NOO Peroxy Isomer Exposed With Velocity-Map Imaging

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- Photodetachment/VMI
- VMI $\text{NO}_2^- \rightarrow \text{NO}_2$
- Peroxy NOO isomer
  - PES
  - PAD
  - Dynamics
$A^- + h\nu \rightarrow A^*^- \rightarrow A^* + e^-$
Spectrometer - photodetachment/photofragmentation

- anion source-
pulsed molecular jet
HV discharge

- mass separation
- TOF

photodetachment: electron
velocity-mapping lens
MCPs and phosphor detector

Fast beam spectrometer (based on Neumark/Continetti design):
Cyr PhD Thesis (UC Berkeley 1993)
Velocity-map imaging lens:
Gating-bunching-rereferencing unit:

Photodetachment:
\[ A^- + h\nu \rightarrow A^* + e^- \]
Velocity-map imaging

VMI lens coaxial with ion-beam

A laser

MCPs + phosphor

CCD camera

Hemispherical Analyser

Grid Electrode Lens

Velocitv Map Imaging Lens

3D Photodetachment

2D Projection of $O_2^-$

3D slice

Inverse Abel transformation: Gascooke/Hansen and Law

Velocity-map imaging

3D Photodetachment

e^- Intensity vs photon energy

Photoelectron spectrum (PES)

PE angular distribution (PAD)

2D Projection of O_2^-

3D slice

Inverse Abel transformation: Gascooke/Hansen and Law

NO$_2$ Photoelectron Spectrum

$\lambda = 519\text{nm}$

**NO$_2$**
- Prominent air pollutant
- Photochemical smog, tropospheric ozone
- Respiratory problems in humans

- Additional $e^-$ structure
- $D_0(\text{ON} \cdots \text{O}^-) = 3.932 \text{ eV} > h\nu = 2.39 \text{ eV}$
NO₂ Photoelectron Spectrum

\[ \lambda = 519 \text{nm} \]

Additional \( e^- \) structure

\[ D_0(\text{ON} \cdots \text{O}^-) = 3.932 \text{ eV} > h\nu = 2.39 \text{ eV} \]
Extra electron structure - Peroxy NOO

\[ \omega_1 \approx 1270(20) \text{ cm}^{-1} \]

\[ \omega_2 \sim 720 \text{ cm}^{-1} \]

\[ \omega_3 \text{ inactive} \]

\[ D_0(\text{NO} \cdots \text{O}^-) = 0.13 \text{eV} \]

Observation fragment O\(^-\) results from dissociation of peroxy NO-O bond
NO$_2$ Photoelectron Spectrum

$\lambda = 519$nm

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

\[ \text{N} + \text{O}_2 \rightarrow \text{NOO} \rightarrow \text{NO} + \text{O} \]  

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.
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(1)

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First direct proof of existence of peroxy NOO isomer
\[ l(\theta, \epsilon) = \frac{\sigma(\epsilon)}{4\pi} [1 + \beta(\epsilon) P_2(\cos \theta)] \]

\( \beta \) anisotropy parameter

\[ \beta = 2 + 12(A_2 \epsilon)^2 - 36(A_2 \epsilon) \cos(\Delta) \]

\[ \frac{5[2 + 3(A_2 \epsilon)^2]}{2} \]

\( \Delta = \) partial wave phase shift

d-orbital electron, \( \Delta \ell = \pm 1 \)

Hanstorp approx: \( A_2 \epsilon \sim R_f / R_p \)

\( \epsilon \) electron kinetic energy (eV)

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

\[ \beta \text{ anisotropy parameter} \]

\[ \text{Hanstorp } A_3 = 0.50(1), \cos = 0.94(1) \]


Photodynamics

O\(^-\) fragmentation √

\[
\text{NOO}^- + h\nu \rightarrow \text{NO} + \text{O}^- \\
\text{O}^- + h\nu \rightarrow \text{O} + e^- \\
\text{NO}^- \text{ fragmentation} \times \\
\text{NOO}^- + h\nu \not\rightarrow \text{NO}^- + \text{O} \\
\text{NOO}^- \text{ detachment} √ \\
\text{NOO}^- + h\nu \rightarrow \text{NOO} + e^- 
\]

Confirmation of peroxy NOO isomer

How abundant is the peroxy isomer in the atmosphere? Possible implications?

=⇒ Further studies needed

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Confirmation of peroxy NOO isomer

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O\(^-\) fragmentation ✓

NOO\(^-\) + h\(\nu\) → NO + O\(^-\)

O\(^-\) + h\(\nu\) → O + e\(^-\)

NO\(^-\) fragmentation ×

NOO\(^-\) + h\(\nu\) → NO\(^-\) + O

NOO\(^-\) detachment ✓

NOO\(^-\) + h\(\nu\) → NOO + e\(^-\)
**Conclusions**

- **NO$_2^-$ detachment**: additional e$^-$ structure observed

- **O$^-$ present**: but $D_0$(ON···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···O$^-$) = 0.13 eV would explain the presence of O$^-$

- **PAD**: NOO$^-$ detachment more isotropic than NO$^-$

- **Photodynamics**: Photofragment O$^-$ produced but no NO$^-$ produced. Gives final confirmation of peroxy NOO isomer

- **Future Studies**: How abundant is the peroxy isomer in nature? Possible implications?