NOO Peroxy Isomer Exposed With Velocity-Map Imaging

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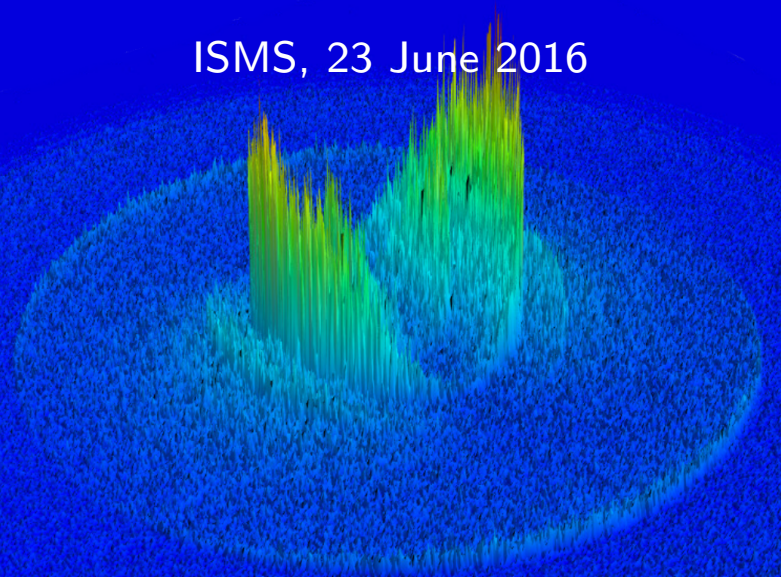
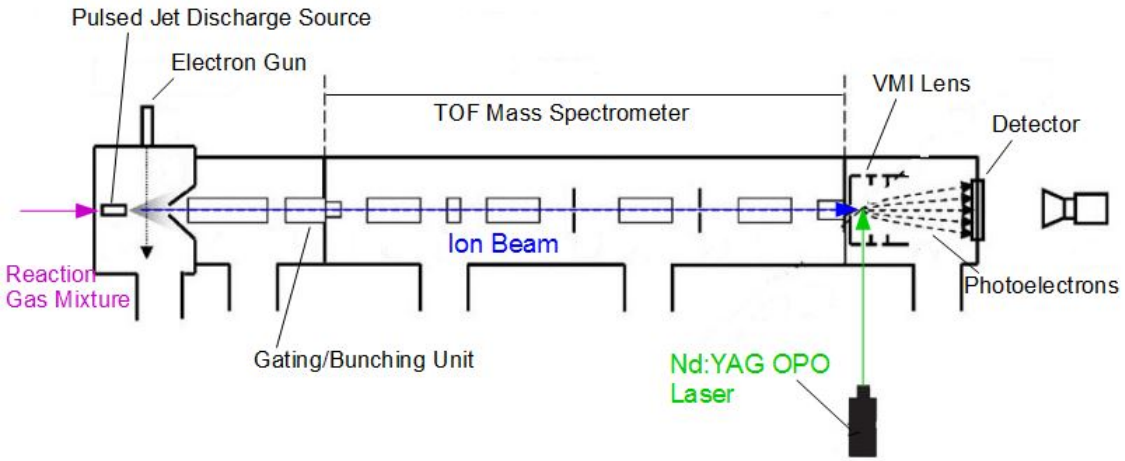
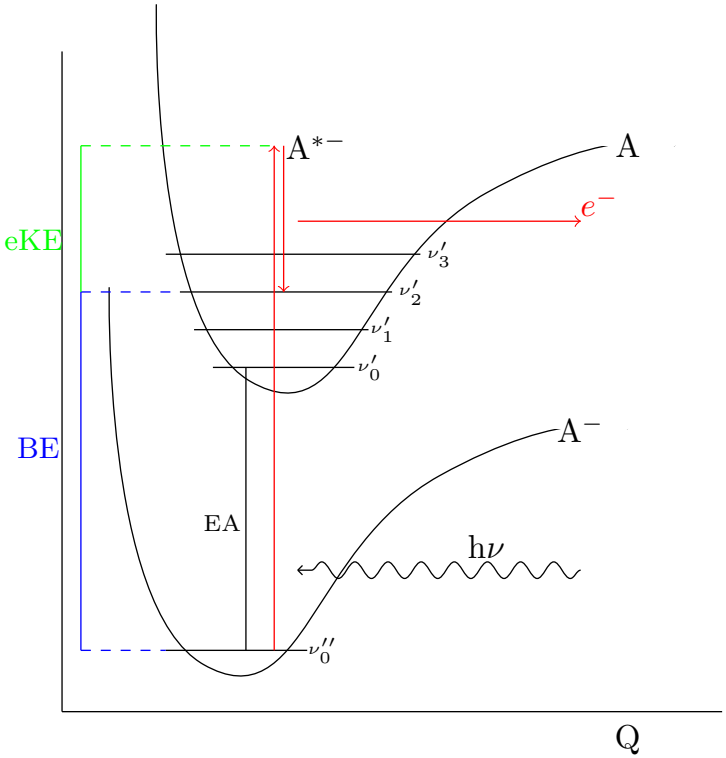
ISMS, 23 June 2016



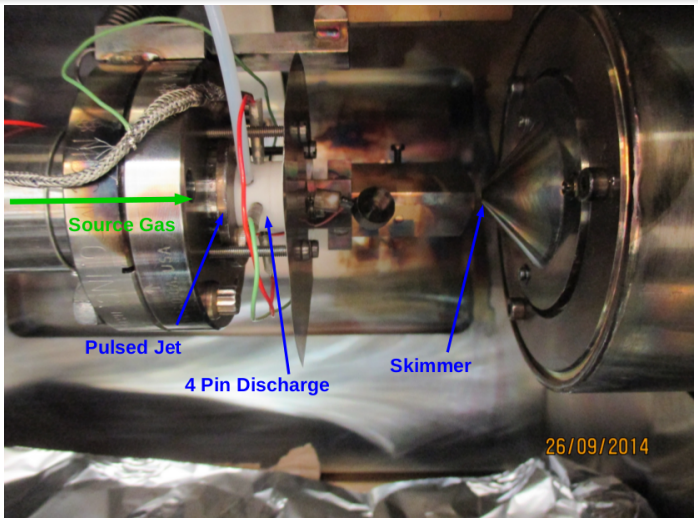
- Photodetachment/VMI
- VMI $NO_2^- \rightarrow NO_2$
- Peroxy NOO isomer
  - PES
  - PAD
  - Dynamics

Photoelectron Spectroscopy

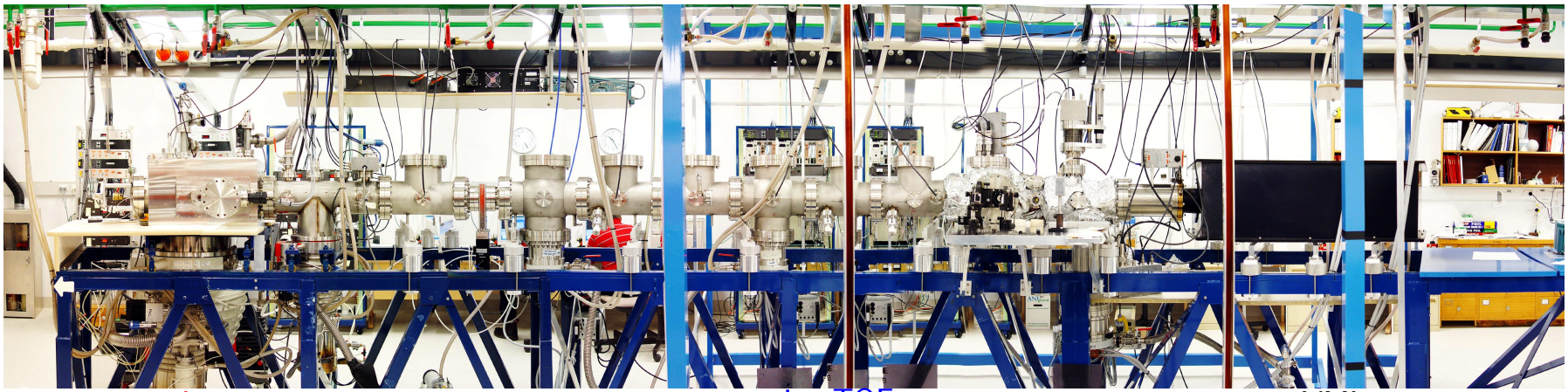




$$A^- + h\nu \rightarrow A^{*-} \rightarrow A^* + e^-$$



Spectrometer - photodetachment/photofragmentation



Fast beam spectrometer (based on Neumark/Continetti design):

Cyr PhD Thesis (UC Berkeley 1993)

Velocity-map imaging lens:

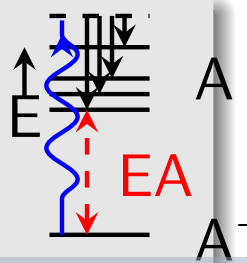
Eppink and Parker Rev Sci Instrum **68** 3477 (1997)

Gating-bunching-rereferencing unit:

(ANU) Dedman *et al.* Rev Sci Instrum **73** 2915 (2001)

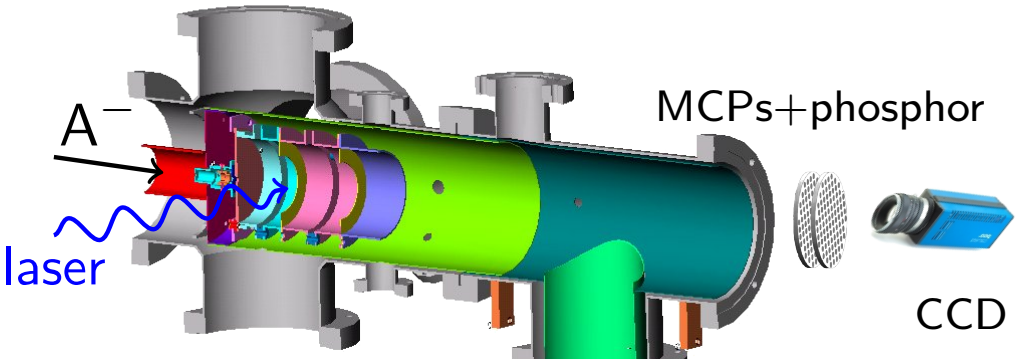
Photodetachment:

$$A^- + h\nu \rightarrow A^* + e^-$$

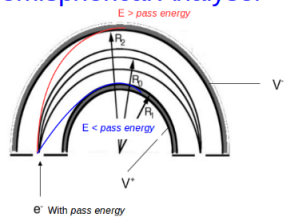


Velocity-map imaging

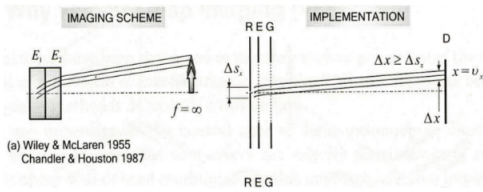
VMI lens coaxial with ion-beam



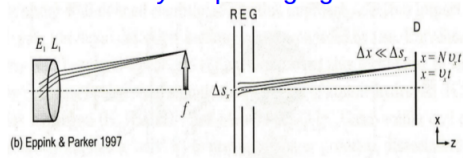
Hemispherical Analyser



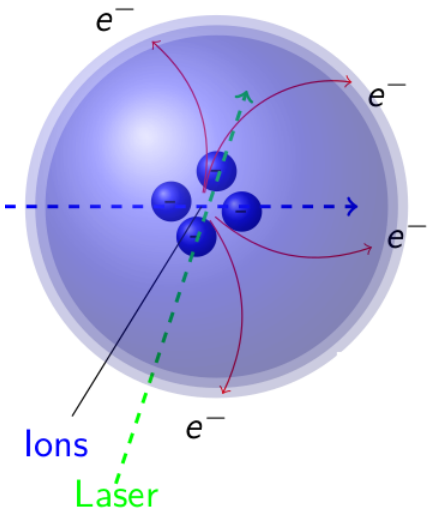
Grid Electrode Lens



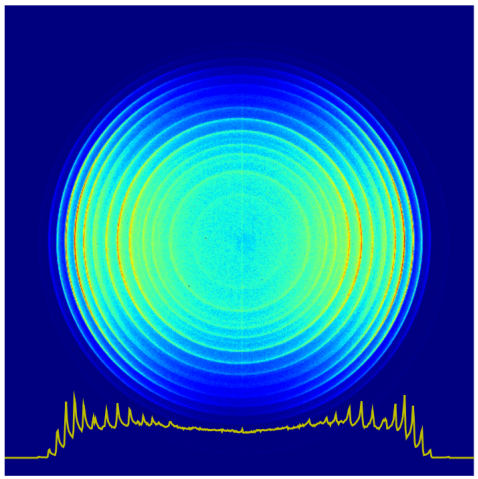
Velocity Map Imaging Lens



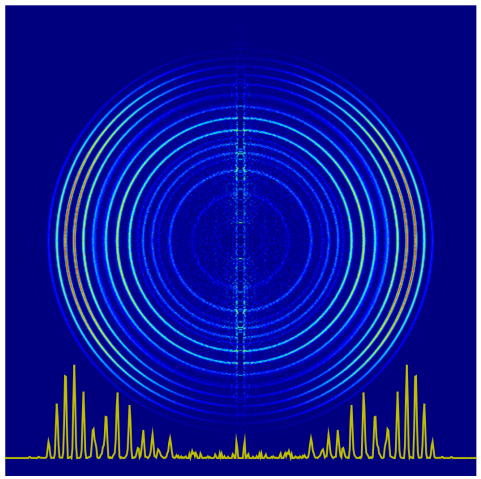
3D Photodetachment



2D Projection of O_2^-



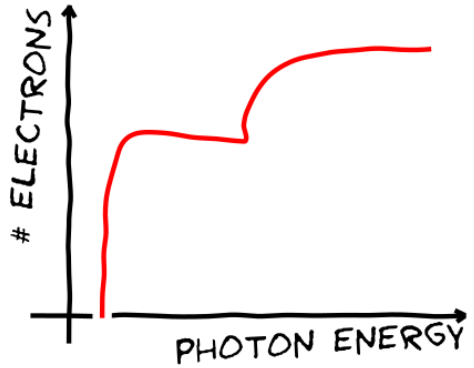
3D slice



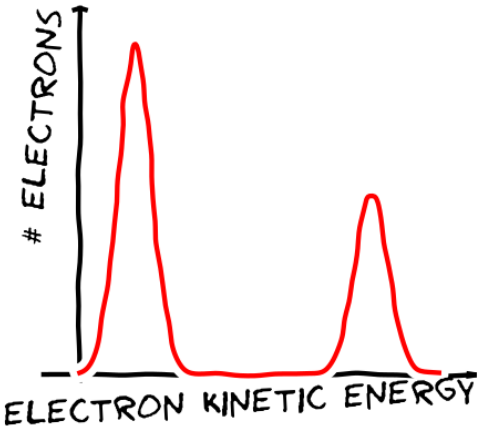
Inverse Abel transformation: Gascooke/Hansen and Law

Velocity-map imaging

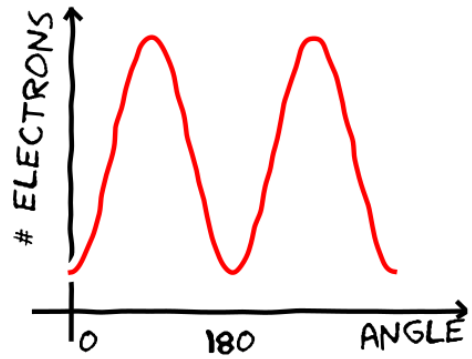
e^- Intensity vs photon energy



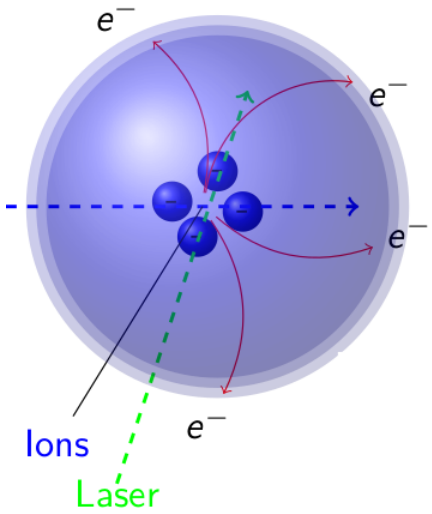
Photoelectron spectrum (PES)



PE angular distribution (PAD)



3D Photodetachment



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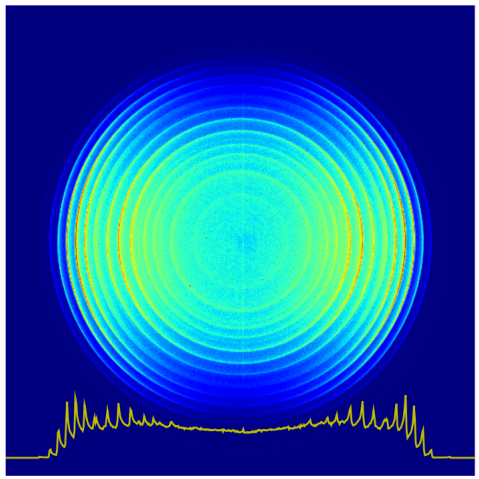
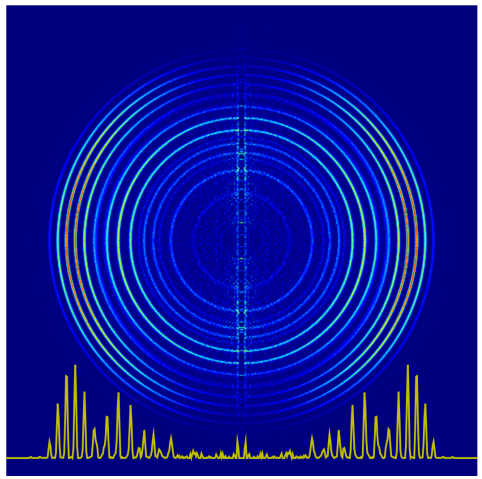


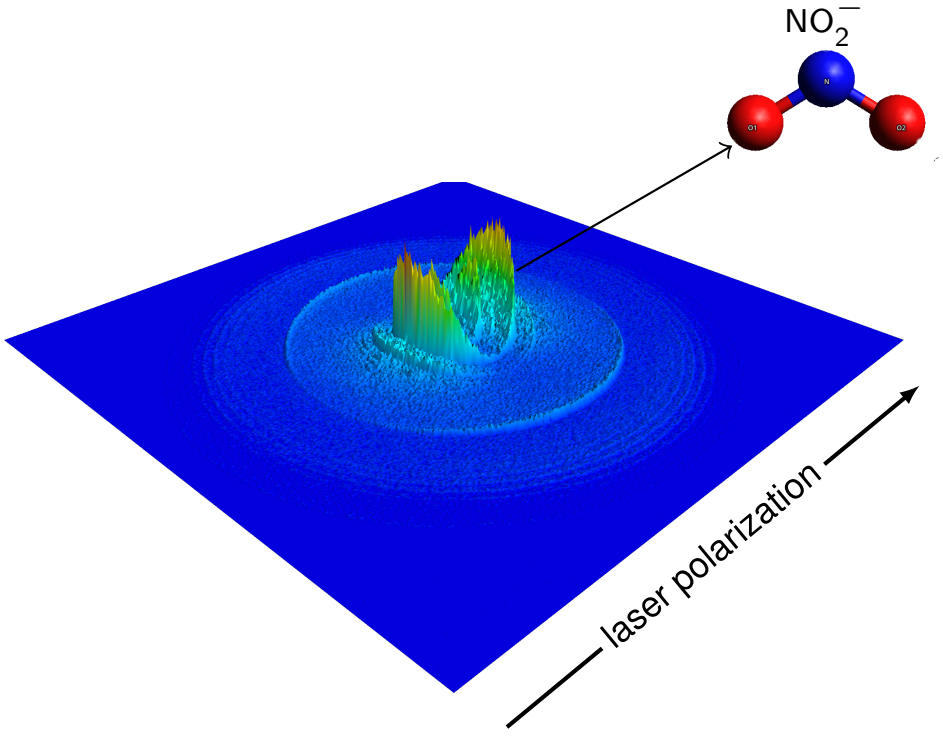
3D slice



Inverse Abel transformation: Gascooke/Hansen and Law

NO_2 Photoelectron Spectrum

$\lambda = 519$nm



- Additional e^- structure
- $D_0(ON\cdots O^-) = 3.932$ eV $> h\nu = 2.39$ eV

NO_2

- Prominent air pollutant
- Photochemical smog, tropospheric ozone
- Respiratory problems in humans

NO_2 Photoelectron Spectrum

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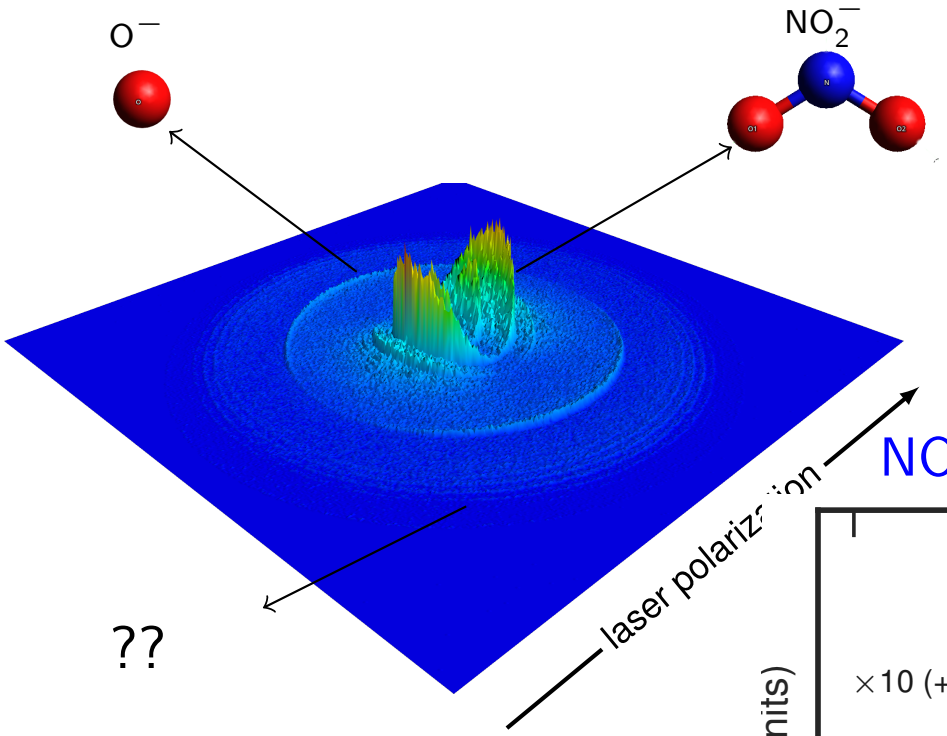

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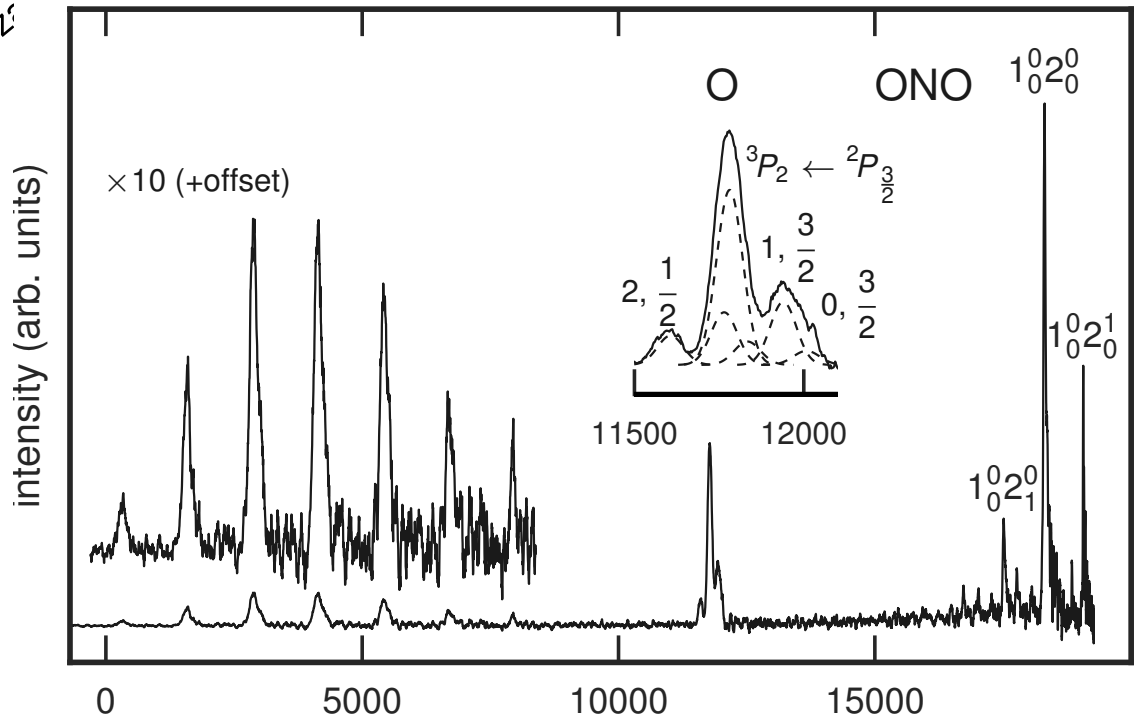
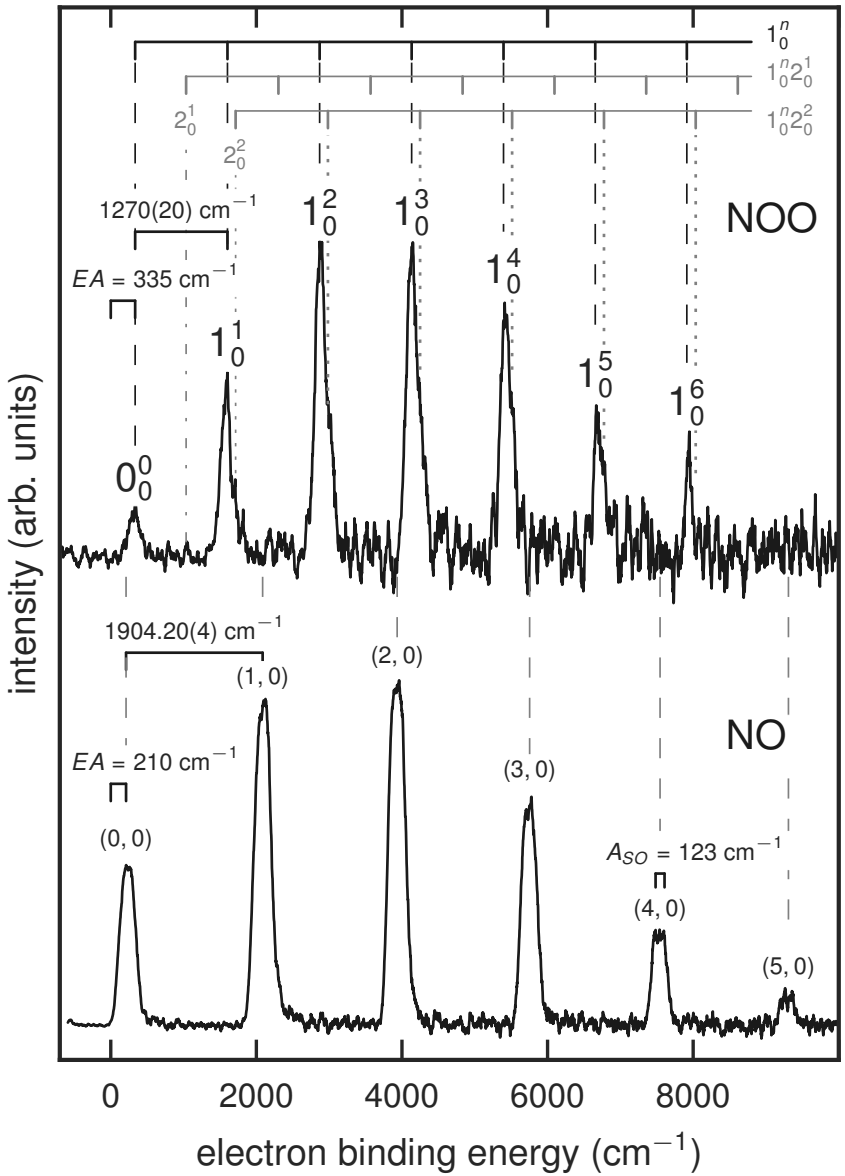
NO_2^- $\lambda = 519$nm Photoelectron Spectrum

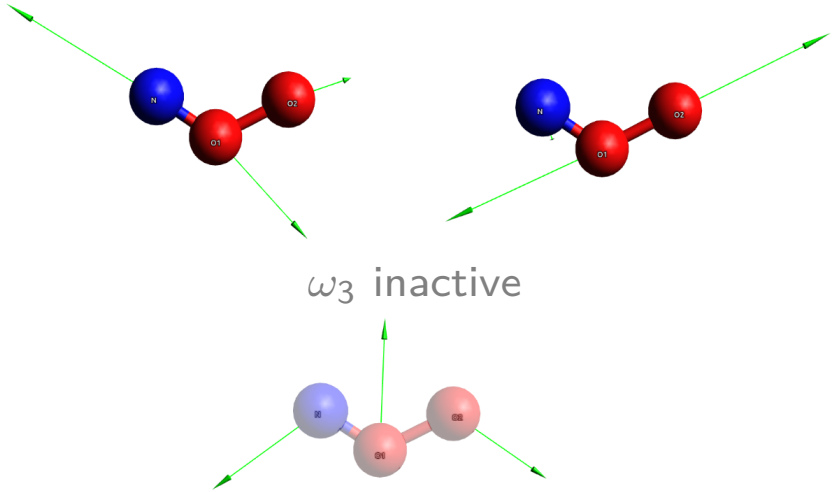


Extra electron structure - Peroxy NOO



$\omega_1 \approx 1270(20)$ cm^{-1}

$\omega_2 \sim 720$ cm^{-1}

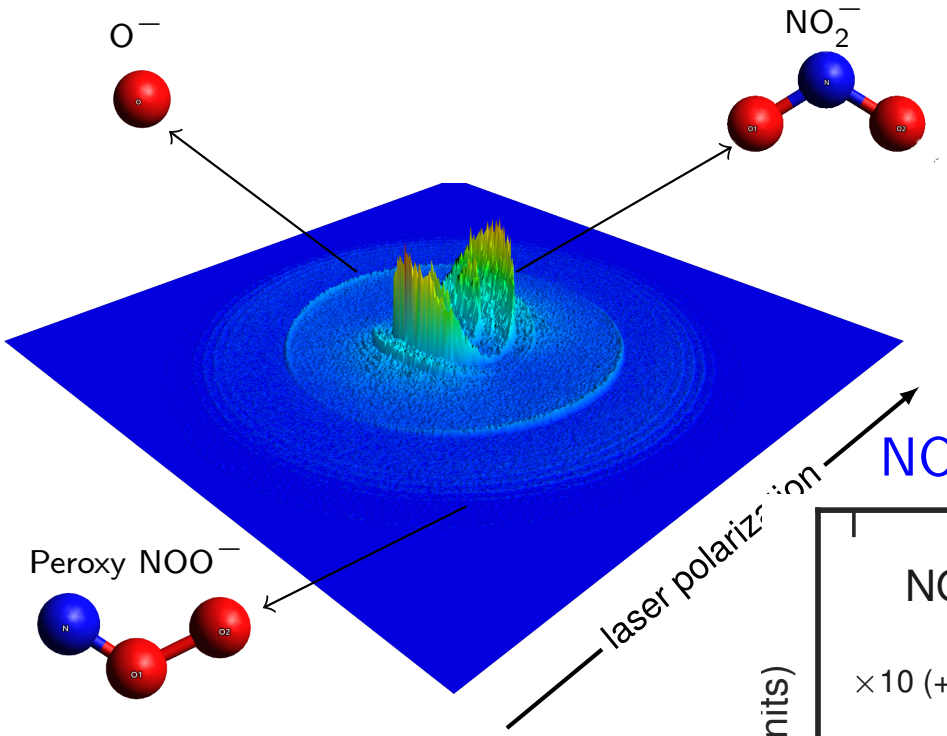


ω_3 inactive

- $D_0(NO\cdots O^-)$=0.13eV
- Observed fragment O^- results from dissociation of peroxy NO-O bond

NO_2 Photoelectron Spectrum

$\lambda = 519$nm



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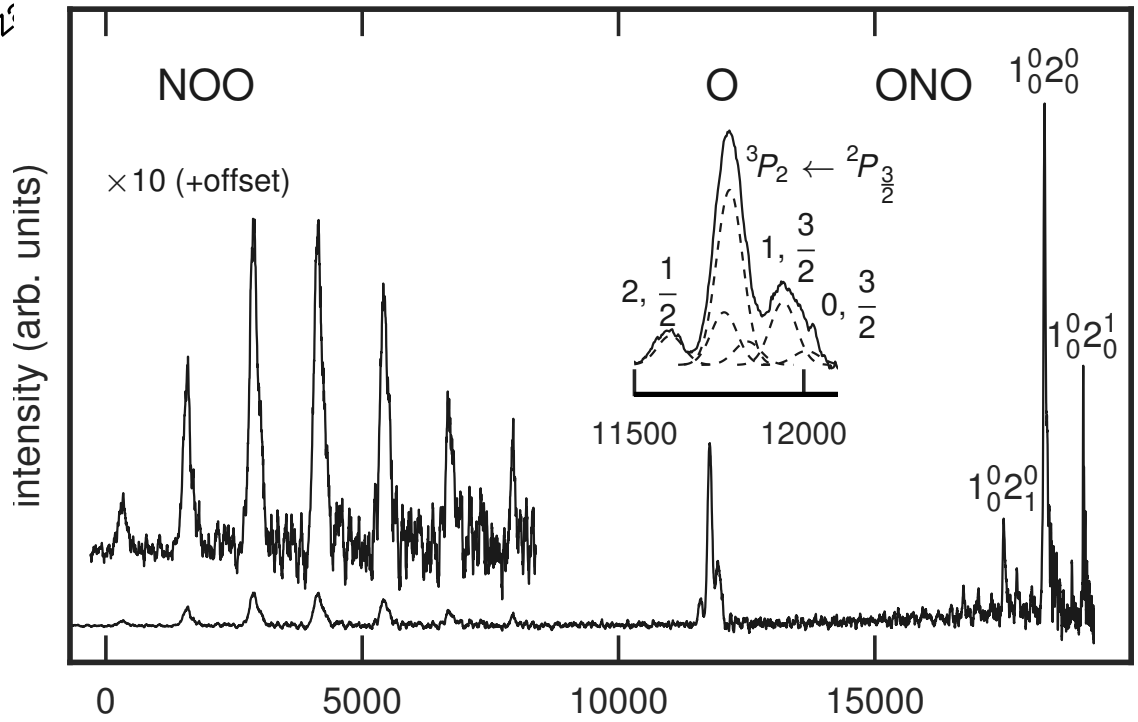
NO_2^- $\lambda = 519$nm Photoelectron Spectrum

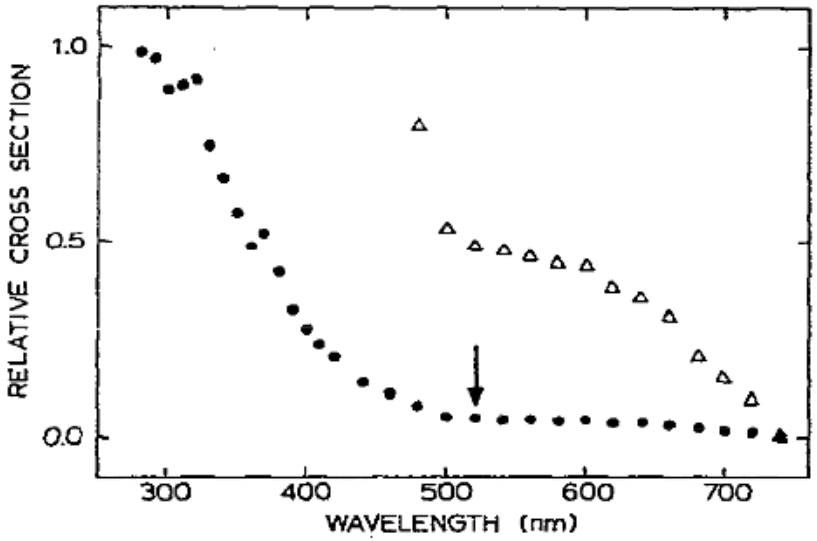


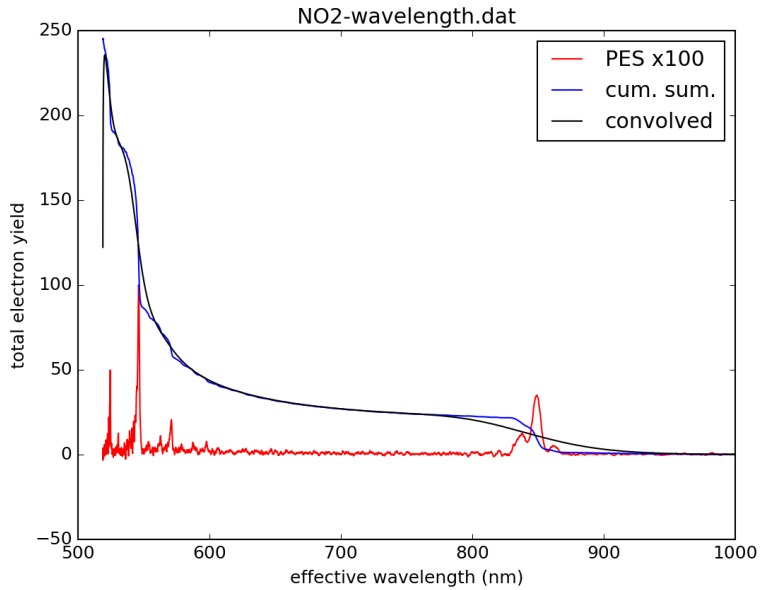
Peroxy NOO isomer

- A peroxy NOO isomer was first proposed by Clynne and Thrush in 1961, as a reaction intermediate in atmospheric chemistry

$$N + O_2 \rightarrow NOO \rightarrow NO + O \quad (1)$$

- However there is still debate about whether NOO is a stable isomer, or just a reaction intermediate
- NOO has been used in past photodetachment cross section experiments to possibly explain observed tails below the EA of NO2





Brauman Chem Phys Lett 25 318 (1974)

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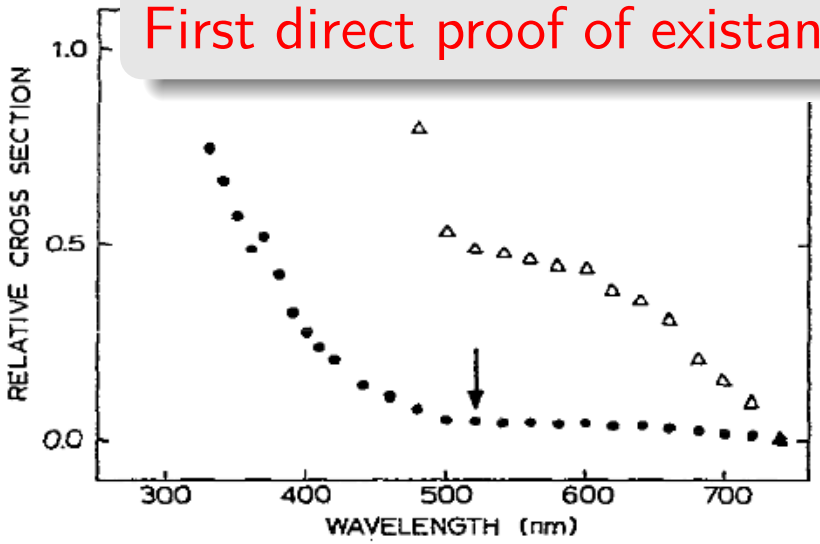
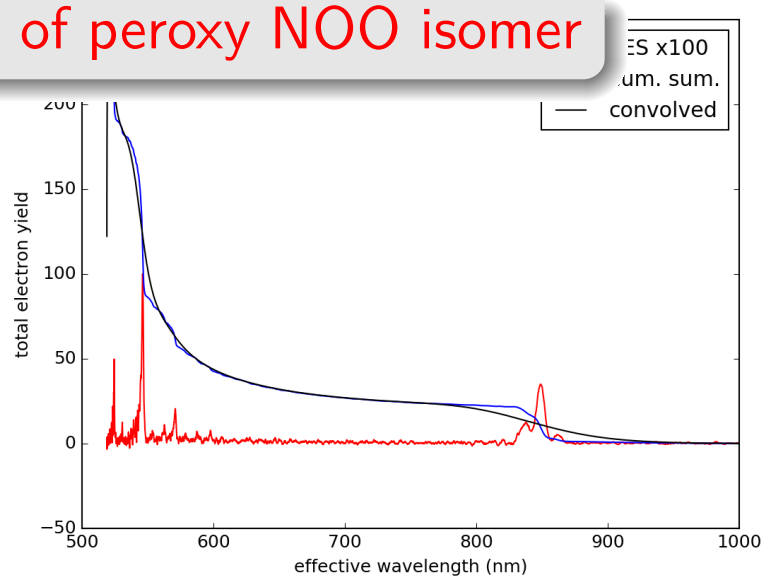
First direct proof of existance of peroxy NOO isomer





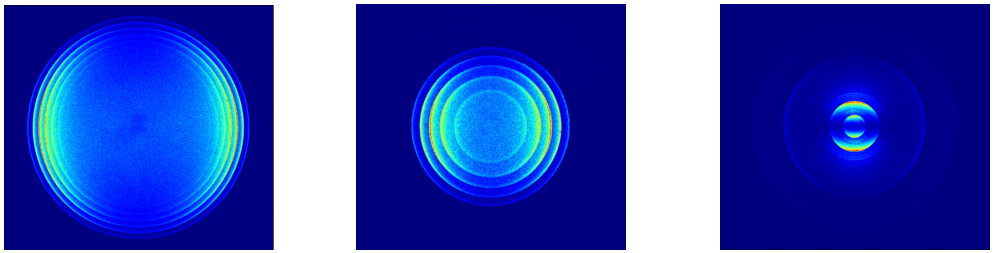
Brauman Chem Phys Lett 25 318 (1974)

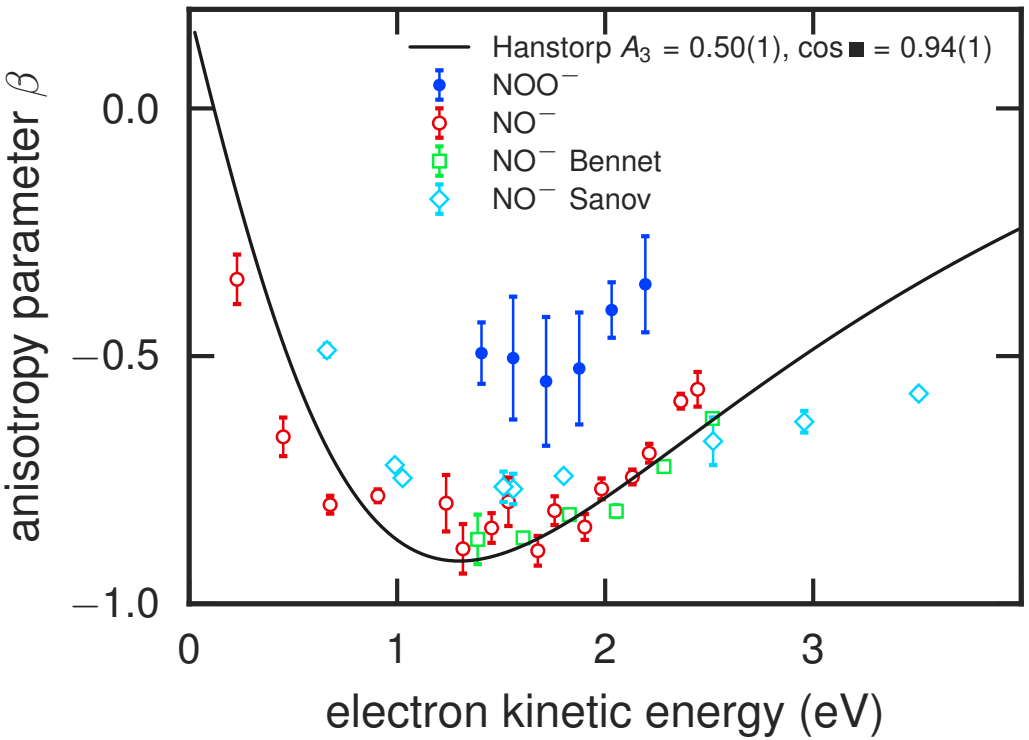
NO^- vs NOO^- PAD

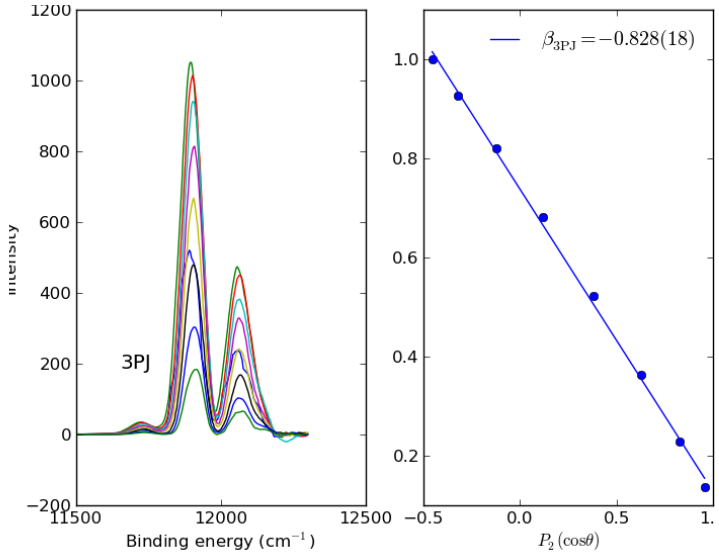
$$I(\theta,\epsilon) = \frac{\sigma(\epsilon)}{4\pi}[1+\beta(\epsilon)P_2(\cos\theta)]$$

β anisotropy parameter

NO 519nm NO 1064nm NO_2 519nm







Hanstorp approx: $A_2\epsilon \sim R_f/R_p$

Δ = partial wave phase shift

d-orbital electron, $\Delta\ell = \pm 1$

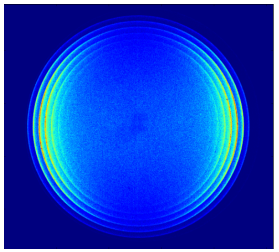
$$\beta(\epsilon) = \frac{2 + 12(A_2\epsilon)^2 - 36(A_2\epsilon)\cos(\Delta)}{5[2+3(A_2\epsilon)^2]}$$

NO^- vs NOO^- PAD

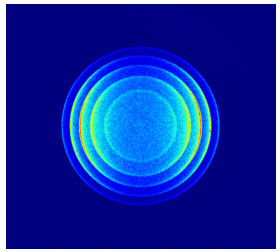
$$I(\theta,\epsilon) = \frac{\sigma(\epsilon)}{4\pi}[1+\beta(\epsilon)P_2(\cos\theta)]$$

β anisotropy parameter

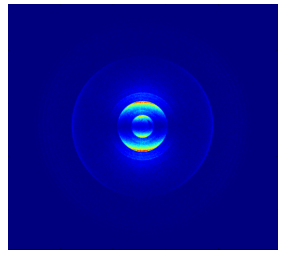
NO 519nm

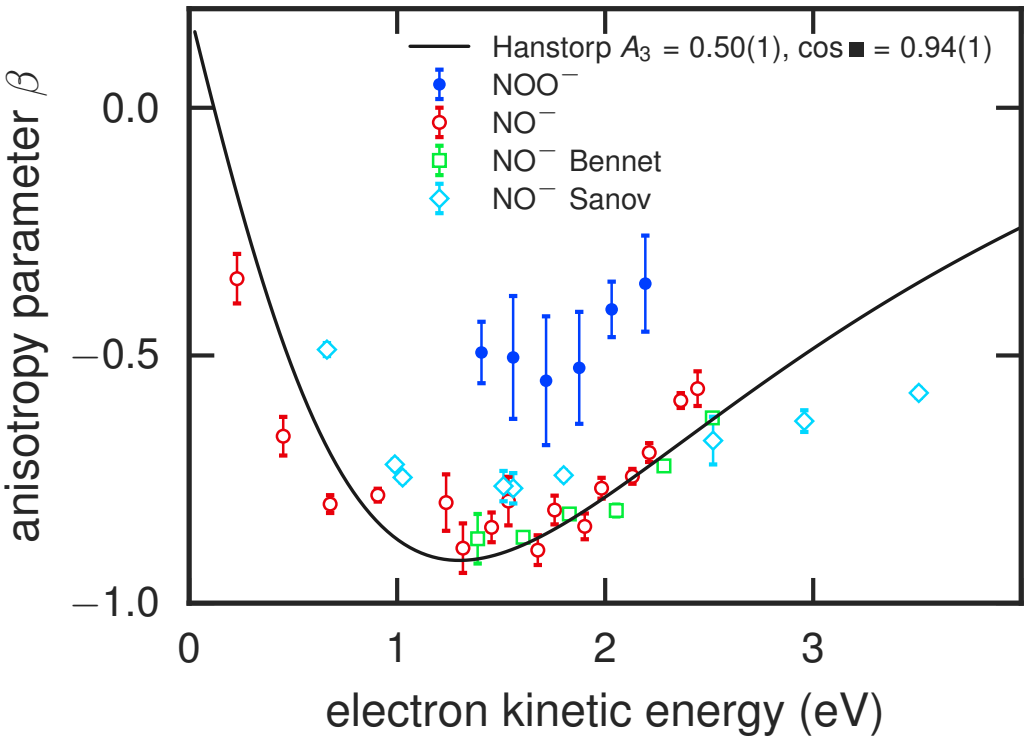


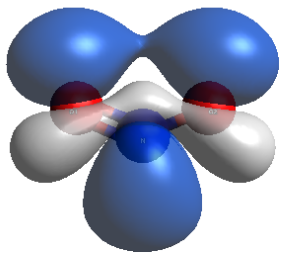
NO 1064nm



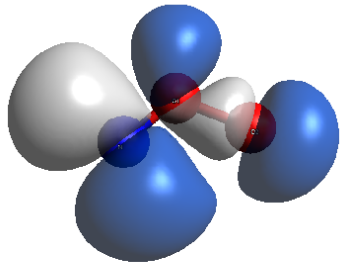
NO_2 519nm







C_{2v} ONO^-

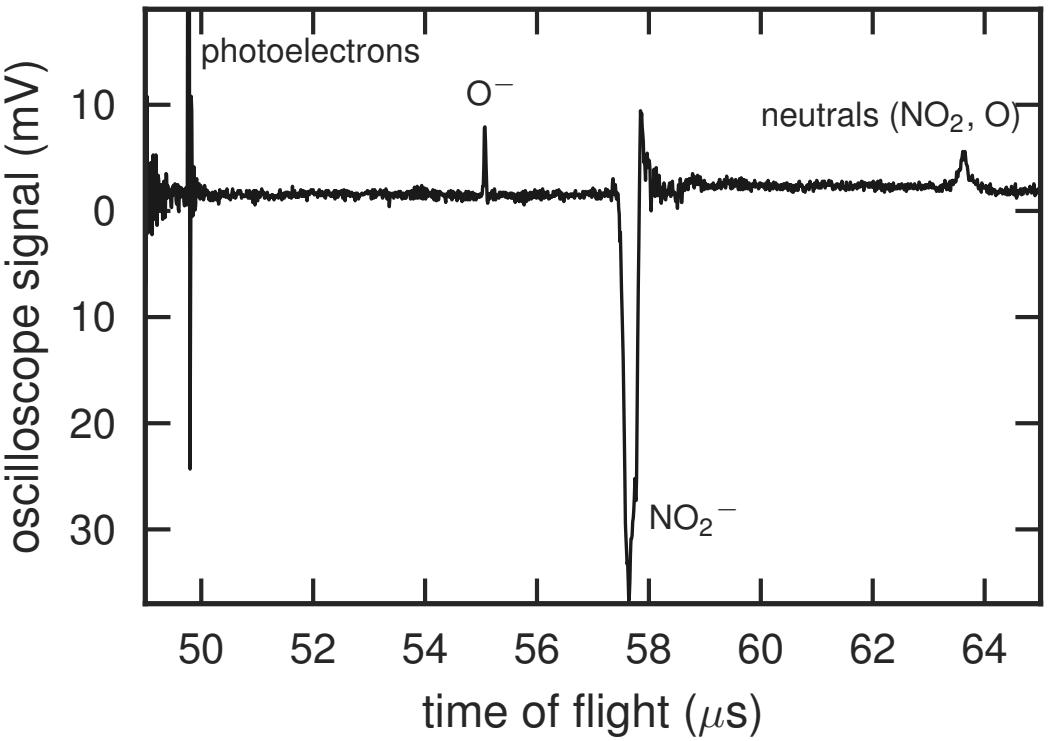


C_s NOO^-

[35] Bennett Phys Rev A 6 670 (1972)

[36] Sanov J Phys Chem A 114 1367 (2010)

Photodynamics



- O^- fragmentation ✓

  $$NOO^- + h\nu \rightarrow NO + O^-$$

  $$O^- + h\nu \rightarrow O + e^-$$

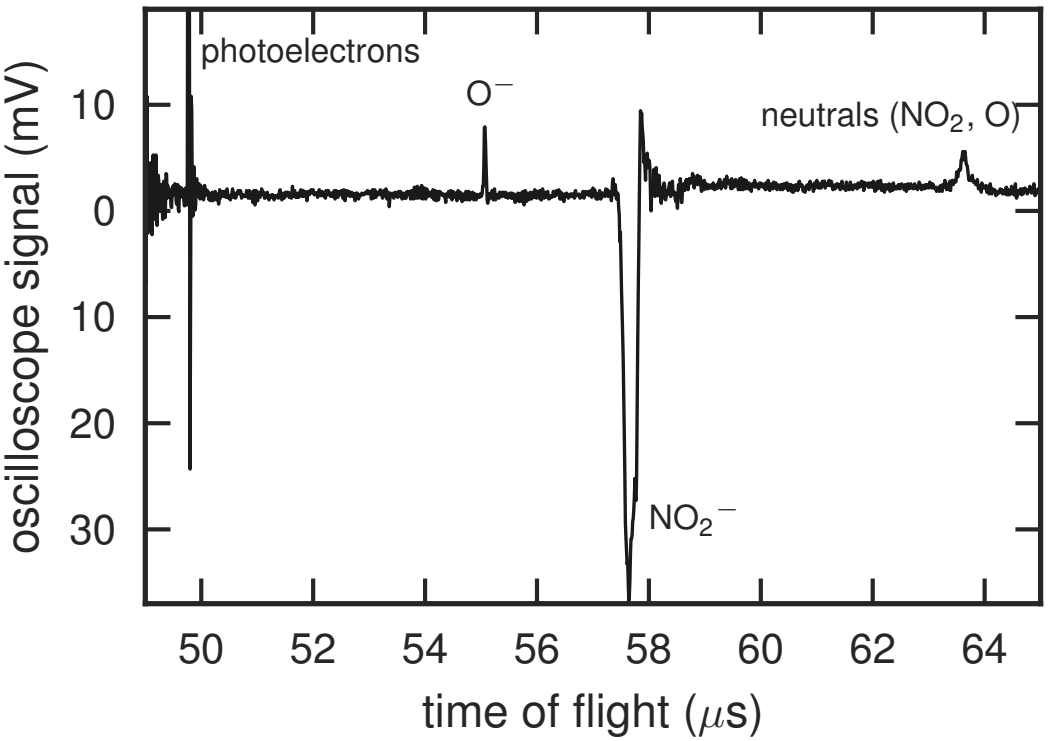
- NO^- fragmentation ×

  $$NOO^- + h\nu \nrightarrow NO^- + O$$

- NOO^- detachment ✓

  $$NOO^- + h\nu \rightarrow NOO + e^-$$

Photodynamics



- O^- fragmentation ✓

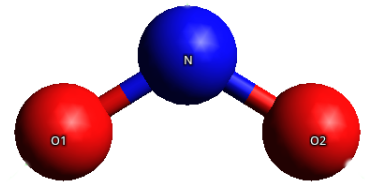
  $NOO^- + h\nu \rightarrow NO + O^-$

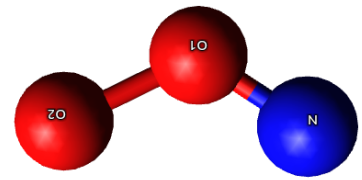
  $O^- + h\nu \rightarrow O + e^-$
- NO^- fragmentation ×

  $NOO^- + h\nu \nrightarrow NO^- + O$
- NOO^- detachment ✓

  $NOO^- + h\nu \rightarrow NOO + e^-$

- Confirmation of peroxy NOO isomer
- How abundant is the peroxy isomer in the atmosphere? Possible implications?
  $\Longrightarrow$ Further studies needed





Conclusions

- **NO_2^- detachment:** additional e^- structure observed
- **O^- present:** but $D_0(ON\cdots O^-) = 3.932$ eV $> h\nu = 2.39$ eV
- **Low BE e^-:** similar to NO, but with a 600 cm^{-1} shift in dominant vibrational frequency. Also evidence of a second mode
- ***ab-initio* calculations:** predicted vibrational frequency for peroxy NOO isomer in agreement with PES. Small $D_0(NO\cdots O^-) = 0.13$ eV would explain the presence of O^-
- **PAD:** - NOO^- detachment more isotropic than NO^-
- **Photodynamics:** Photofragment O^- produced but no NO^-. Gives final confirmation of peroxy NOO isomer
- **Future Studies:** How abundant is the peroxy isomer in nature? Possible implications?