

On the Ionization Mechanism in Negative Ion Atmospheric Pressure Mass Spectrometry and the Role of Cluster Formation



Physical & Theoretical Chemistry

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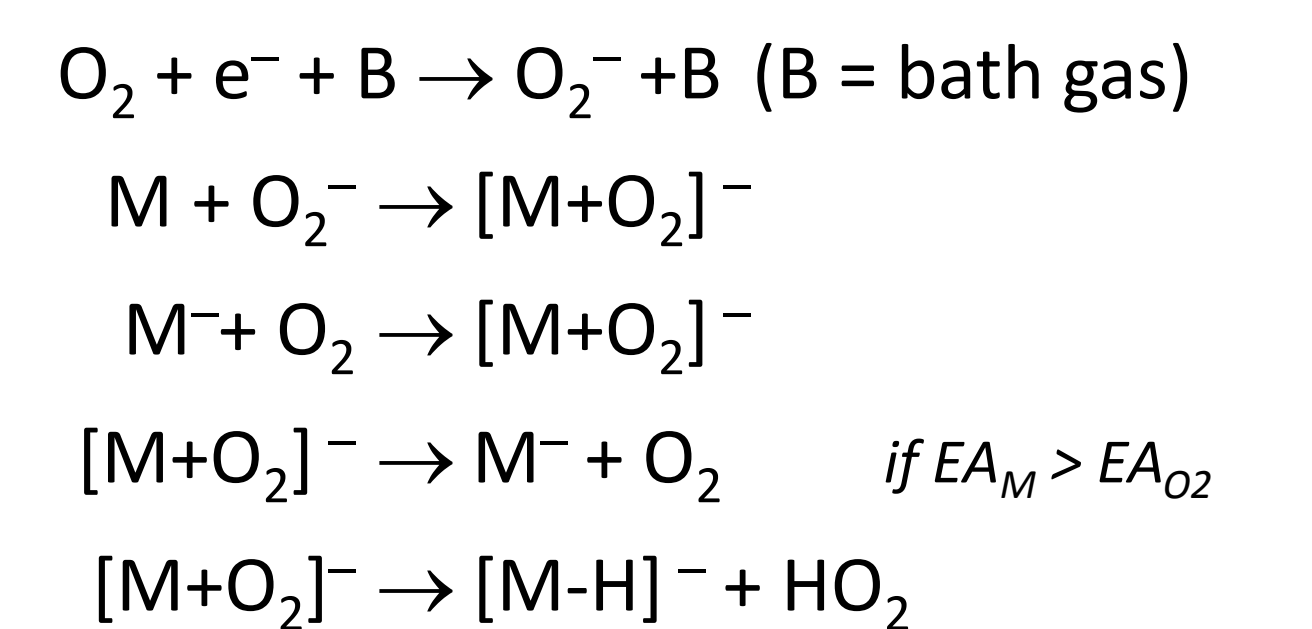
Introduction

Questions:

- 1) How does ionization proceed in negative ion mode mass spectrometry after generation of thermal electrons?
- 2) What is the role of O_2^- water clusters?

State of Knowledge:

After generation of thermal electrons at atmospheric pressure:



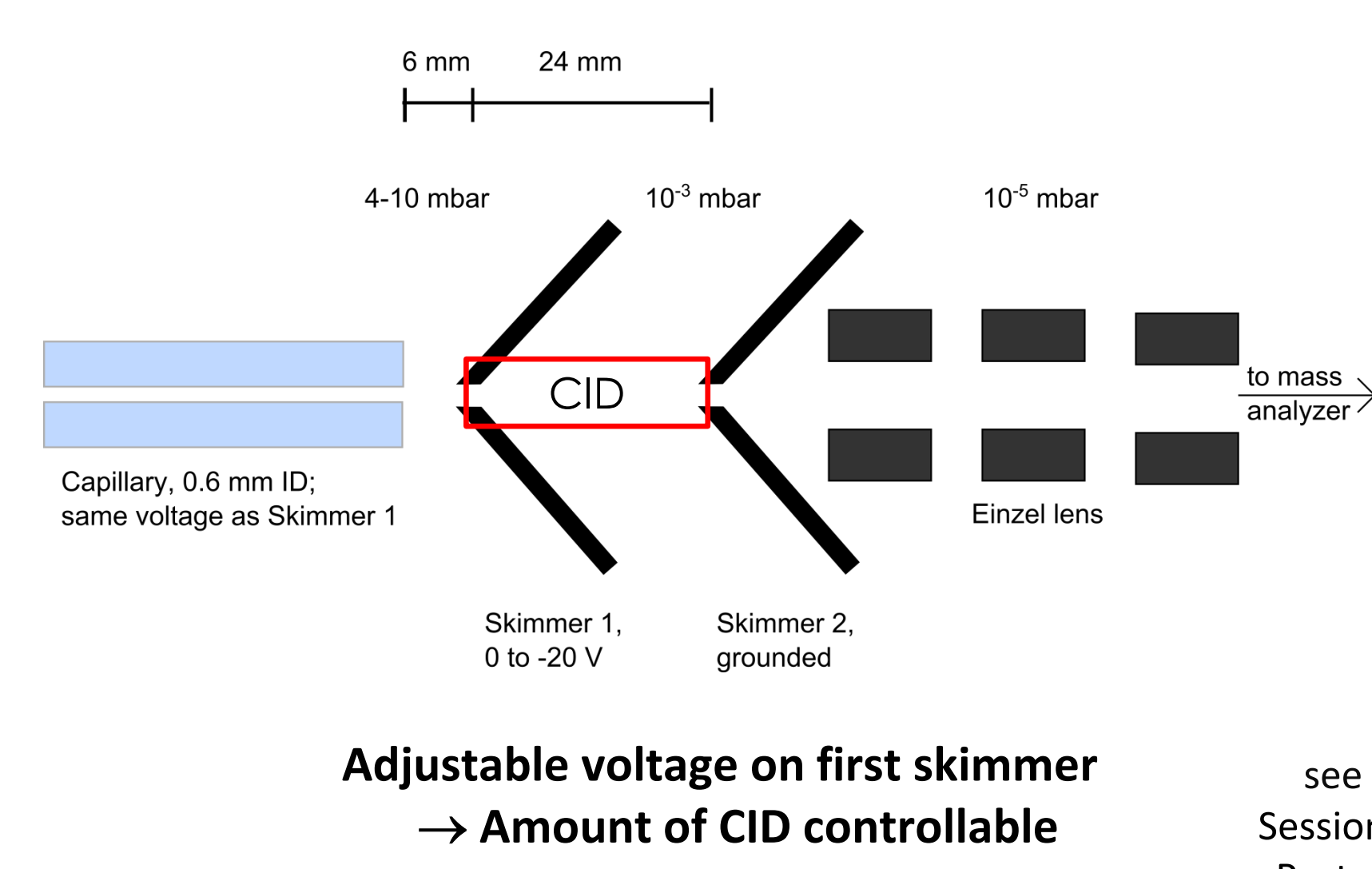
- Adduct formation $[M+O_2]^-$ is not always assumed
- Superoxide water clusters are often mentioned to be generated but are not included in the ionization mechanism

Experimental:

- Thermally sampling MS, which does not change the ion distribution by
 - collision induced dissociation (CID)
 - adiabatic expansions
- See also Session MP29, Poster #669
- Laser ionization of toluene, generating solely thermal electrons and toluene radical cations
 - negligible generation of neutral radicals compared to APPI, APCI etc.
- Comparison with mass spectra obtained with a standard MS (Ion Trap)
 - CID processes inevitably occur
- See also Session MP01, Poster #674

Thermal sampling

Schematic of the custom built ion optics which allows thermal sampling

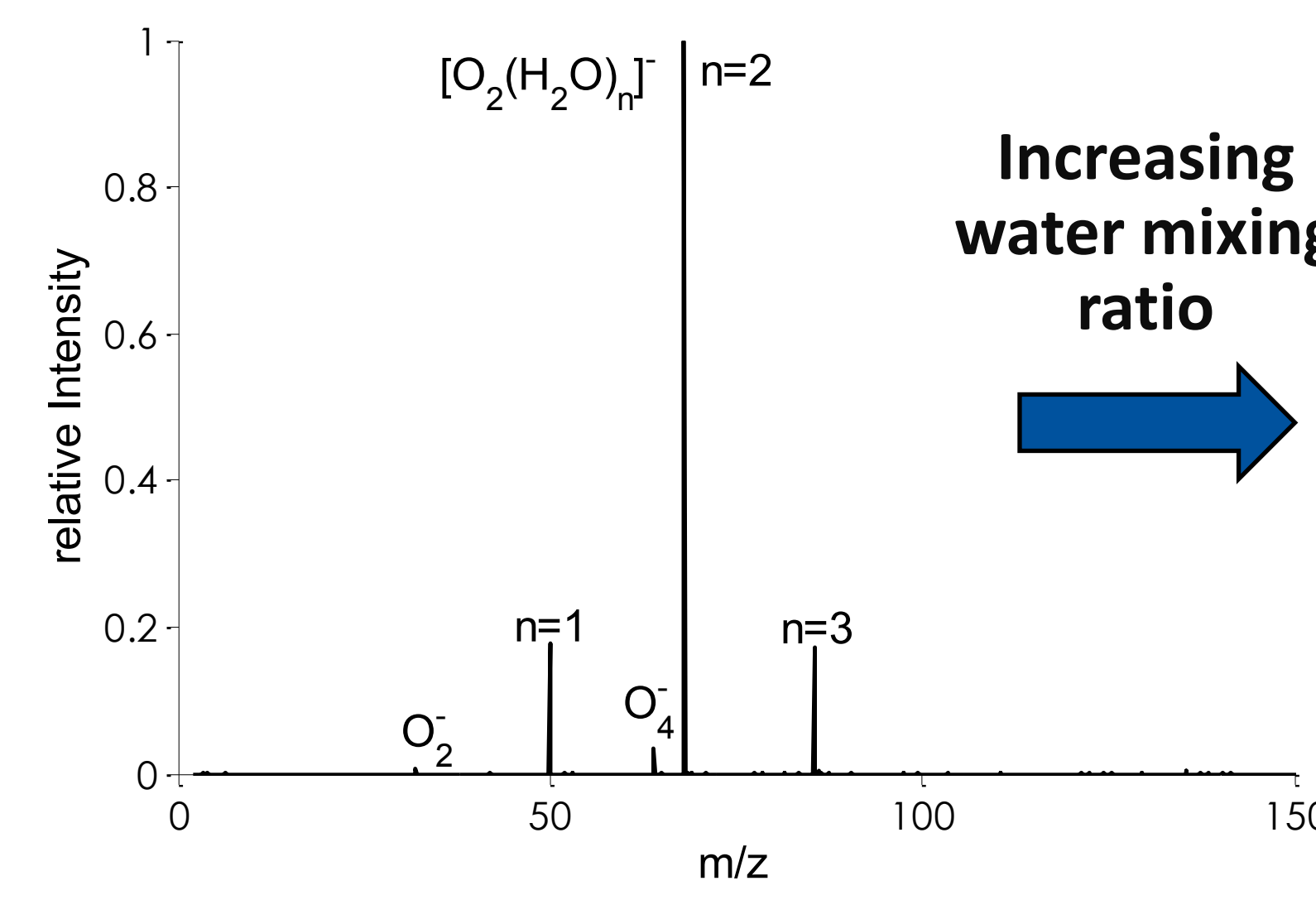


see also:
Session MP29
Poster #669

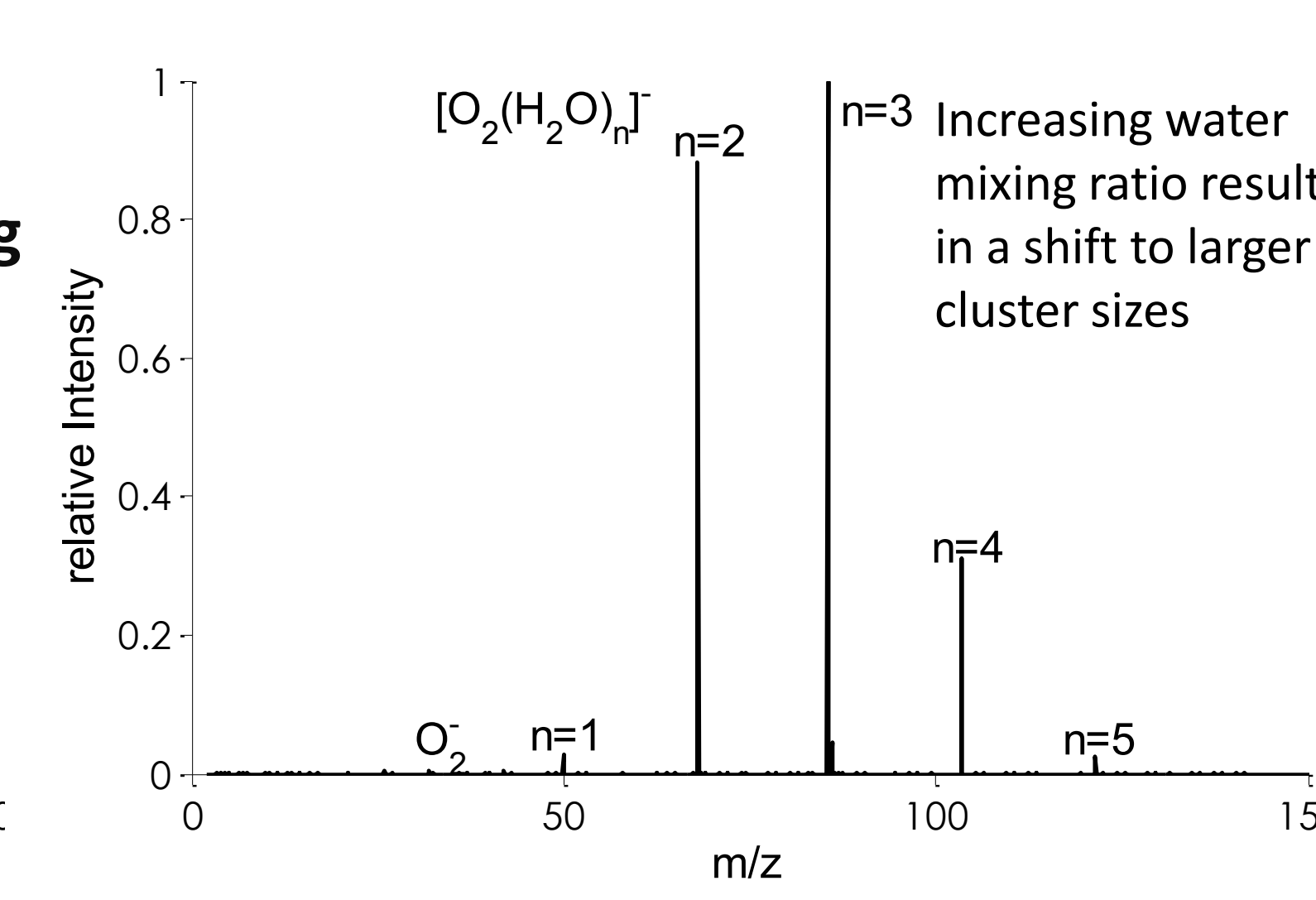
Background Mass Spectra

Background water concentration

(several hundred ppmV)

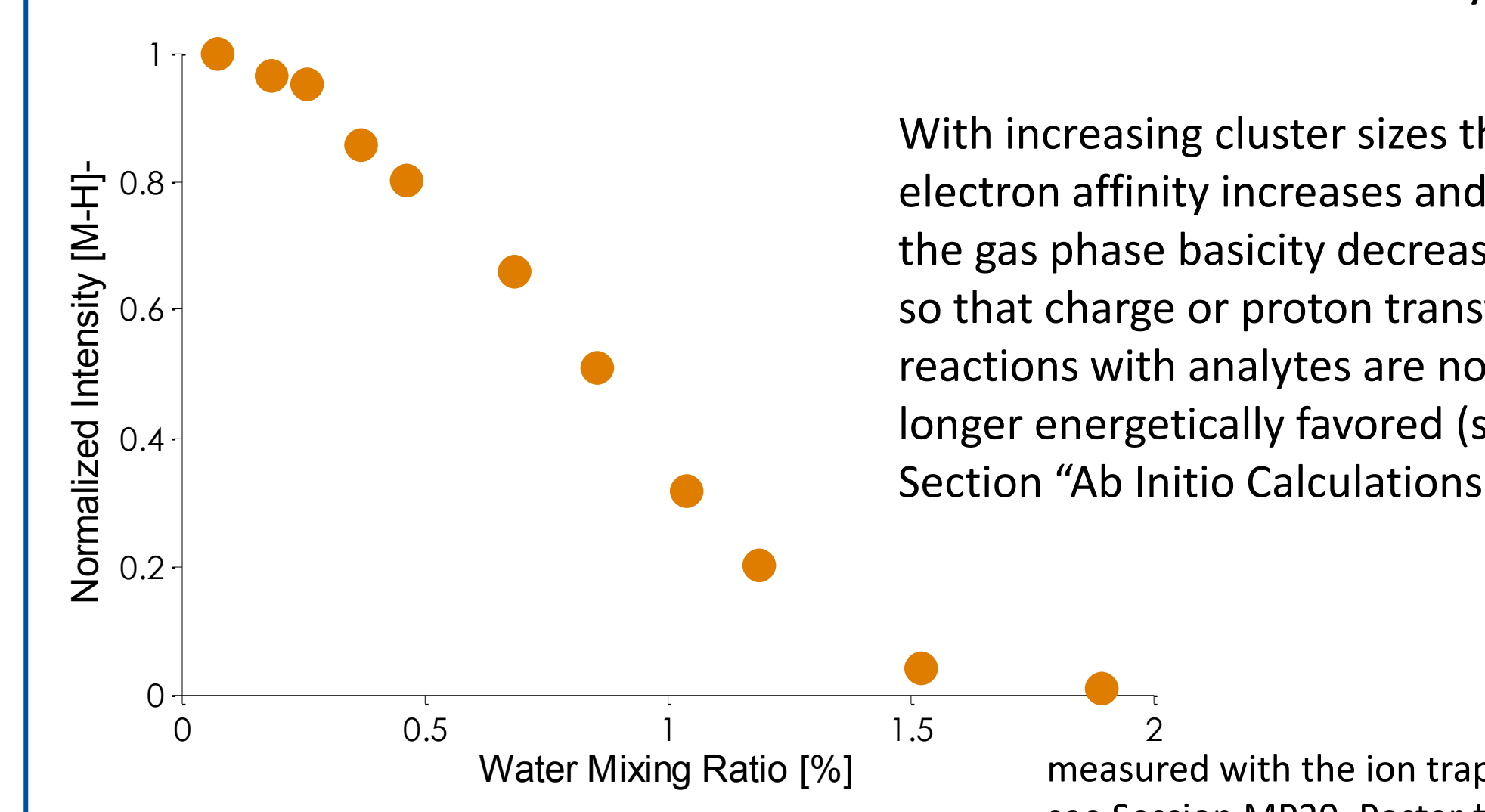


0.2 % water



Water Concentration

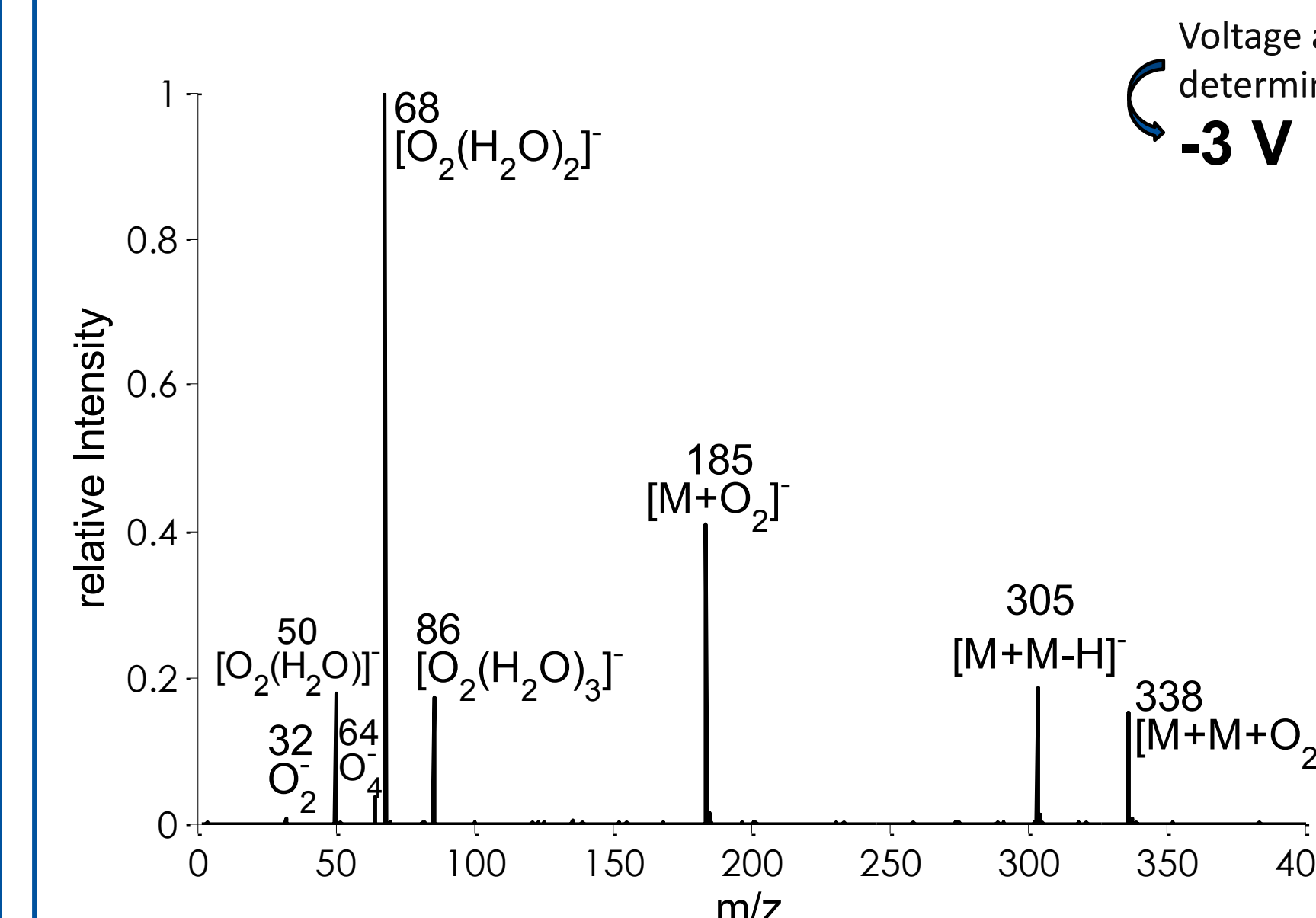
Increasing water mixing ratio → Increasing cluster sizes → Decreasing ionization efficiency



Conclusions

- Primary ion-water clusters are always present in negative ion atmospheric pressure mass spectrometry sources
- Understanding of the ionization mechanism leading to M^- and $[M-H]^-$ formation
 - $[M-H]^-$ formation
 - $[M+O_2]^-$ adduct formation
 - Decomposition of $[M+O_2]^-$ only with additional energy (→ CID necessary)
 - M^- can be formed, but will react back to $[M+O_2]^-$ very fast (20 % oxygen)
- M^- formation
 - Direct ionization by primary ions, e.g., O_2^- , O_4^- , $[O_2(H_2O)]^-$
 - Possibly clustering with water after analyte ion generation
- CID processes change the ion distribution prevailing in the ion source
- Increasing water mixing ratios shift the O_2^- cluster distribution to larger cluster sizes
- With increasing water cluster sizes:
 - Electron affinity increases
 - Gas phase basicity decreases
 - Reaction with analytes is no longer energetically favored
 - Decreasing ionization efficiency

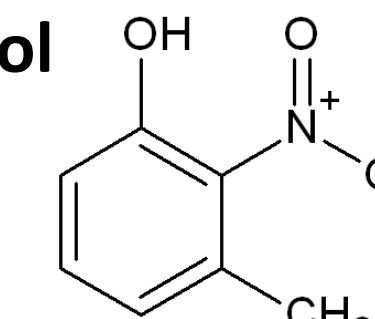
$[M-H]^-$ formation



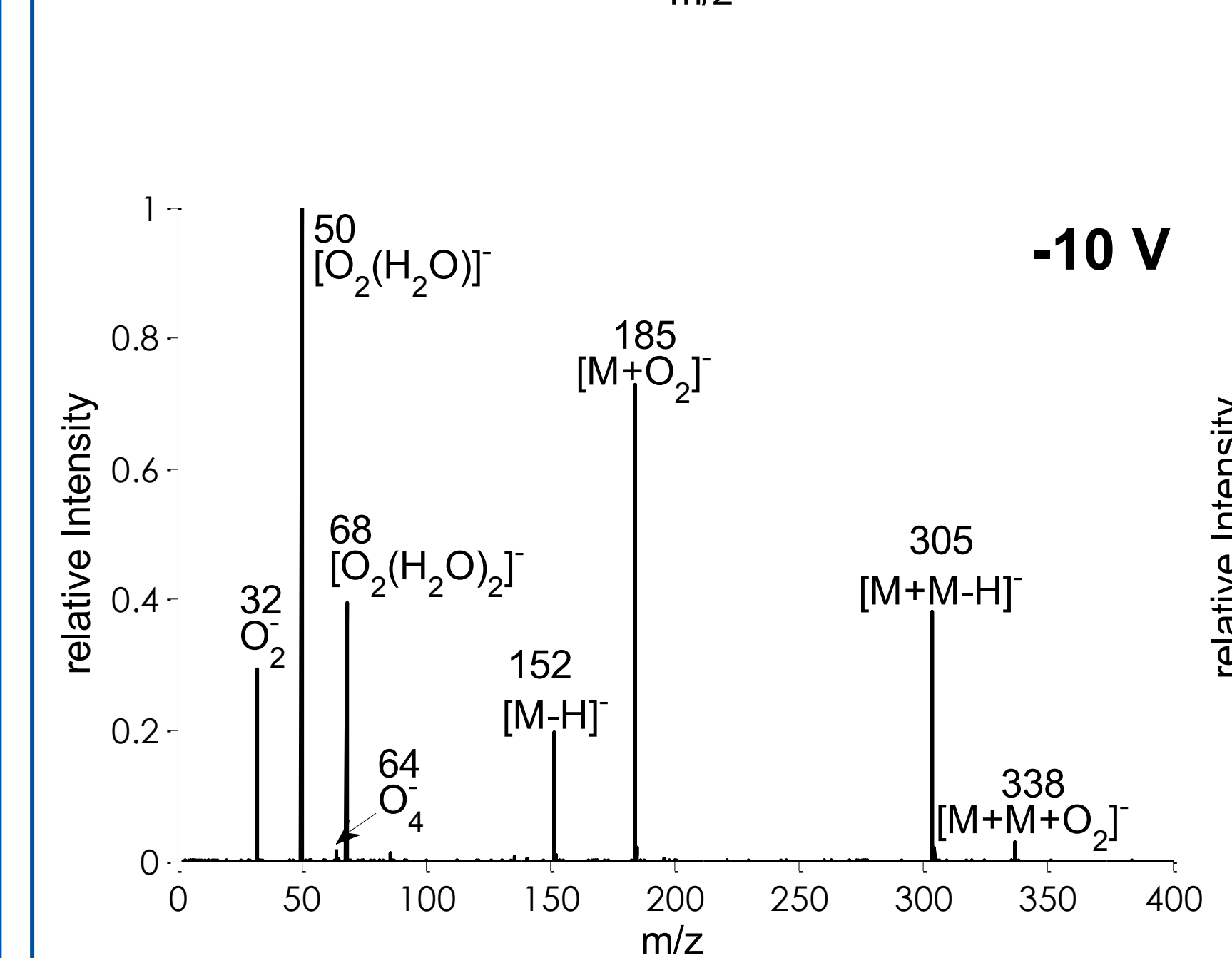
Voltage applied on the first Skimmer; determines amount of CID
-3 V

Without CID processes the O_2^- adduct is the main analyte signal. Due to the high analyte mixing ratio, dimer signals are observed.

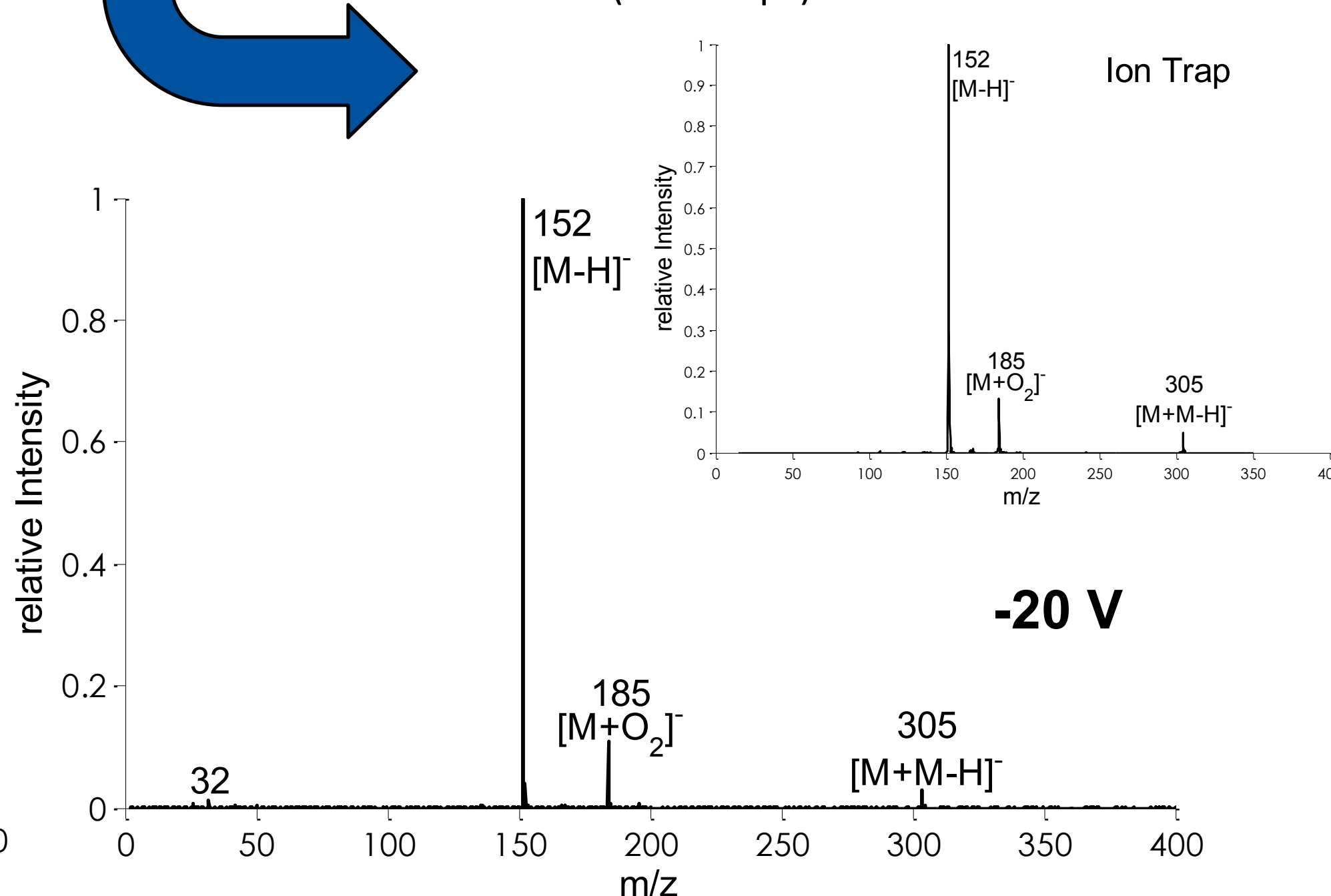
2-Methyl-3-Nitrophenol
Molar Mass: 153 g/mol



Increasing the amount of CID results in a shift of the superoxide water clusters to smaller cluster sizes, up to $n=0$ and to a shift from adduct ions to $[M-H]^-$ as main signal in the mass spectrum. With -20 V applied on the first skimmer the spectrum is nearly identical to that of a standard MS ("Ion Trap").

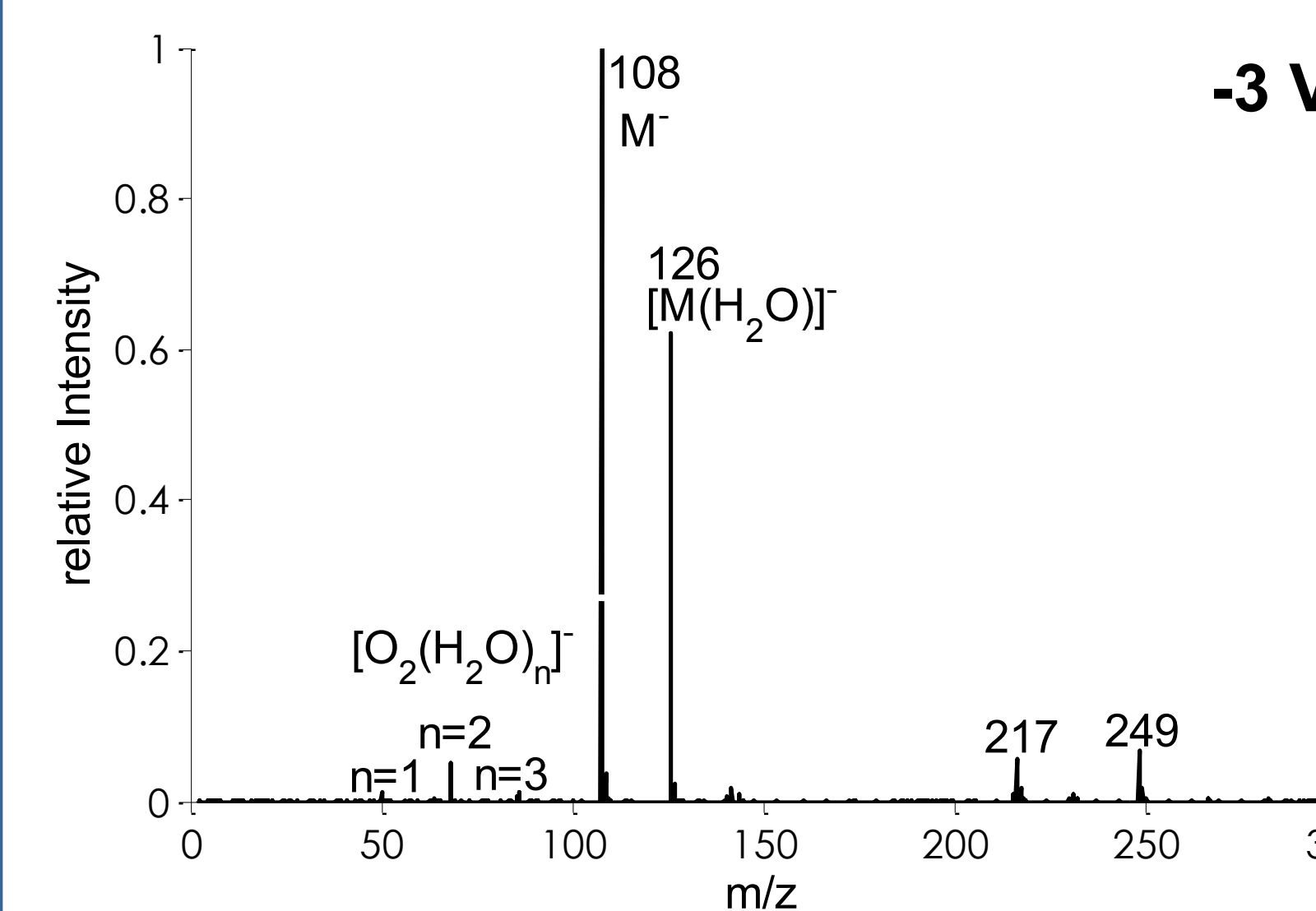


-10 V



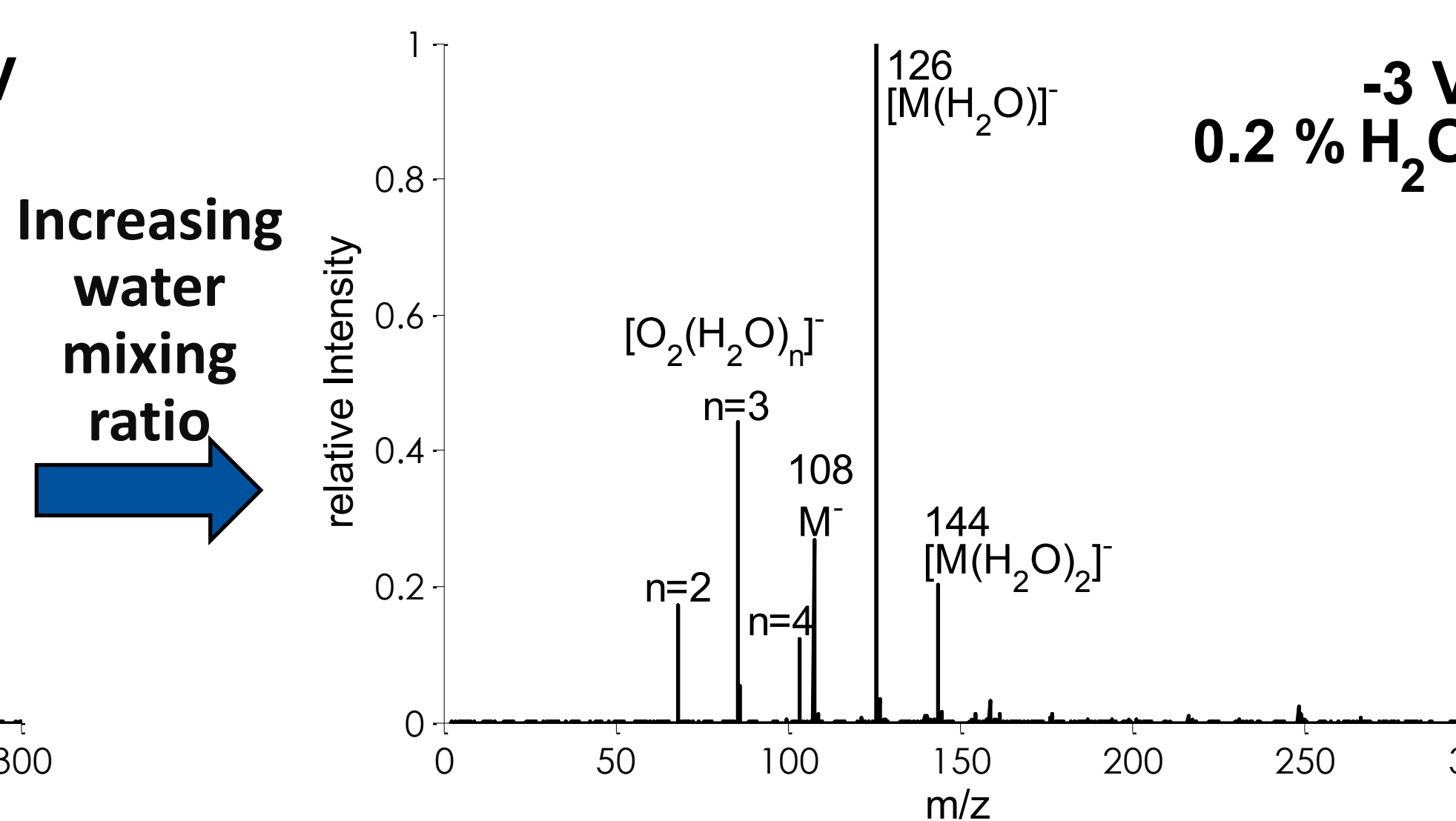
-20 V

M^- formation



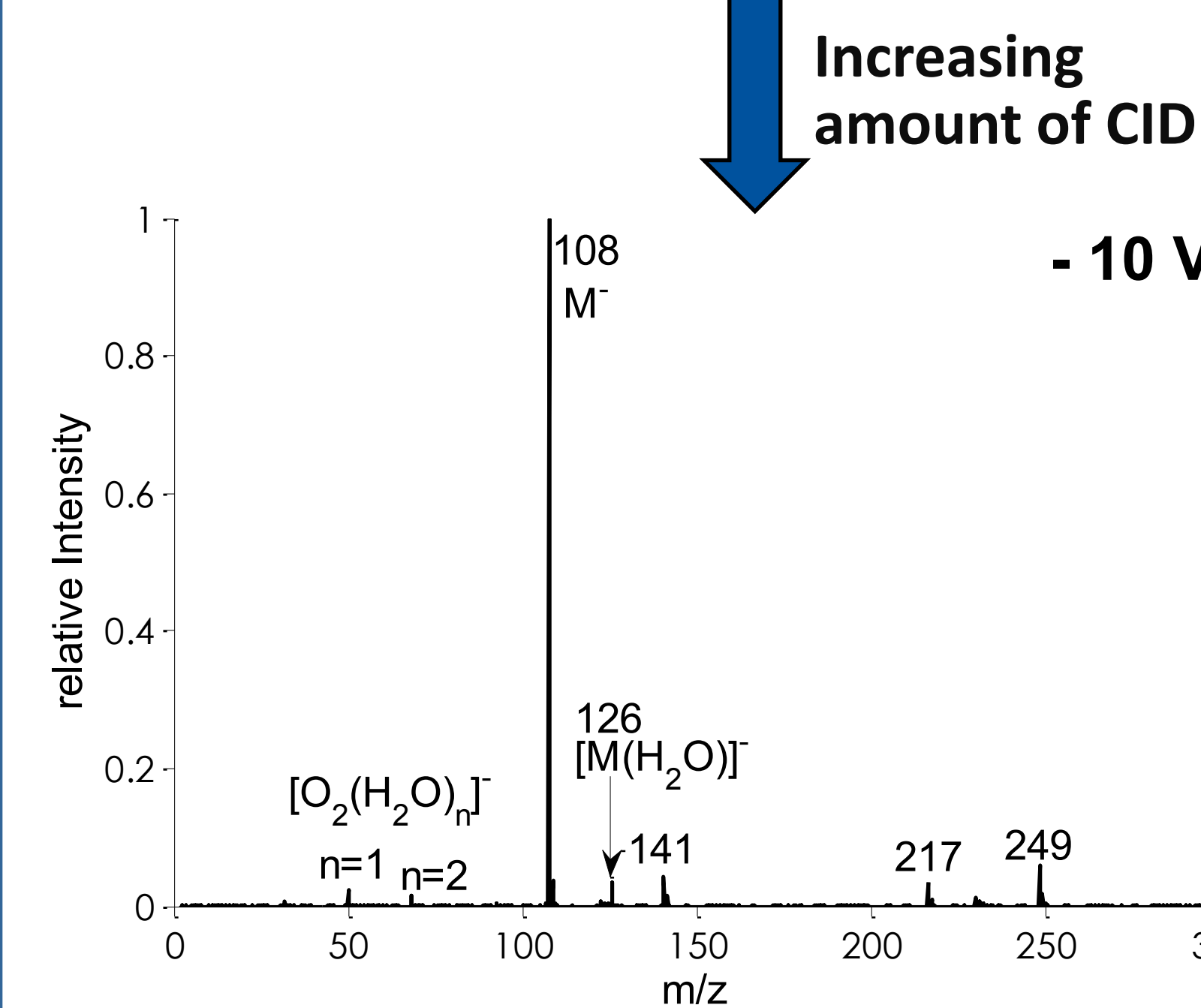
-3 V

Increasing water mixing ratio

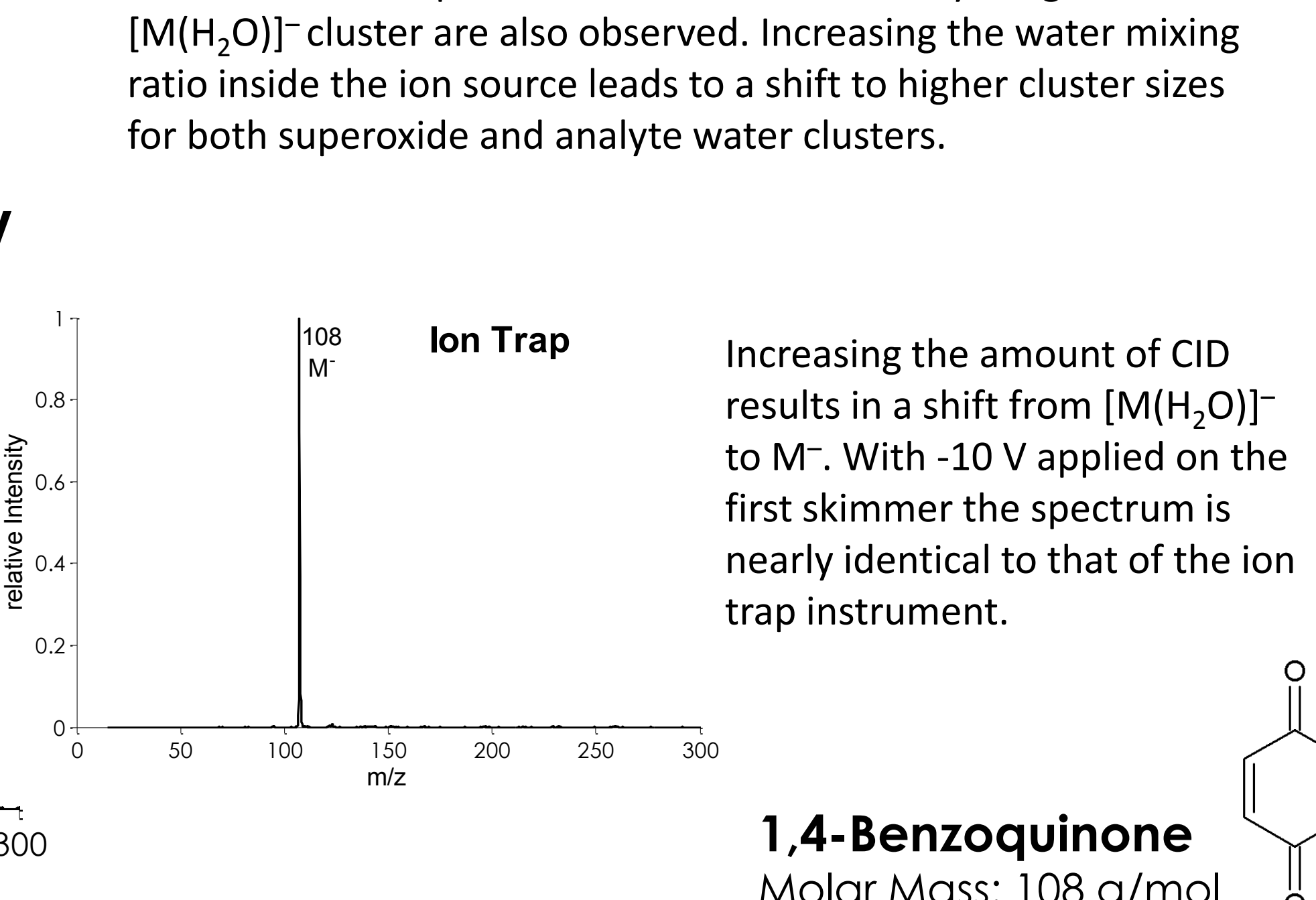


-3 V
0.2 % H₂O

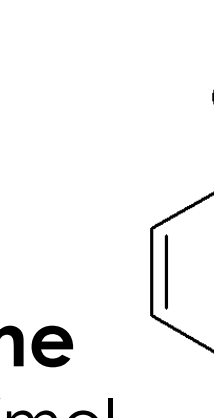
Even without CID processes M^- is the main analyte signal. $[M(H_2O)]^-$ cluster are also observed. Increasing the water mixing ratio inside the ion source leads to a shift to higher cluster sizes for both superoxide and analyte water clusters.



-10 V



1,4-Benzoquinone
Molar Mass: 108 g/mol



Methods

- Experimental Setup**
- MS:** ToFwerk HTOF equipped with custom built ion optic; see also Session MP29 Poster #669
- Ion Source:** Custom laminar flow ion source made of aluminum
- Laser:** 266 nm, CryLas FQSS 266-50 Nd:YAG
- Numerical Calculations**
- Software:** Gaussian03; Gaussian, Inc.
- Basis Set:** B3LYP 6-31+G(d,p)

Ab Initio Calculations

Reaction	Gibbs free energy of reaction ($\Delta_r G$) [eV]
$3M2NP + O_4^- \rightarrow [3M2NP-H]^- + HO_2 + O_2$	-0.77
$3M2NP + O_2^- \rightarrow [3M2NP-H]^- + HO_2$	-0.59
$3M2NP + O_2^- \rightarrow [3M2NP+O_2]^-$	-1.30
$[3M2NP+O_2]^- \rightarrow [3M2NP-H]^- + HO_2$	0.71
$[3M2NP+O_2]^- \rightarrow 3M2NP^- + O_2$	0.38
$3M2NP + [O_2(H_2O)]^- \rightarrow [3M2NP-H]^- + HO_2 + H_2O$	0.02
$3M2NP + [O_2(H_2O)_2]^- \rightarrow [3M2NP-H]^- + HO_2 + 2 H_2O$	2.85
$3M2NP + [O_2(H_2O)_3]^- \rightarrow [3M2NP-H]^- + HO_2 + 3 H_2O$	3.71

Mechanism

- $[M-H]^-$ formation**
- Ionization via adduct formation**
- $$M + O_2^- \rightarrow [M+O_2]^-$$
- $$[M+O_2]^- \rightarrow M^- + O_2$$
- $$[M+O_2]^- \rightarrow [M-H]^- + HO_2$$
- $$M^- + O_2 \rightarrow [M+O_2]^-$$
- Higher analyte concentrations:**
- $$[M+O_2]^- + M \rightarrow [M+M+O_2]^-$$
- $$[M+M+O_2]^- \rightarrow [M+M-H]^- + HO_2$$
- Only possible with additional energy**
- Possible without additional energy**
- M^- formation**
- Direct ionization**
- $$M + O_2^- \rightarrow M^- + O_2$$
- $$M^- + H_2O \rightarrow [M(H_2O)]^-$$
- $$[M(H_2O)_n]^- + H_2O + M \leftrightarrow [M(H_2O)_{n+1}]^- + M$$
- Mean value of n depends on water mixing ratio**

Ab Initio Calculations

Reaction	Gibbs free energy of reaction ($\Delta_r G$) [eV]
$BQ + O_4^- \rightarrow BQ^- + O_2 + O_2$	-0.77
$BQ + O_2^- \rightarrow BQ^- + O_2$	-1.61
$BQ + O_2^- \rightarrow [BQ+O_2]^-$	-1.45
$[BQ+O_2]^- \rightarrow BQ^- + O_2$	-0.16
$BQ + [O_2(H_2O)]^- \rightarrow BQ^- + O_2 + H_2O$	-1.00
$BQ + [O_2(H_2O)_2]^- \rightarrow BQ^- + O_2 + 2 H_2O$	1.83
$BQ + [O_2(H_2O)_3]^- \rightarrow BQ^- + O_2 + 3 H_2O$	2.69
$BQ^- + H_2O \rightarrow [BQ(H_2O)]^-$	-0.21
$[BQ(H_2O)]^- + H_2O \rightarrow [BQ(H_2O)_2]^-$	-0.17

Literature

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