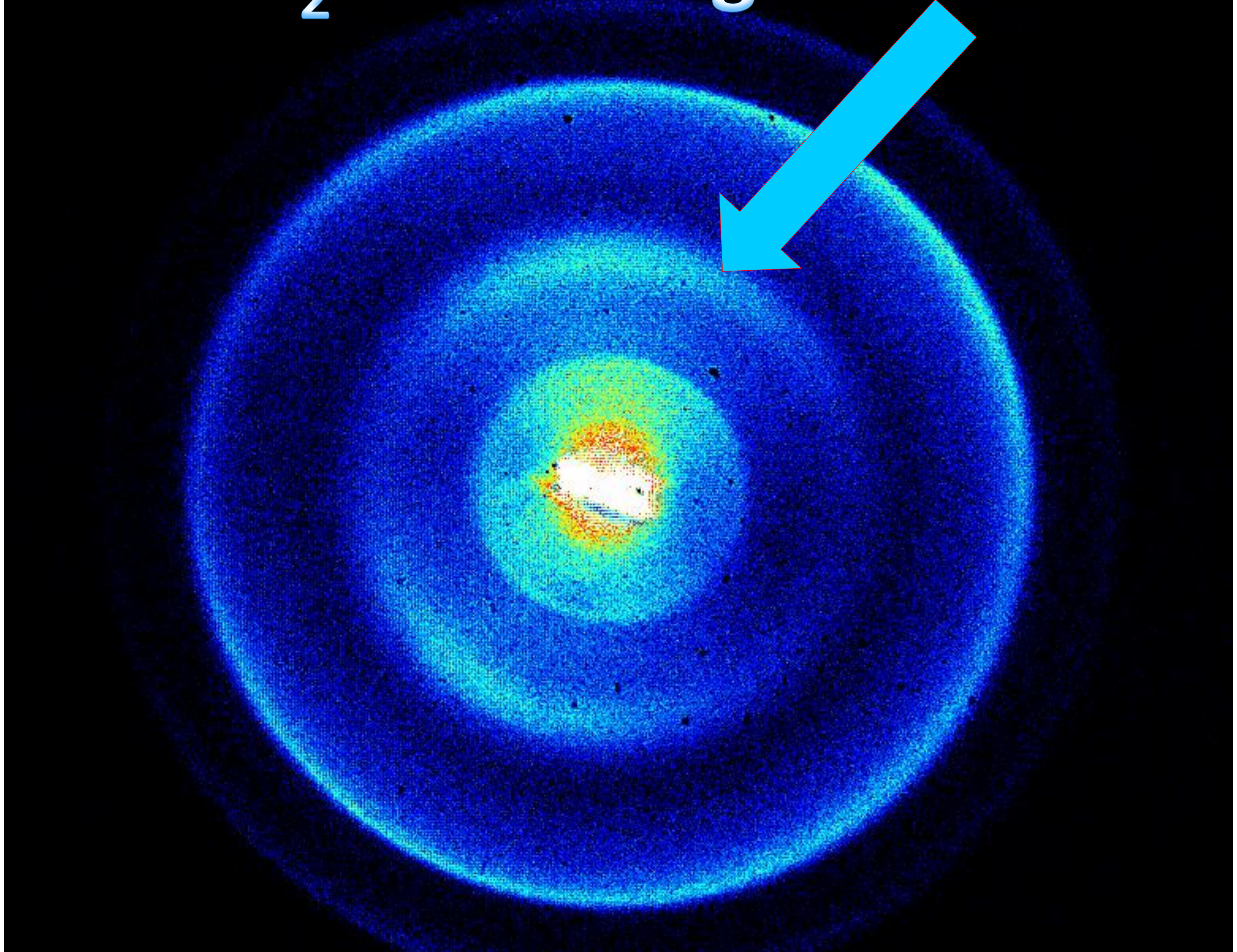


Procedure

1. Grow Ice surface
2. Characterize by
   a) RAIRS
   b) TPD-QMS
3. Irradiate (pulsed or cw)
4. Characterize by
   a) RAIRS
   b) TPD-QMS
   c) post-ioniz. TOF-MS
   d) VMI

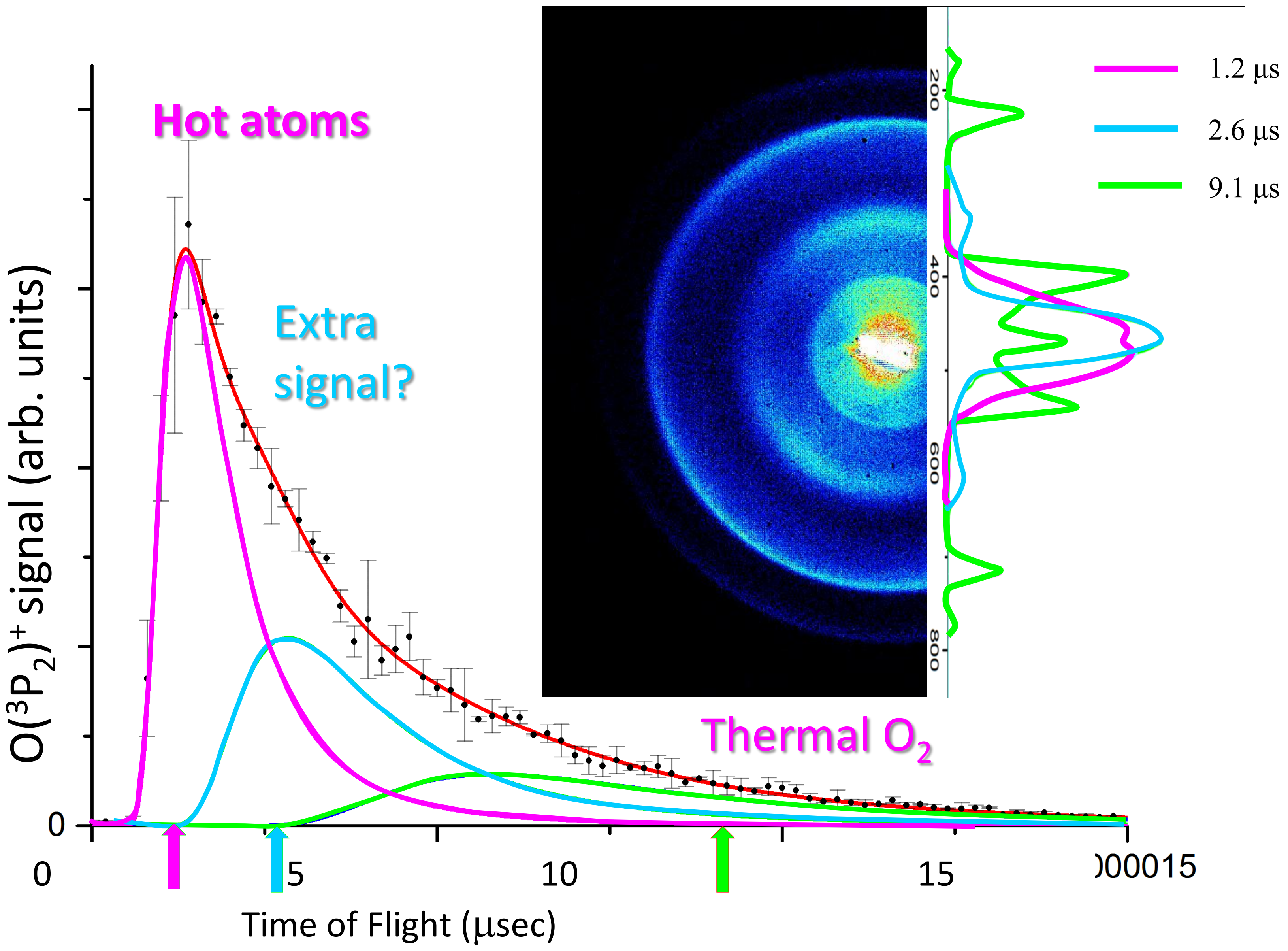

Δt_{steps} = 500ns

O_2 a-state signature

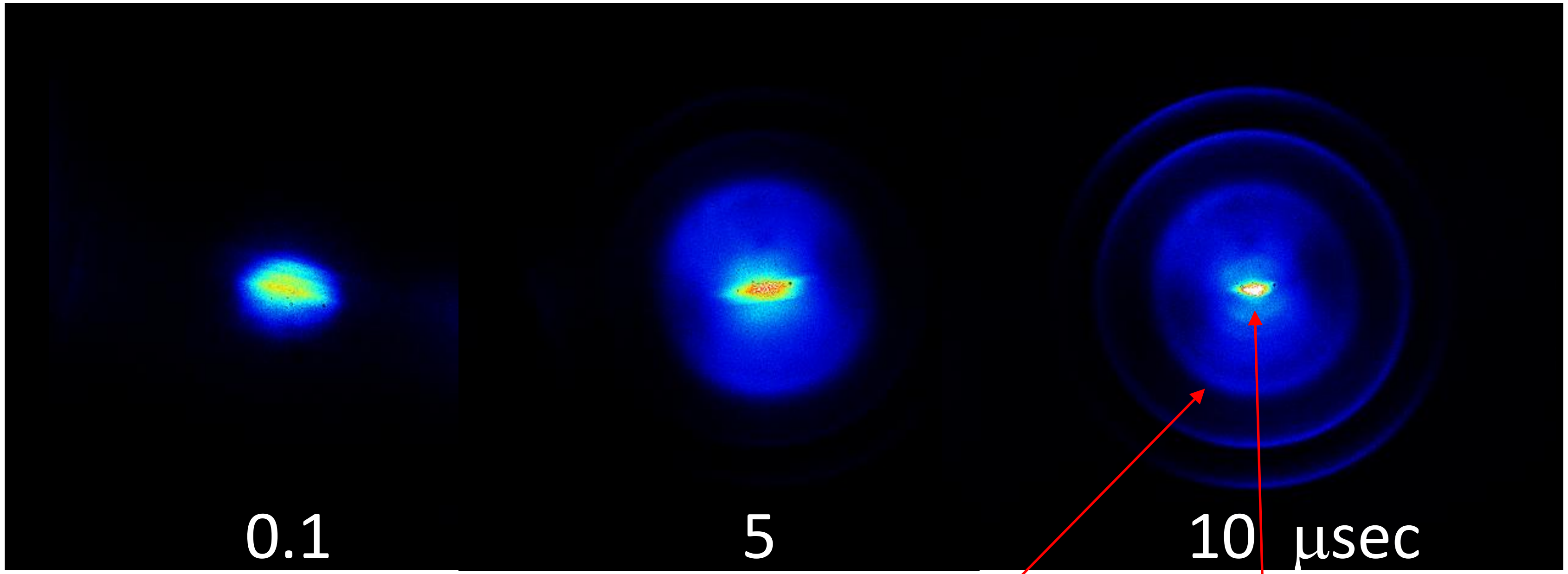


Occurs at 250 nm and 320 nm
and from H_2O-ice and CO_2-ice at 250nm!

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



O(^{1}D) signatures 250 nm desorption

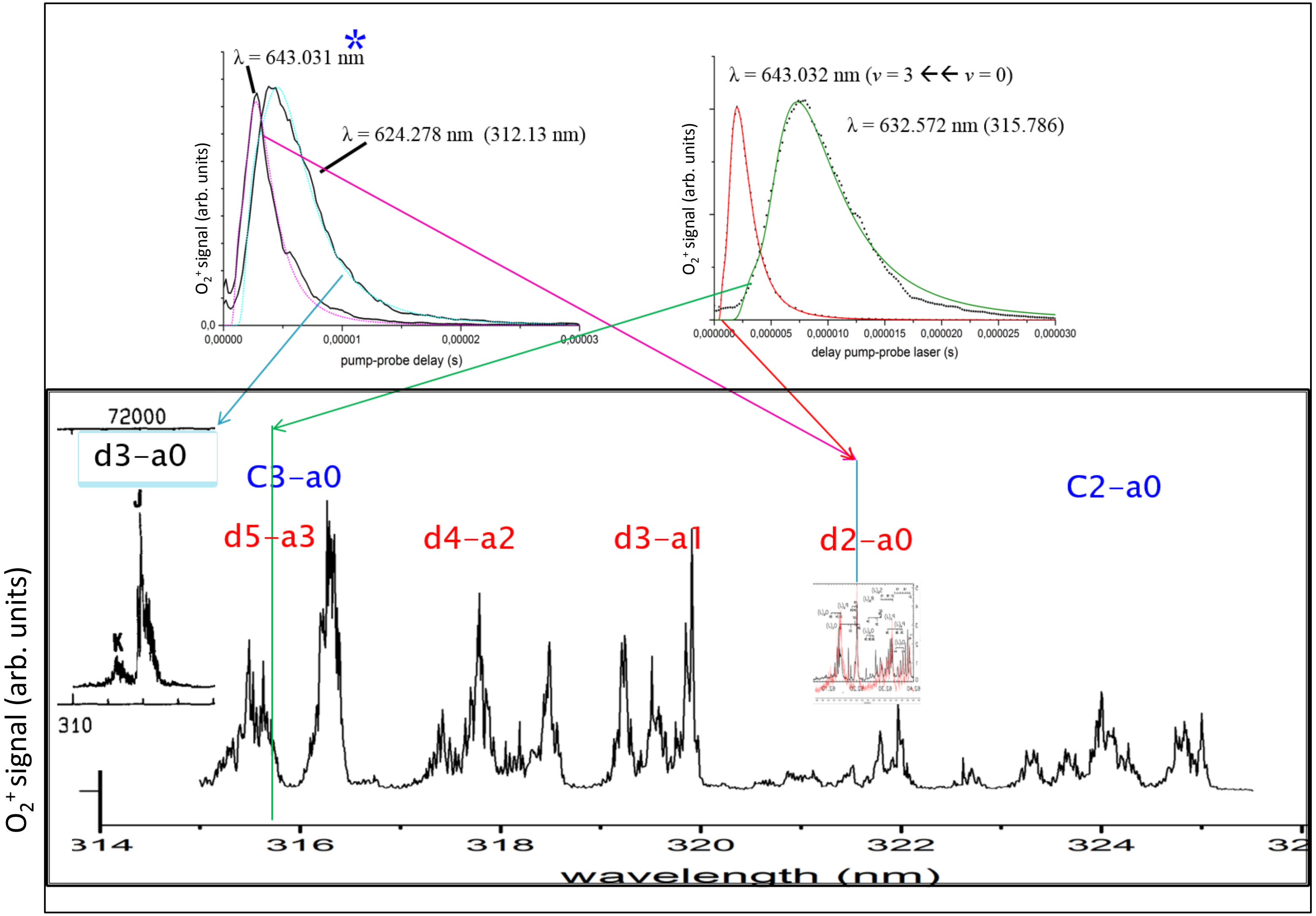


Hot O(^{1}D)

O_2 X(v>5)

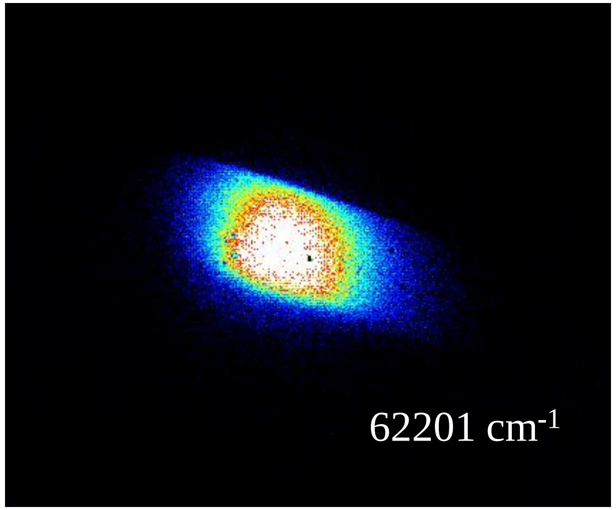
O_2 H1 ??

REMPI spectrum in a-state region

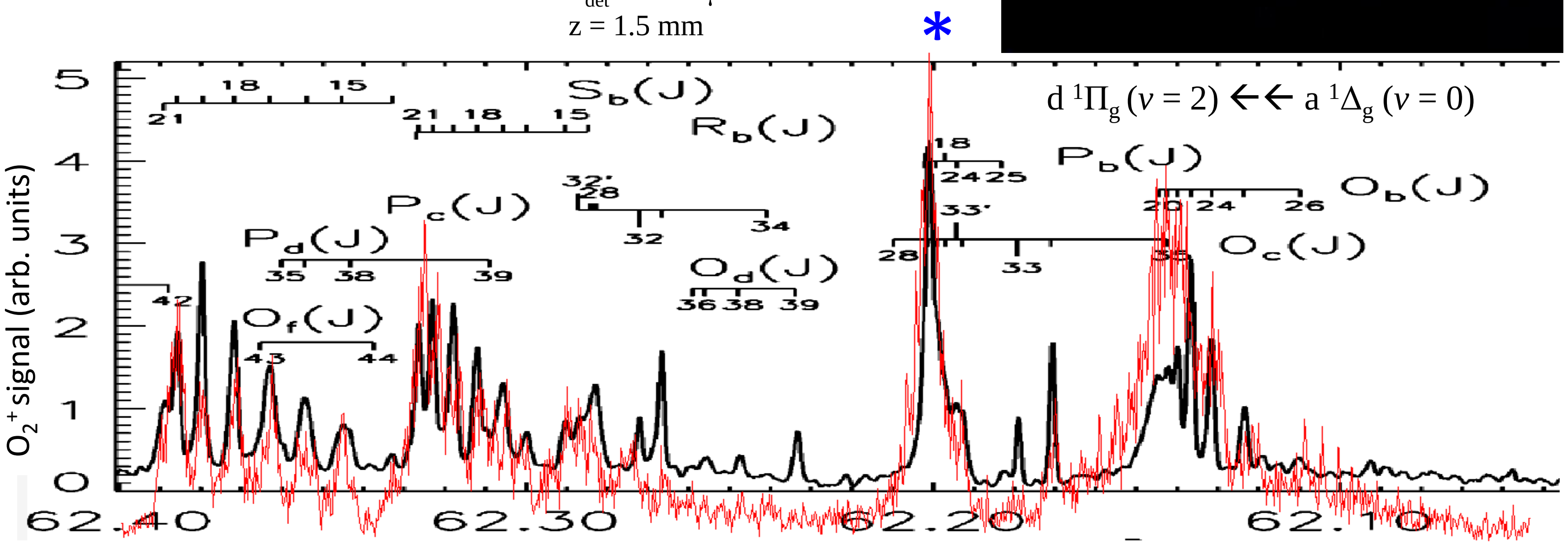


REMPI spectrum: confirmation of O-a($^1\Delta_g$) state

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

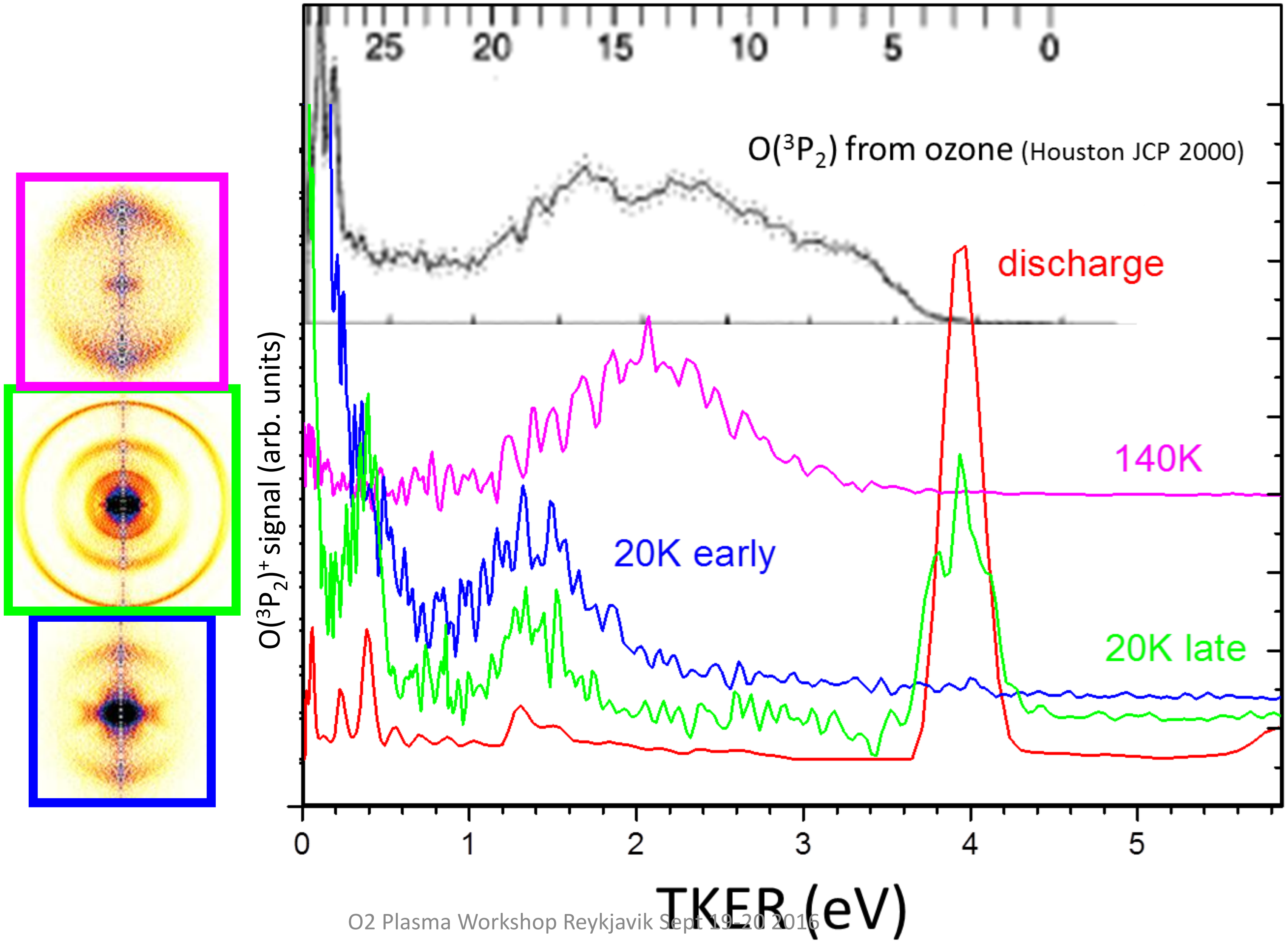


T_s = 10 K, ~80 ML O_2-ice
λ_{des} = 250 nm, P = 600 μJ
λ_{det} = REMPI 641 – 645 nm[O_2^+],
P_{det} = 1500 μJ
z = 1.5 mm



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

Desorption of $O(^3P_2)$ from 20K and 140K O_2-ice at 320 nm



Finally, O_2 discharges

A study of arrested development

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PAPER

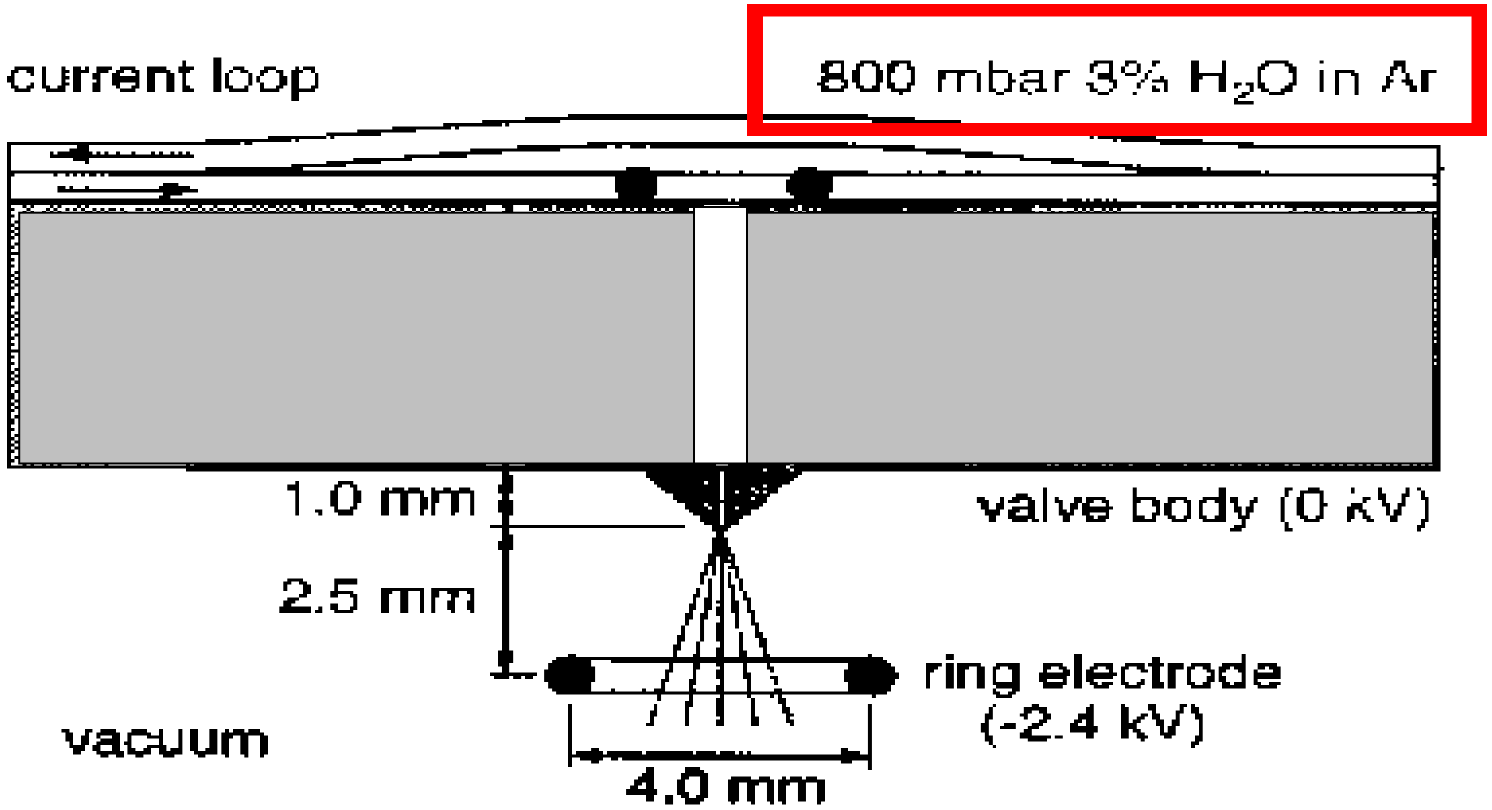
Photodissociation of singlet oxygen in the UV region

Cite this: *Phys. Chem. Chem. Phys.*, 2014, **16**, 3305

Zahid Farooq, Dimitri A. Chestakov, Bin Yan, Gerrit C. Groenenboom, Wim J. van der Zande and David H. Parker*

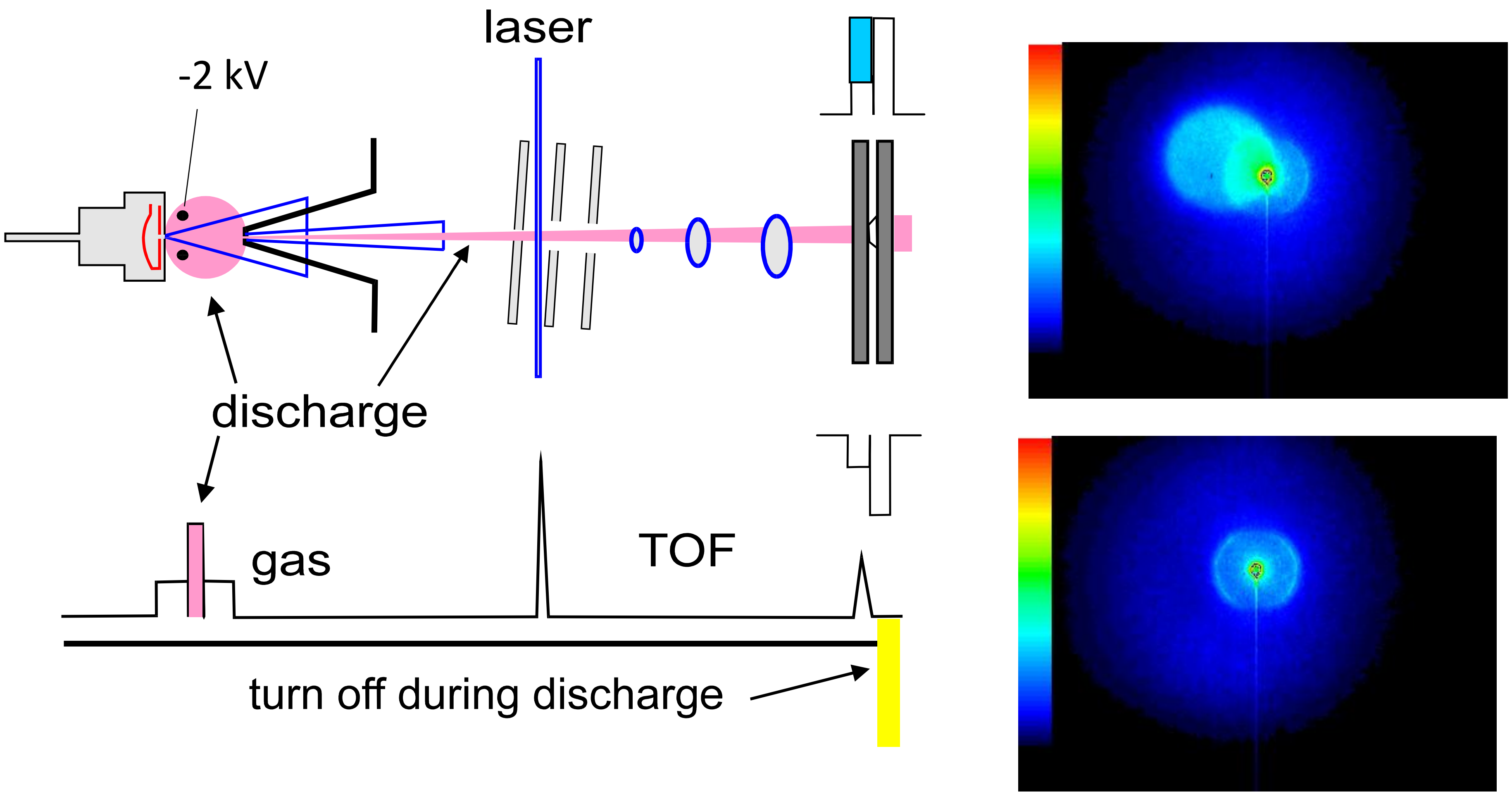
4.0 mm

M.van Beek & J.J ter Meulen CPL 2001



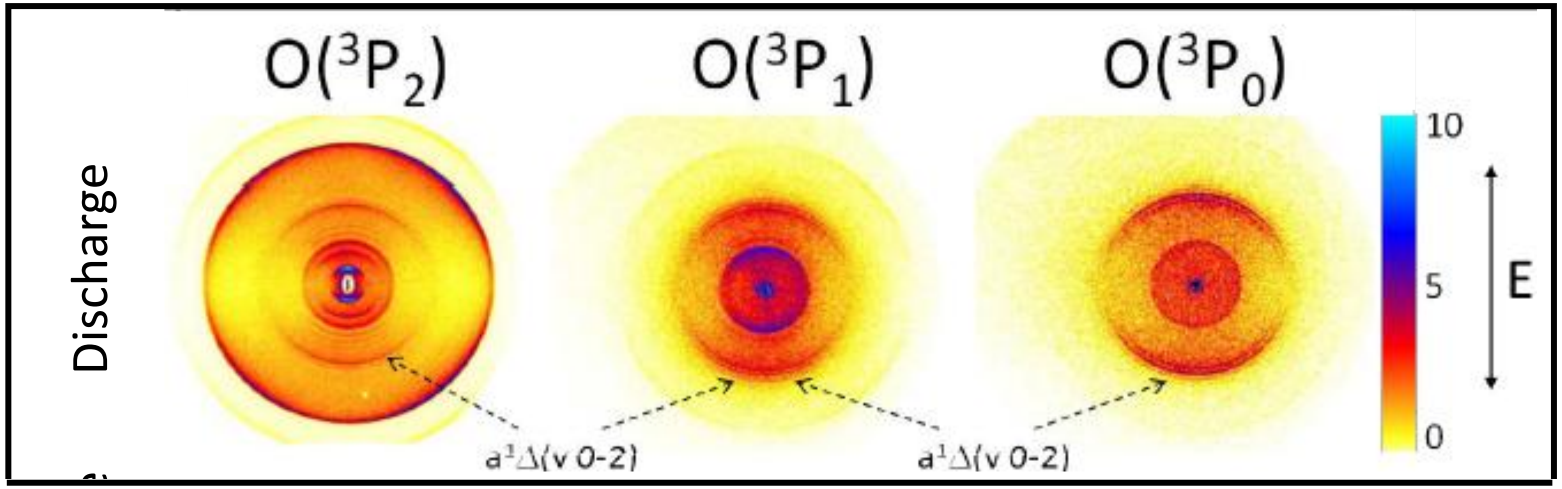
OH flux = $2 \cdot 10^{17}$ #/ster.sec !!

Experiment: Pulsed expansion of water/Ar, HV discharge pulse during middle of expansion, skimmed, cross with one or two UV lasers, image $O(^3P_J)$ products. Turn off channelplates during discharge to avoid looking at XUV photons. Lots of cold $O(^3P_2)$ atoms formed, and Fe* from electrodes.

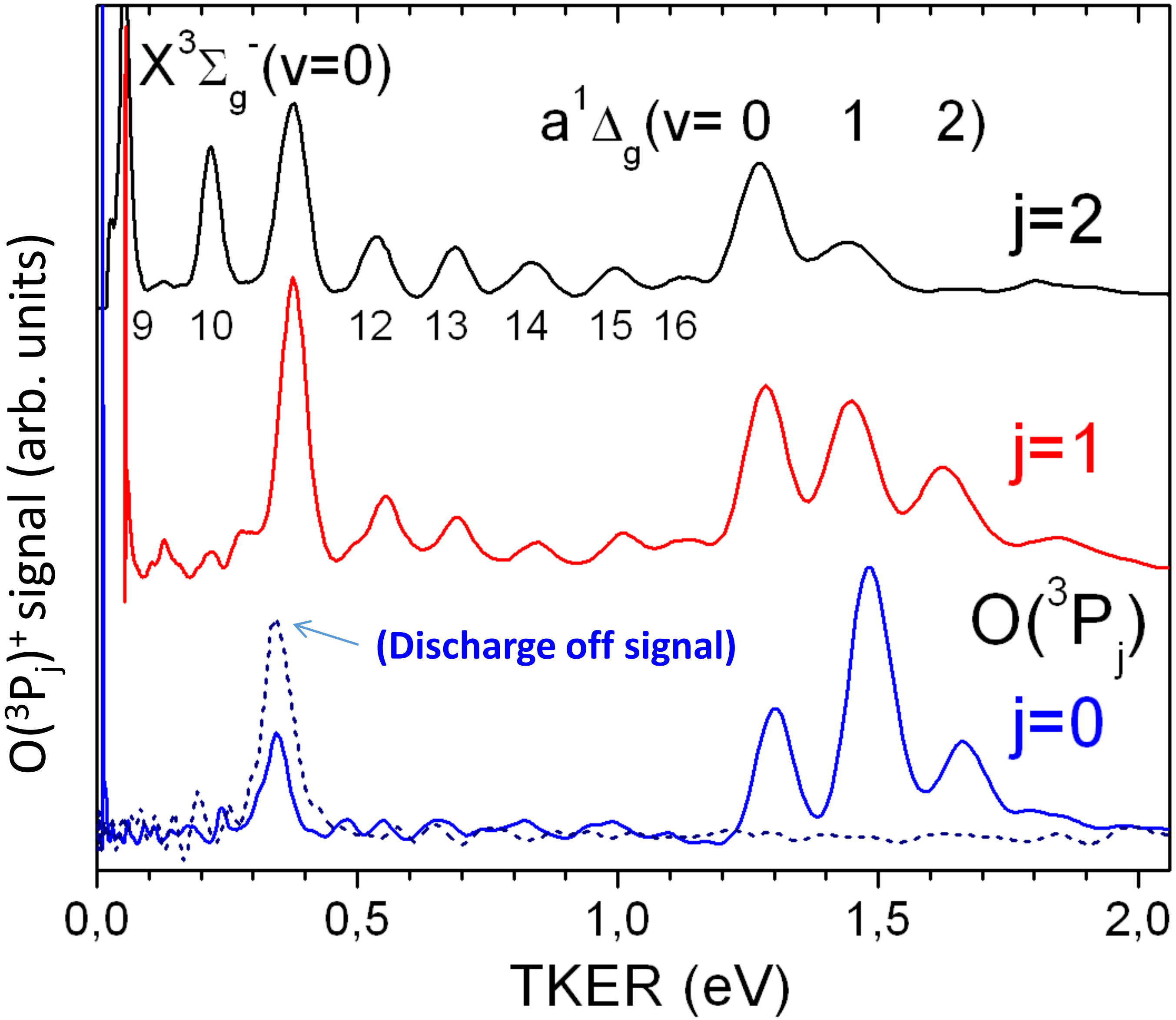


Photodissociation of singlet oxygen in the UV region

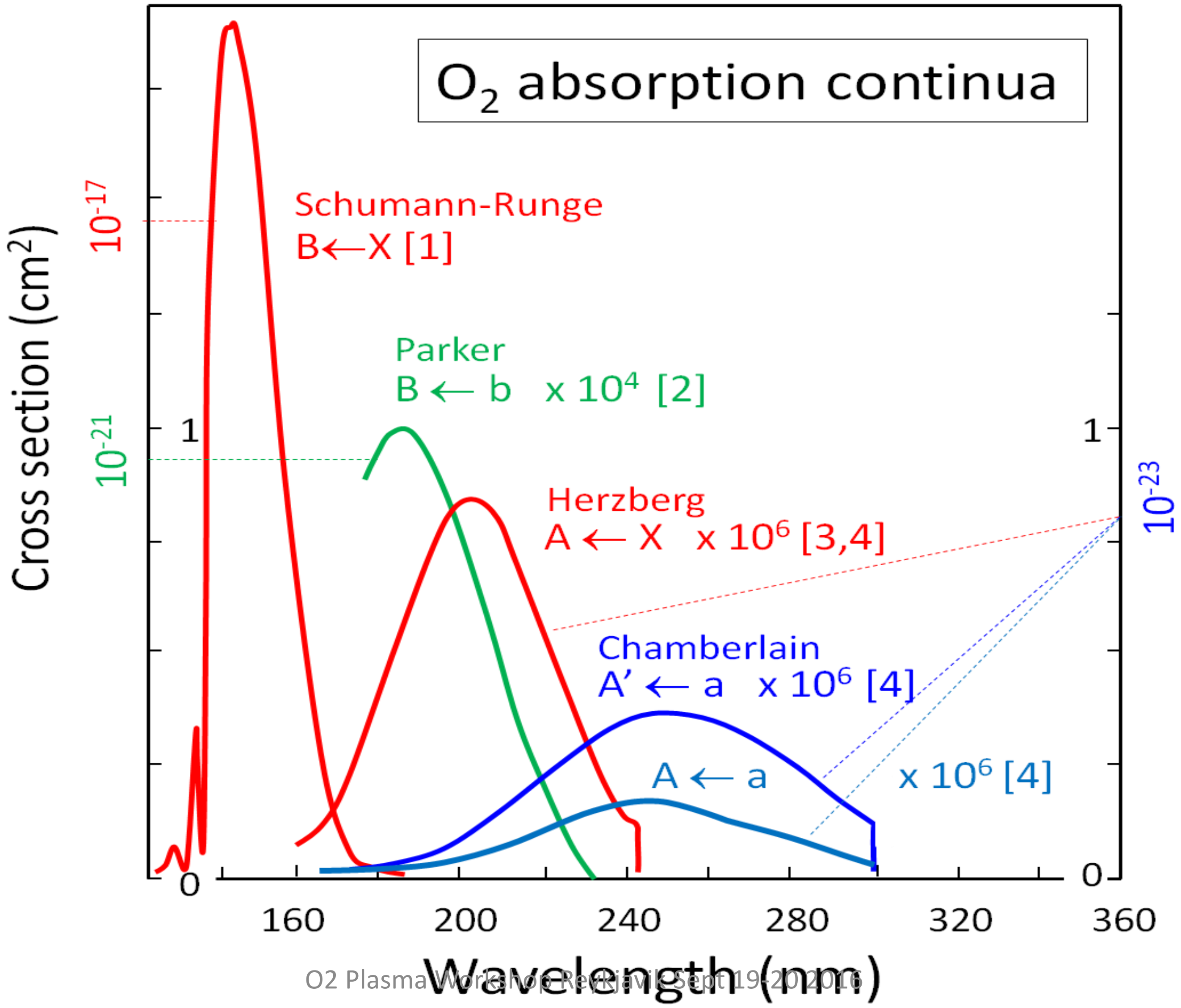
Zahid Farooq, Dimitri A. Chestakov, Bin Yan, Gerrit C. Groenenboom, Wim J. van der Zande and David H. Parker* *Phys. Chem. Chem. Phys.*, 2014, 16, 3305



Energy distributions $O(^3P_j)$ from O_2 discharge



Photodissociation cross sections for the O_2 X, a, b states



Conclusions

- Many forms of O_2 can be identified in an O atom image
- Enhanced absorption in O_2-van der Waals clusters efficiently produces singlet oxygen in a spin flip process
- Laser desorption at 10K O_2-ice surfaces leads to atom recombination to produce significant amounts of singlet oxygen, along with O atoms and hot X O_2
- Atom recombination in discharge produces a significant amount of singlet oxygen, hot ground state molecules, and $O(^3P_2)$ atoms

NWO
Netherlands Organisation for Scientific Research

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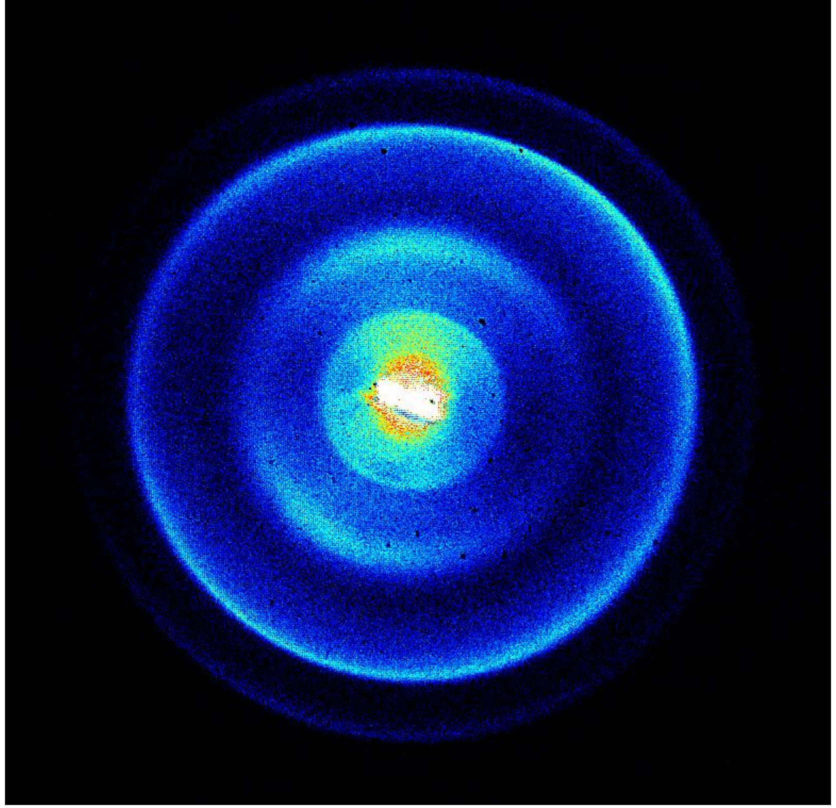

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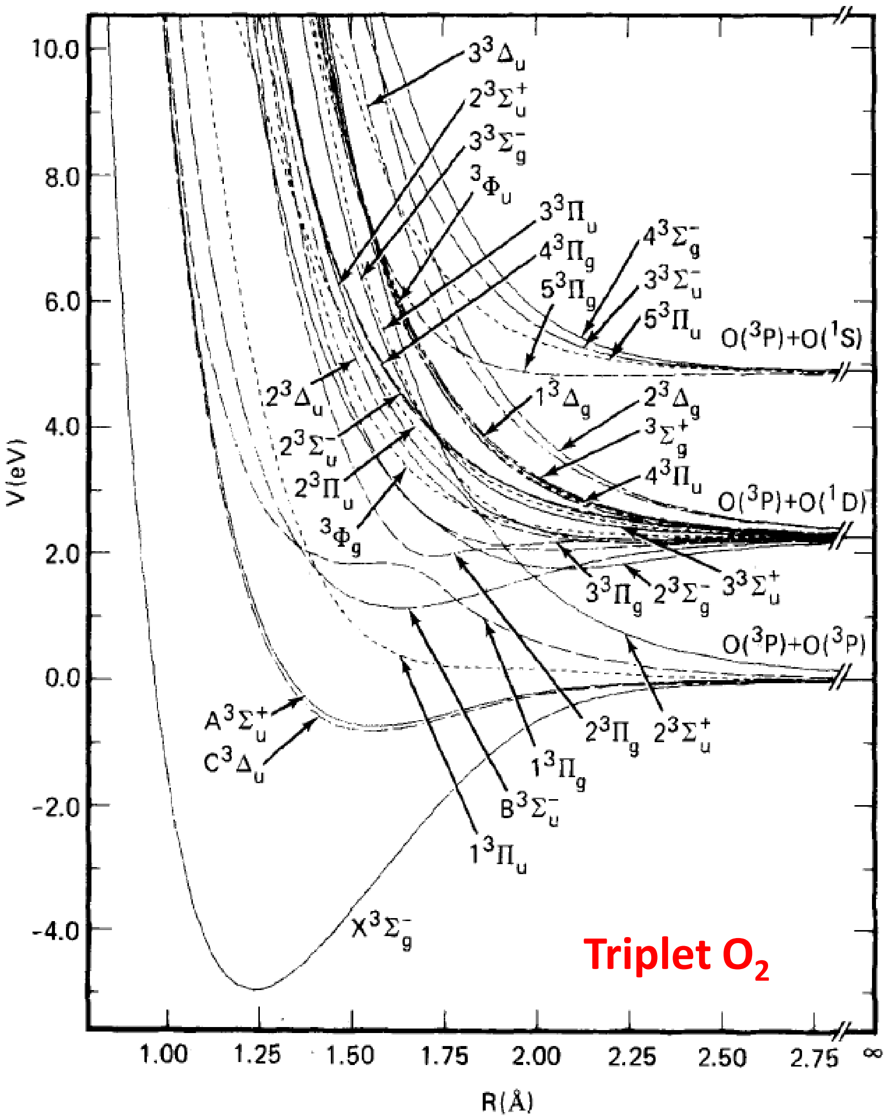
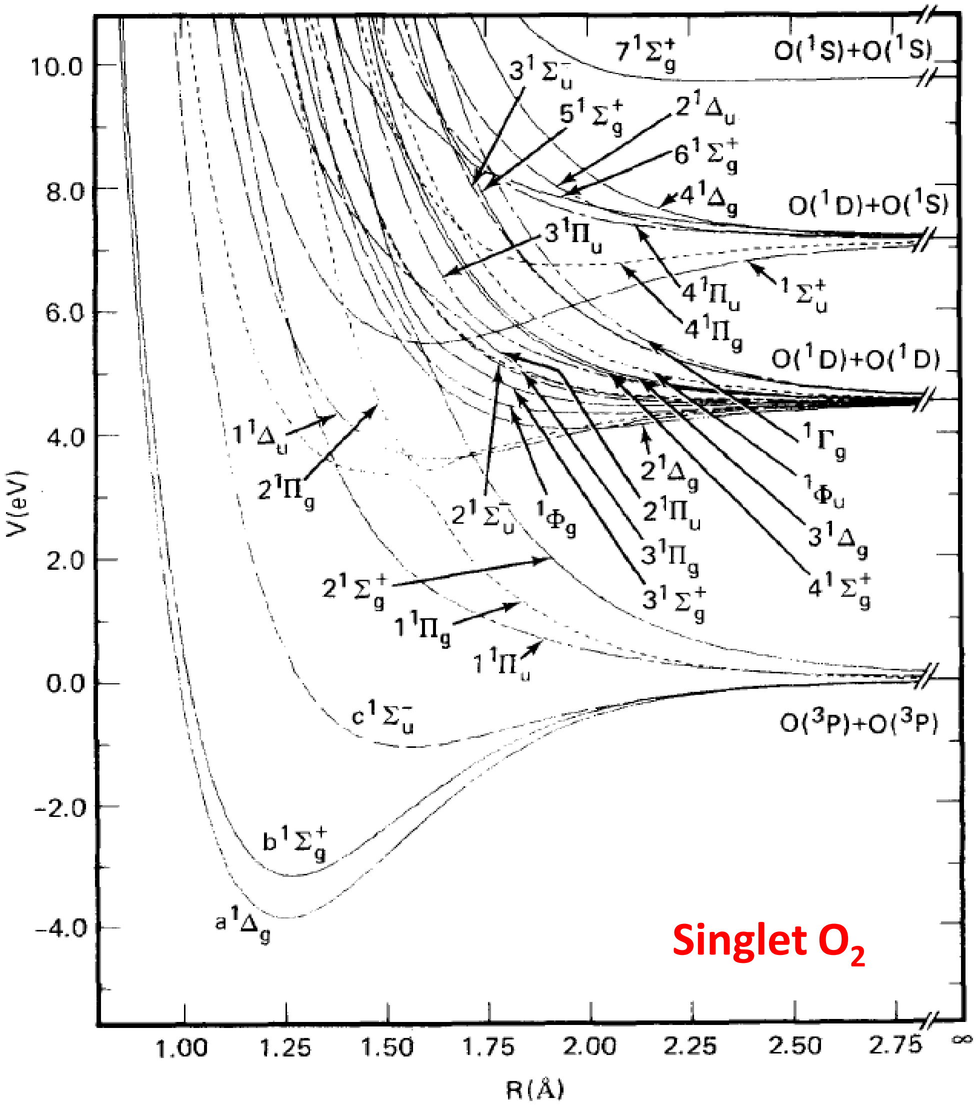
Thanks for your attention!

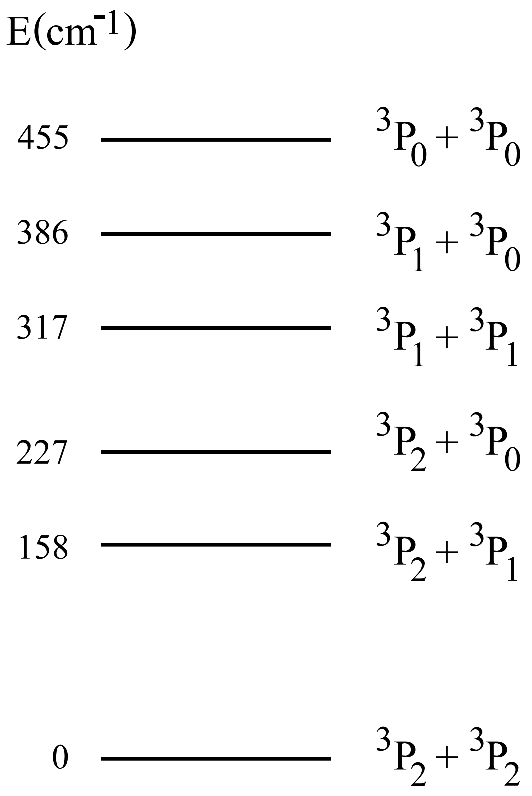
There are many more non-bound states than bound states!





$O_2 + h\nu \rightarrow O(^3P) + O(^3P)$

Fine structure dissociation limits



(2+1) REMPI detection scheme