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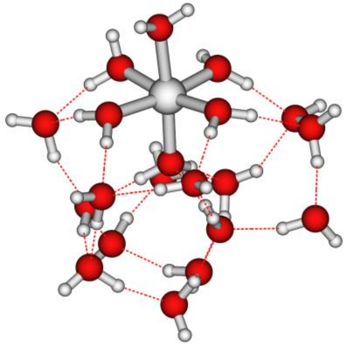
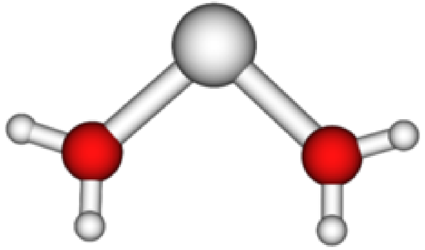
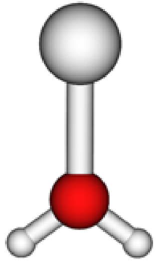
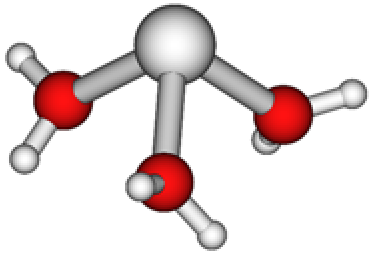
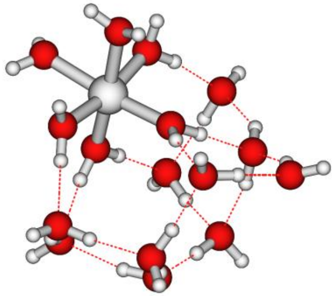
Photochemistry and Spectroscopy of Hydrated Metal Ions

Thomas Taxer

Institute for Ion Physics and Applied Physics
Supervisors: Martin Beyer, Milan Ončák

22.01.2020

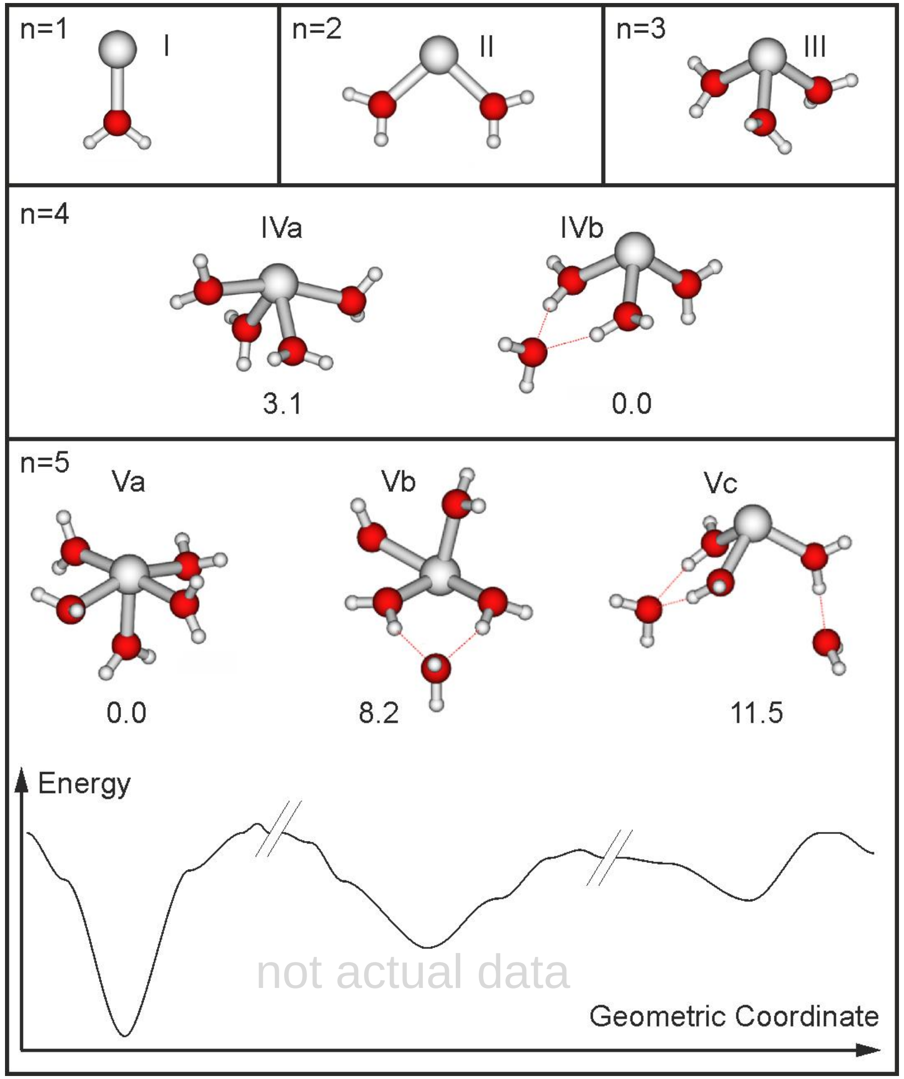
Content

- Motivation
- Theoretical Background
- Experimental Setup / Data Generation
- Hydrated Magnesium Ions
- Hydrated Zinc Ions
- Outlook

Motivation

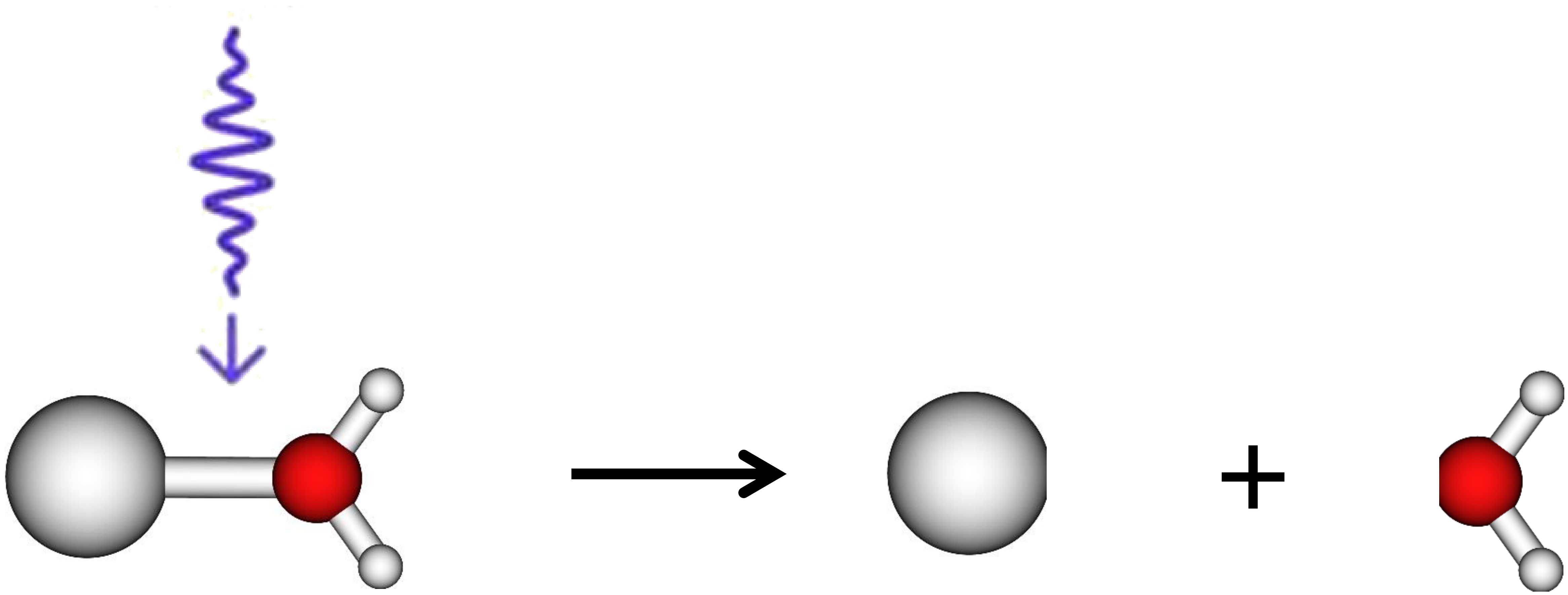
- Basic research on the photochemistry of hydrated metal ions
  - Solvation under well defined conditions
  - Properties from the gas phase to bulk
  - Model for photocorrosion
- Questions:
  - Structures
  - Photochemical Reaction Processes
  - Hydrated Electron?

Hydrated Metal Ions

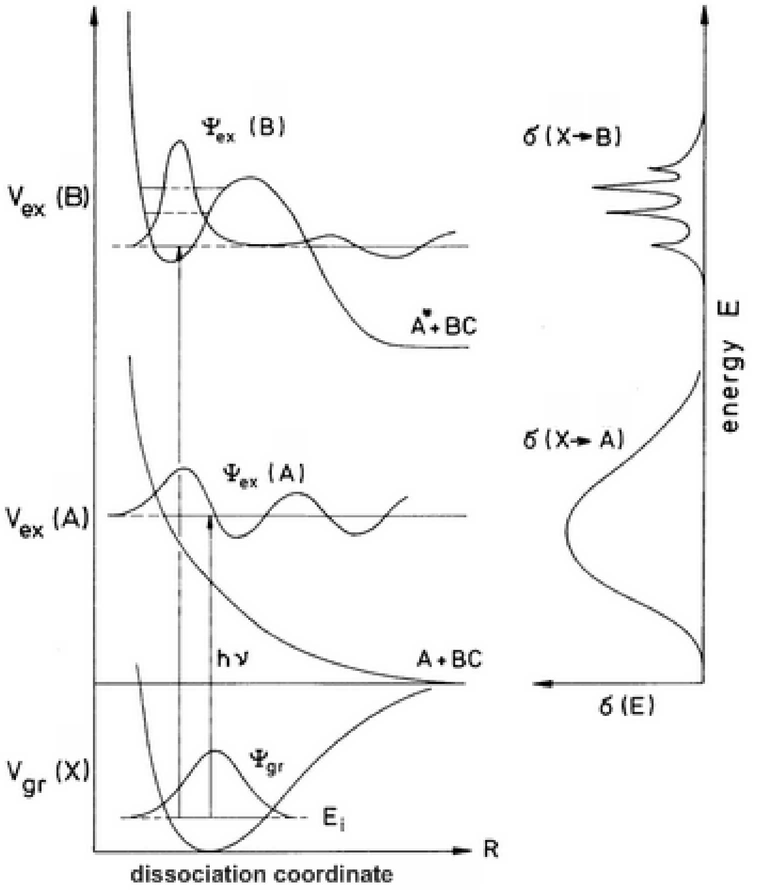


Energies in kJ/mol // B3LYP/6-31**

Photodissociation of Molecules



UV Photodissociation



F.A. Gianturco; Collision Theory for Atoms and Molecules; Springer Science & Business Media 2012

For cw lasers:

$$I_0 = \sum_{i=0}^{n} I_i \; e^{-\sigma\phi t}$$

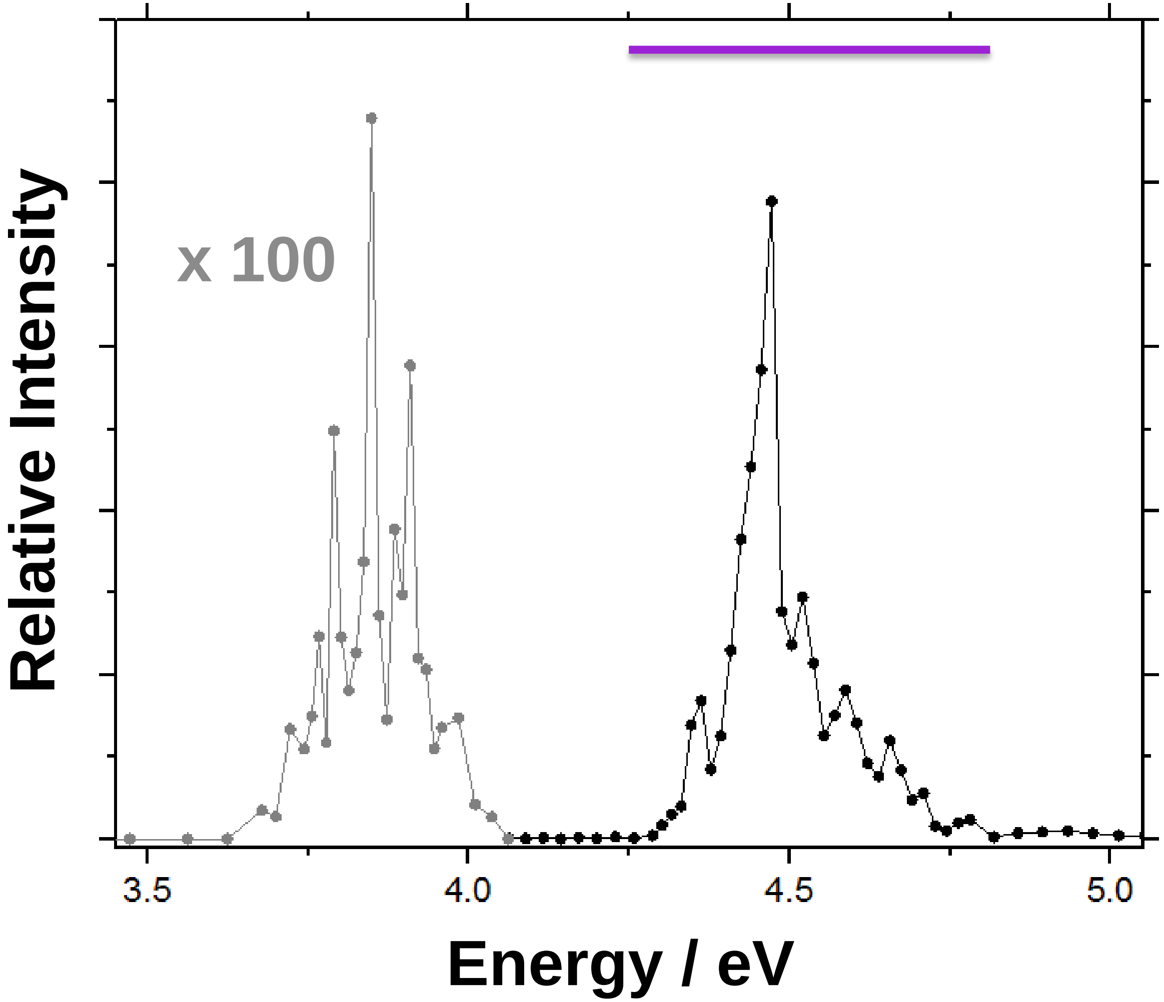
For pulsed lasers:

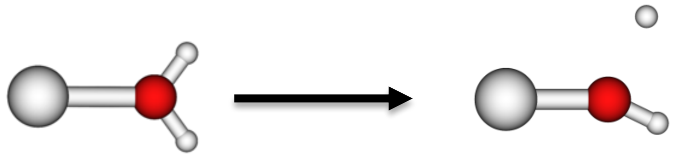
$$I_0 = \sum_{i=0}^{n} I_i \; e^{-\sigma\frac{\lambda p E}{hcA}}$$

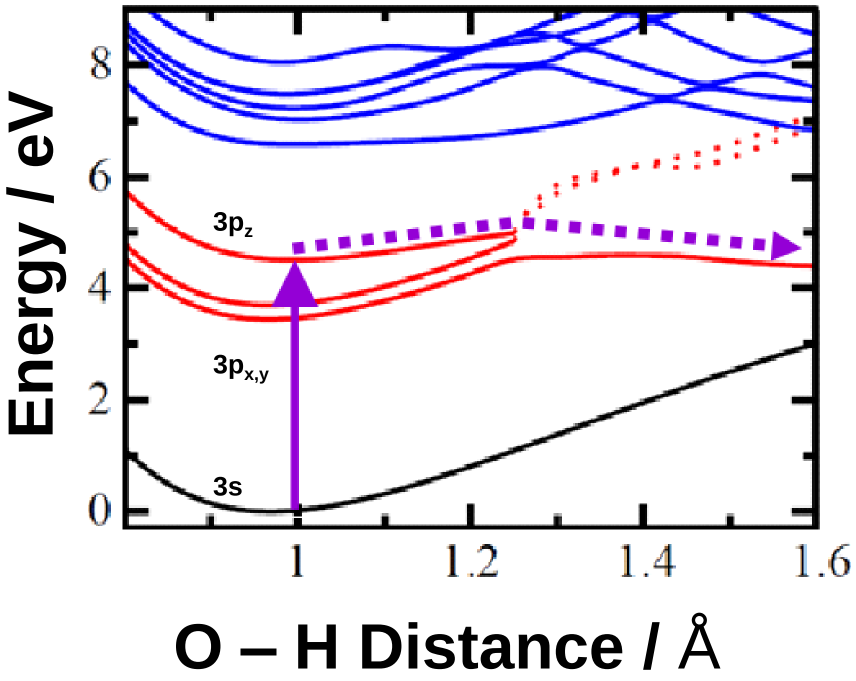
For pulsed lasers, also considering BIRD:

$$I_0 = \sum_{i=0}^{n} I_i \; e^{-\sigma\frac{\lambda p E}{hcA} - k_{BIRD}\, t}$$

$[MgH_2O]^+$ in Detail







Theory: EOM-CCSD/aug-cc-pVD(T)Z, MRCI/aug-cc-pVTZ

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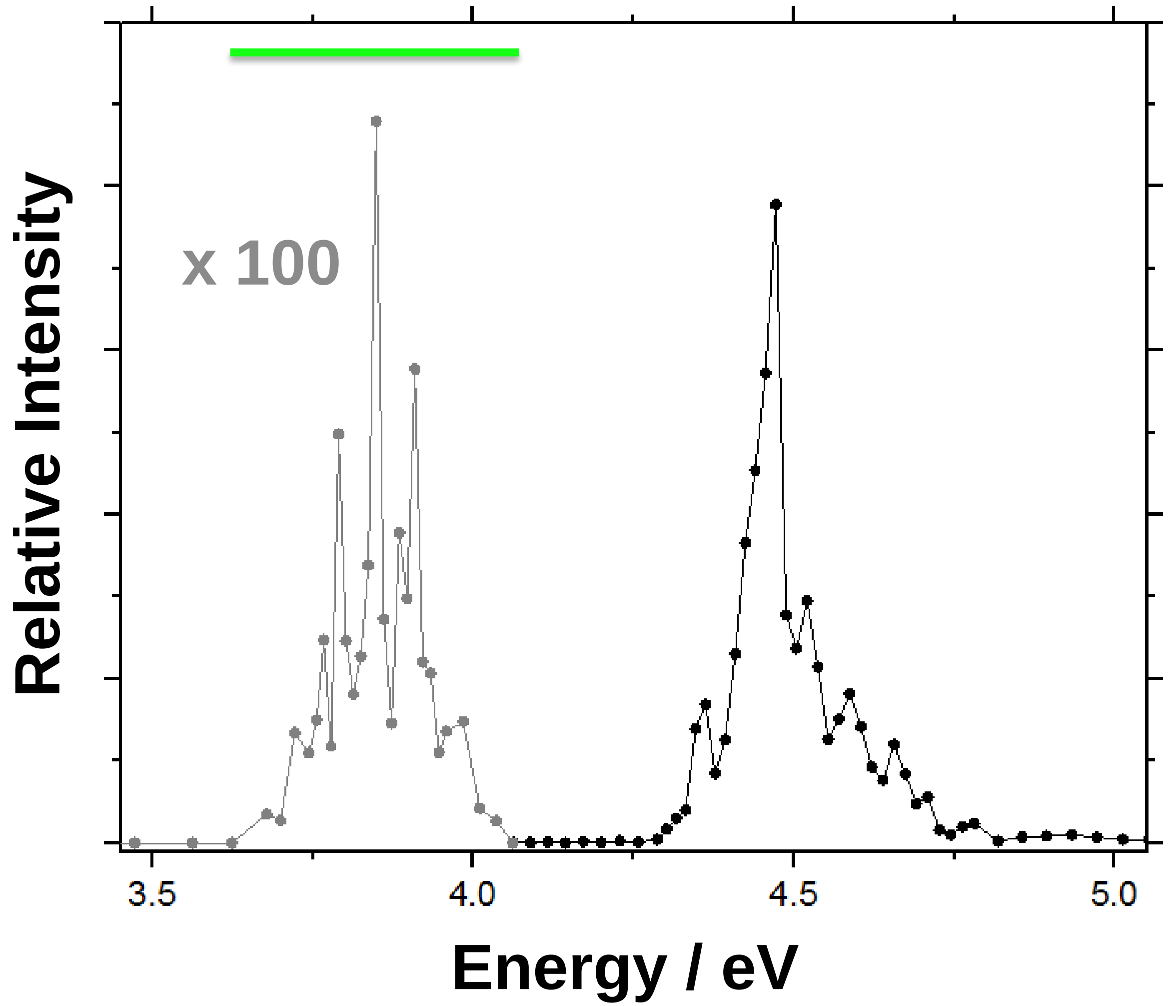
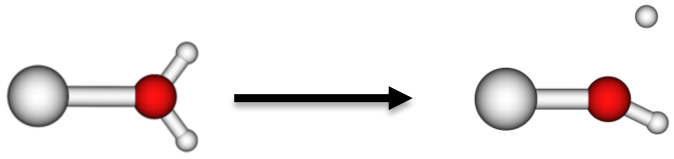
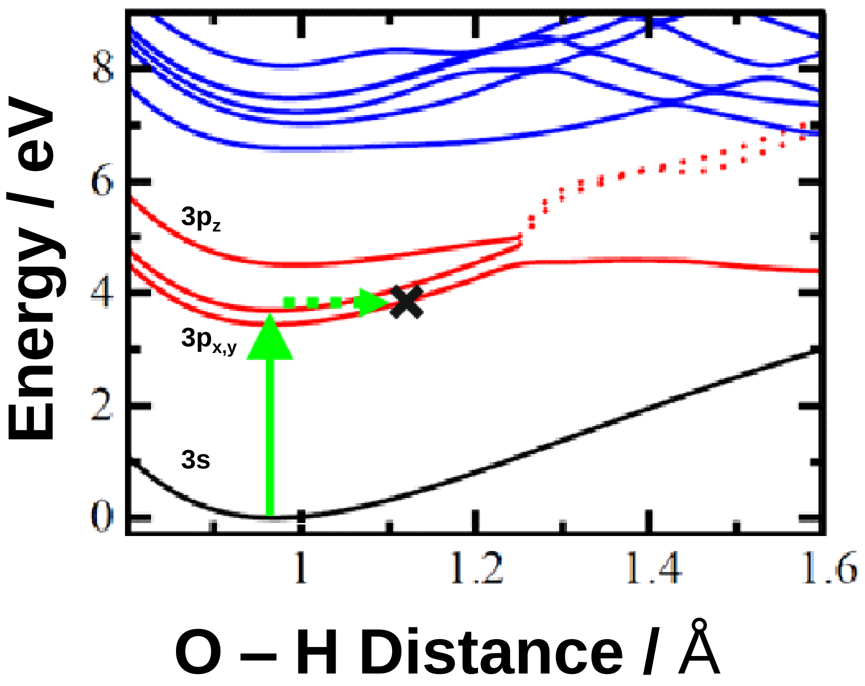
$[MgH_2O]^+$ in Detail

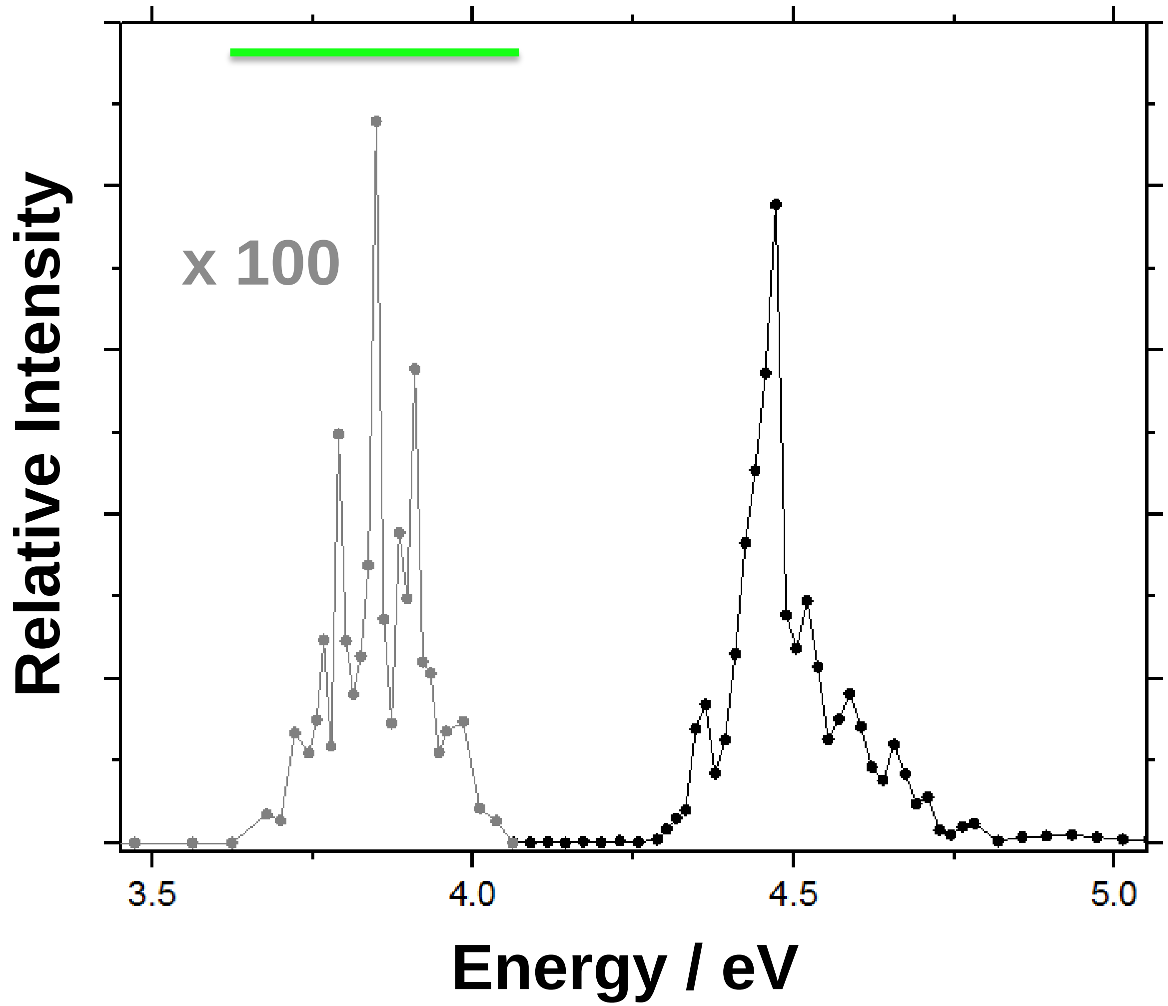


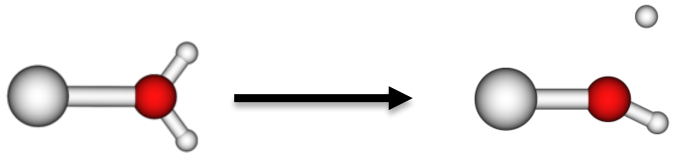


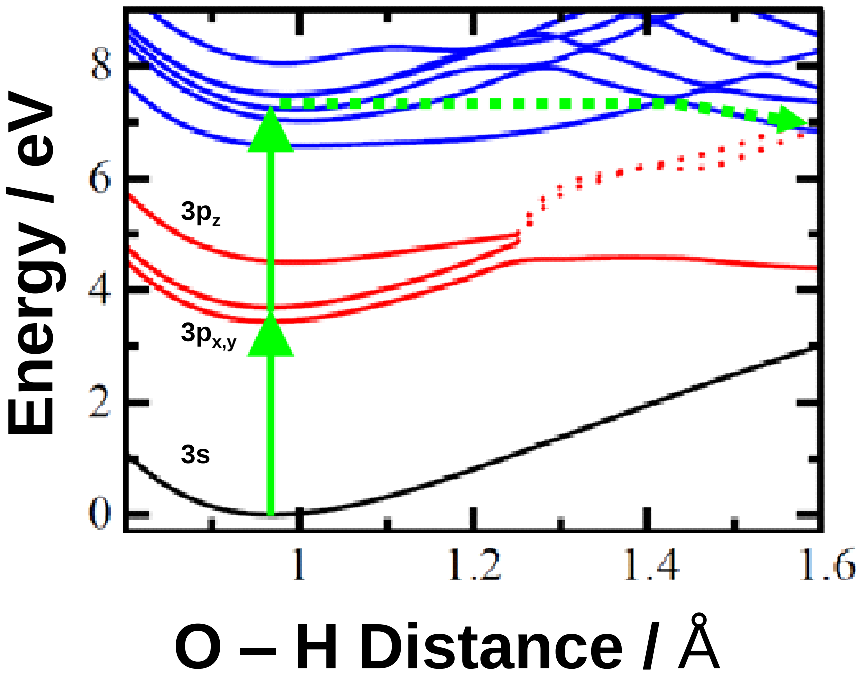


Theory: EOM-CCSD/aug-cc-pVD(T)Z, MRCI/aug-cc-pVTZ

$[MgH_2O]^+$ in Detail

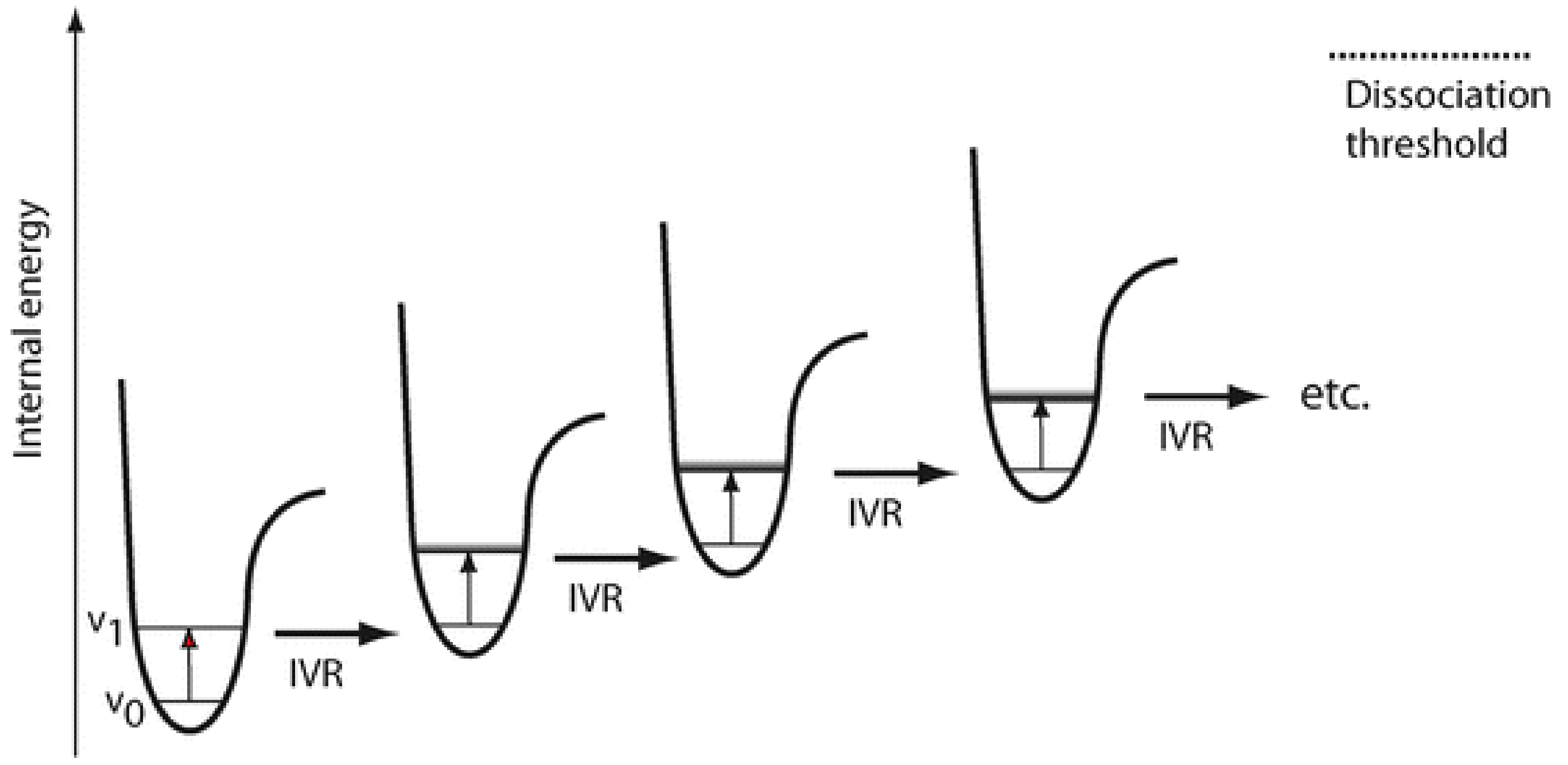






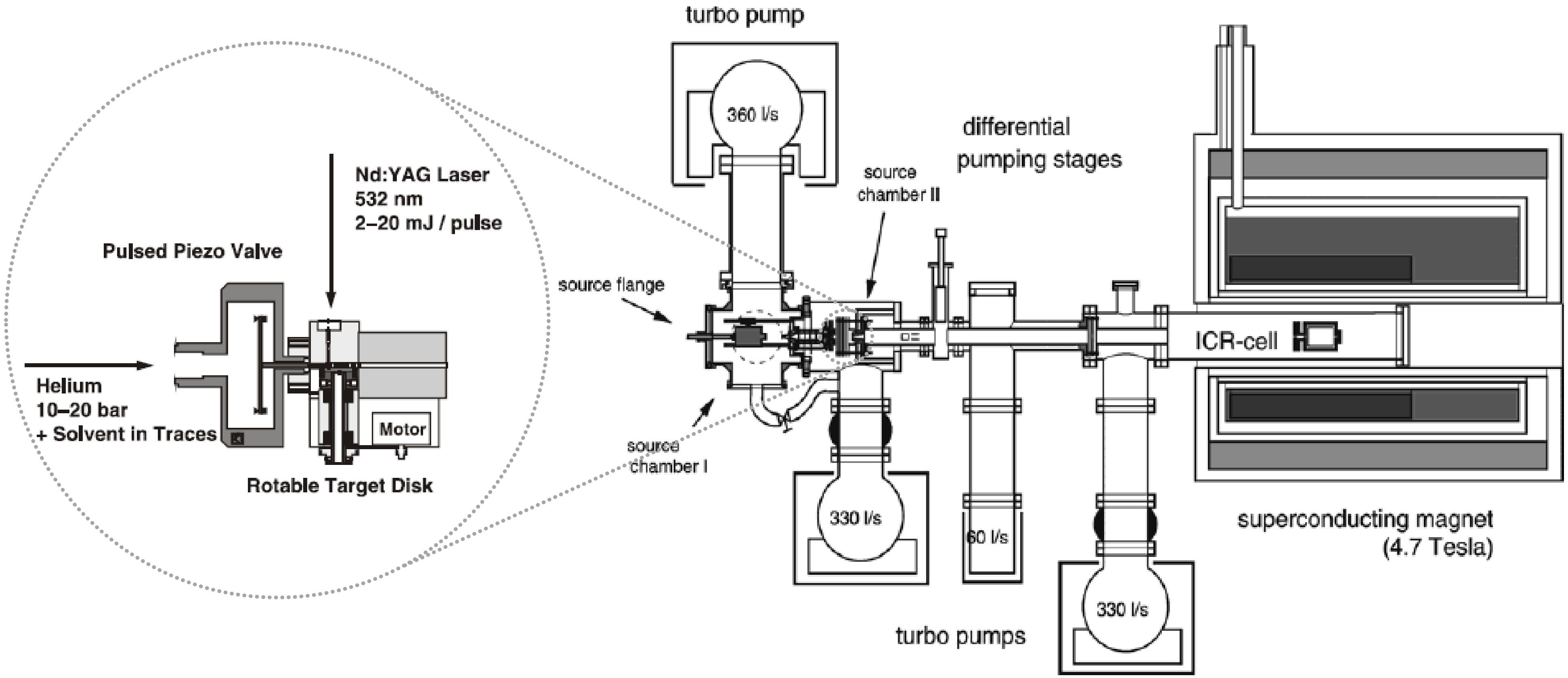
Theory: EOM-CCSD/aug-cc-pVD(T)Z, MRCI/aug-cc-pVTZ

IR Photodissociation

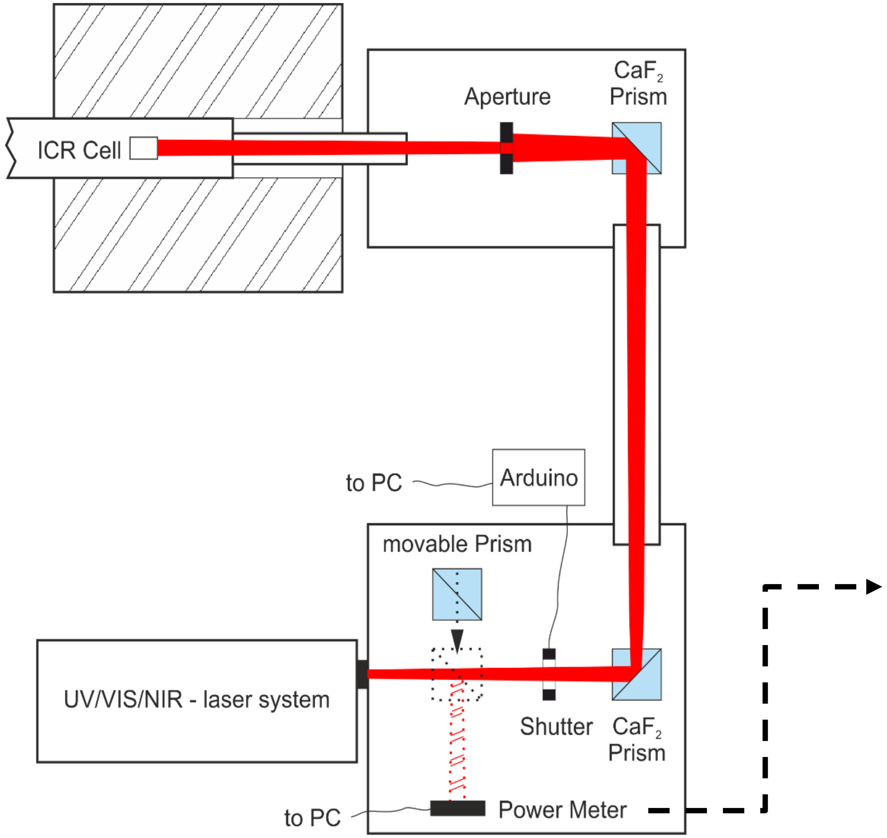


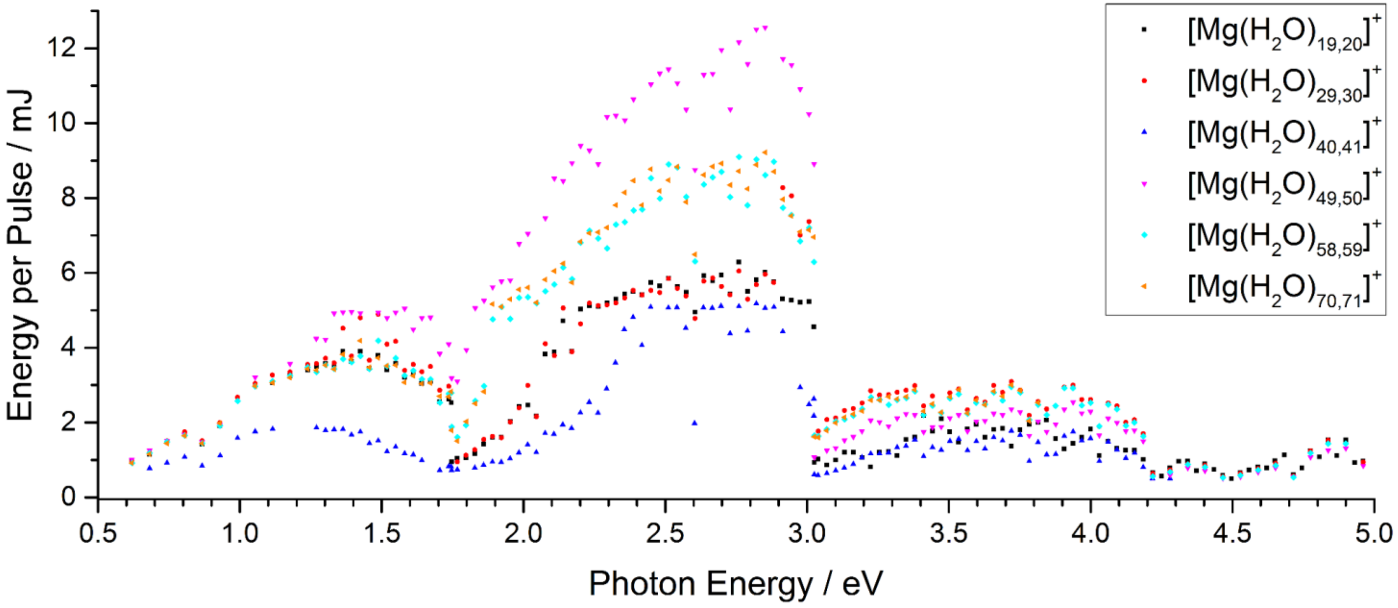
N.C. Polfer; Infrared multiple photon dissociation spectroscopy of trapped ions; Chem. Soc. Rev. 5, 2011

Experimental Setup

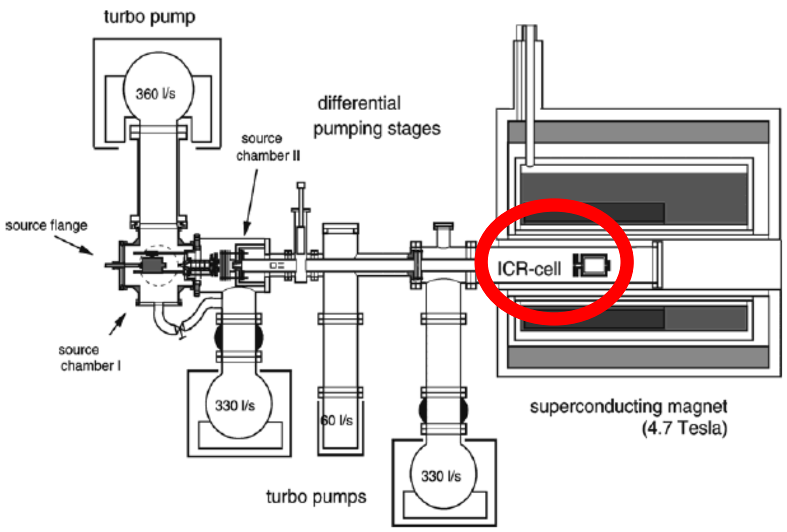


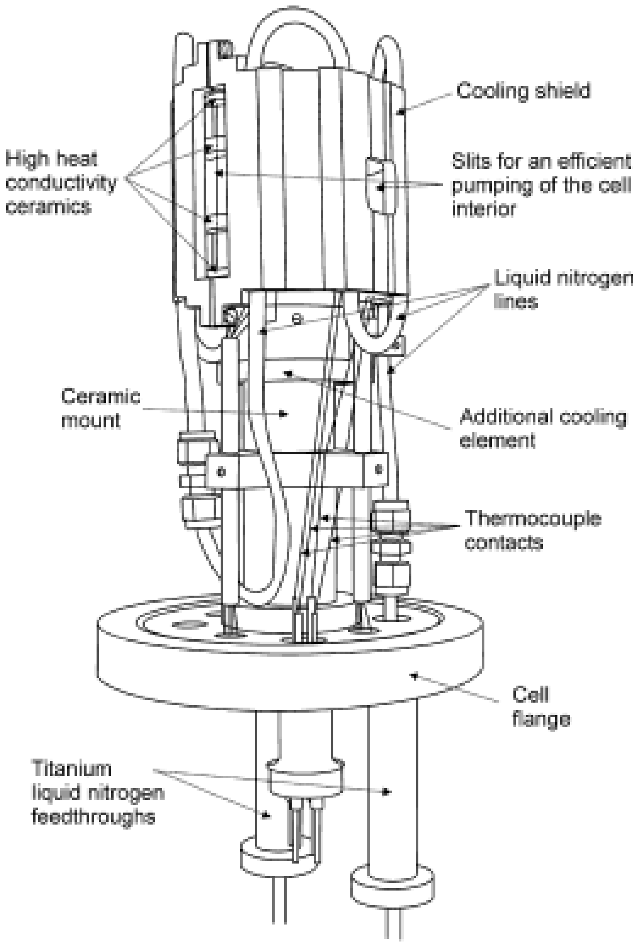
Experimental Setup



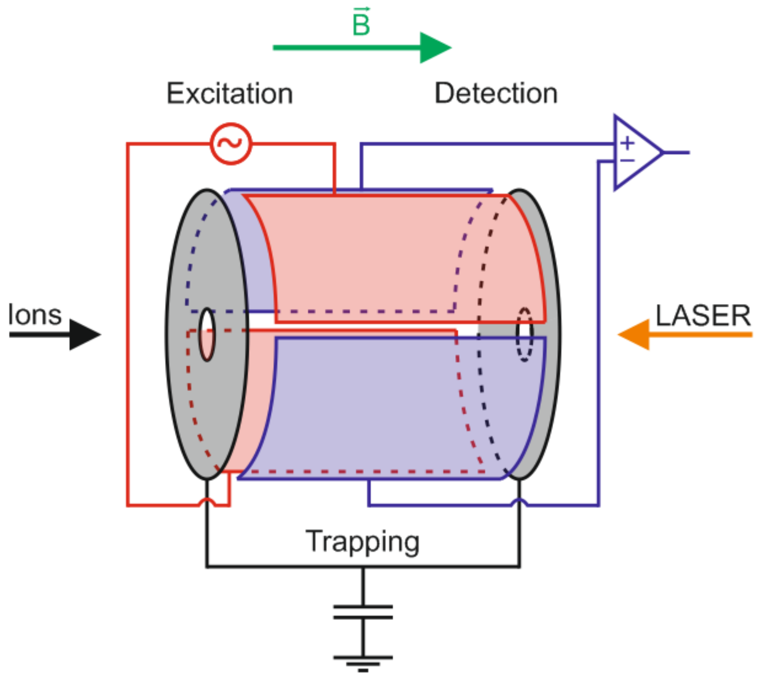


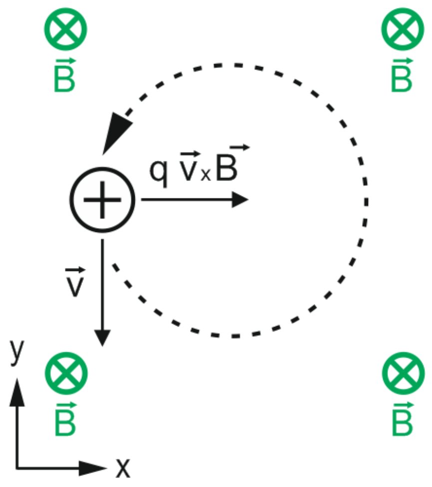
Liquid N_2 cooled ICR Cell





Basic Principles of FT-ICR-MS

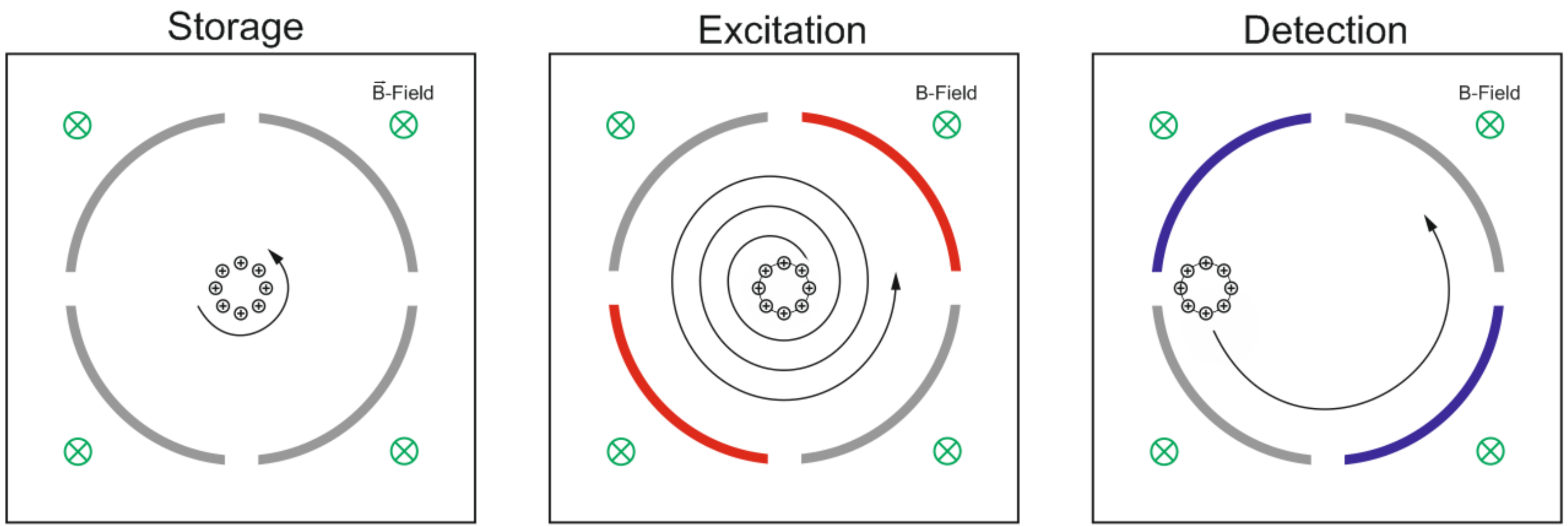


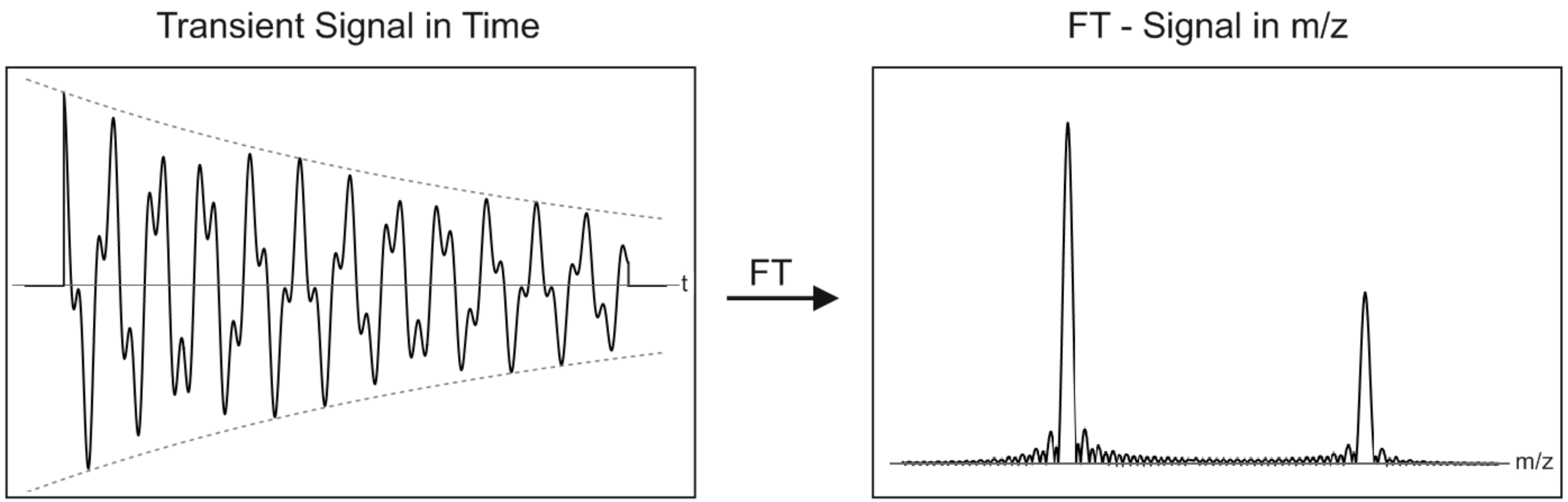


$$\vec{F} = q\left(\vec{E} + \vec{v} \times \vec{B}\right)$$

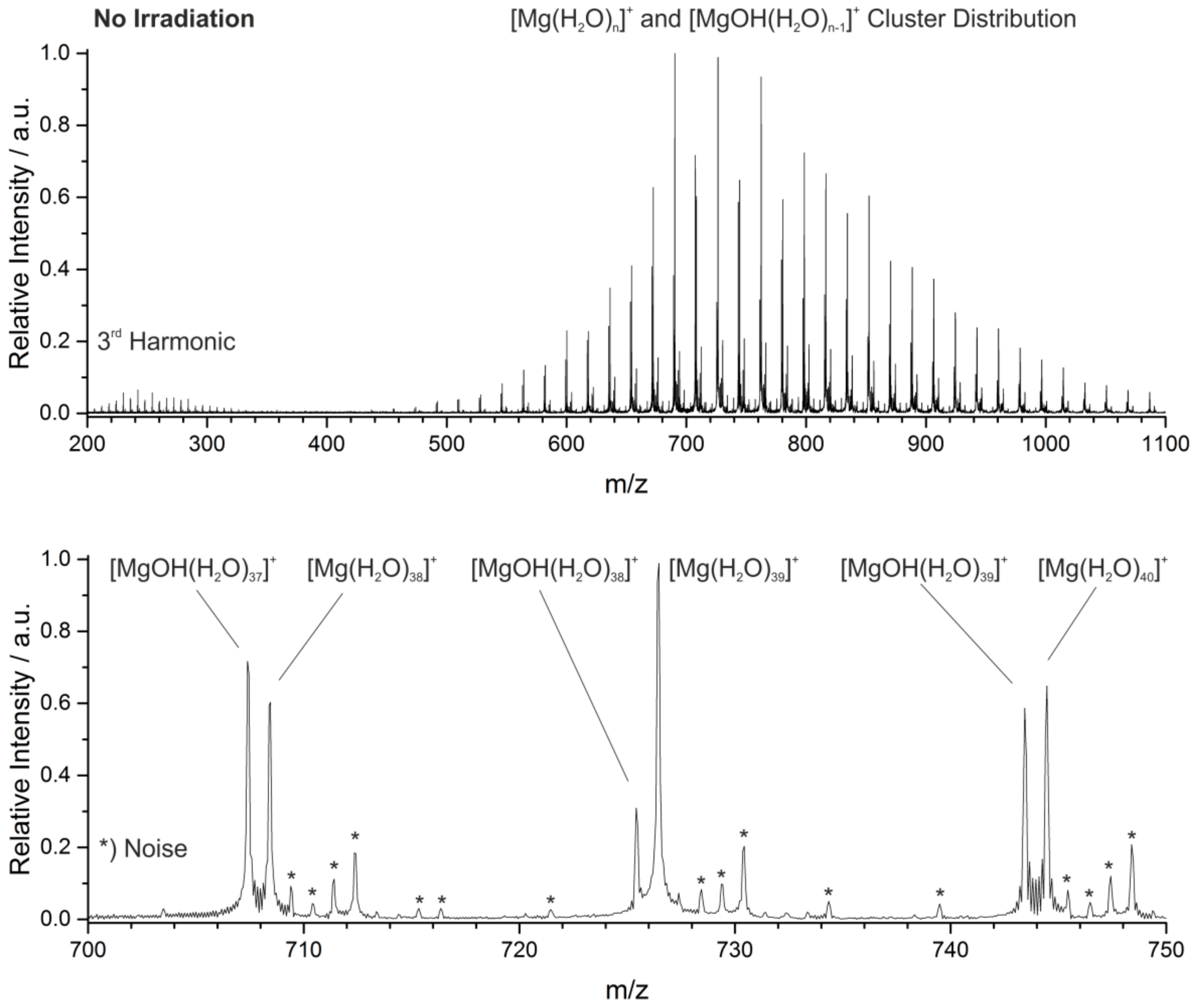
$$\omega \propto \frac{B}{m/z}$$

Experimental Setup



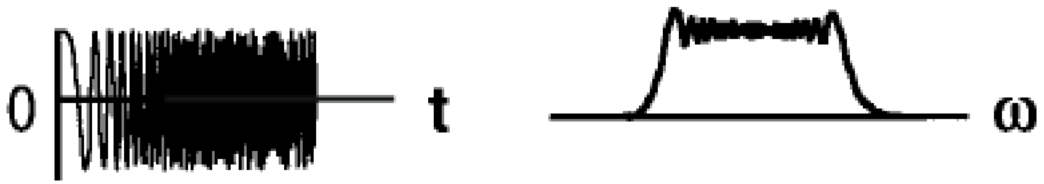


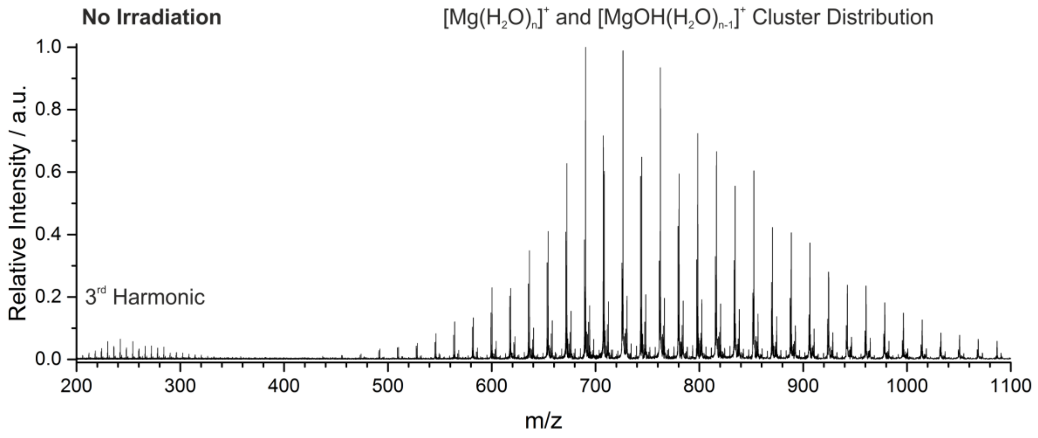
Experimental Setup



Cluster Isolation

Broad Band Excitation: Frequency Sweep / Chirp





A.G. Marshall, C.L. Hendrickson, G.S. Jackson; Fourier Transform Ion Cyclotron Resonance Mass Spectrometry: A Primer

Cluster Isolation

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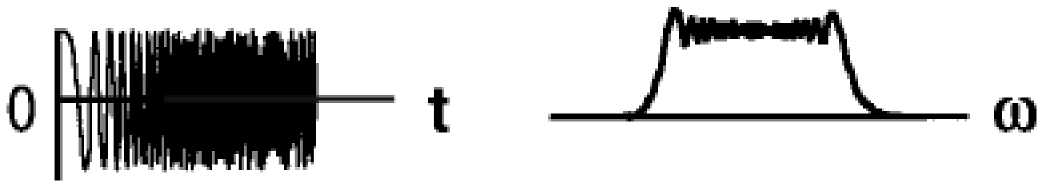

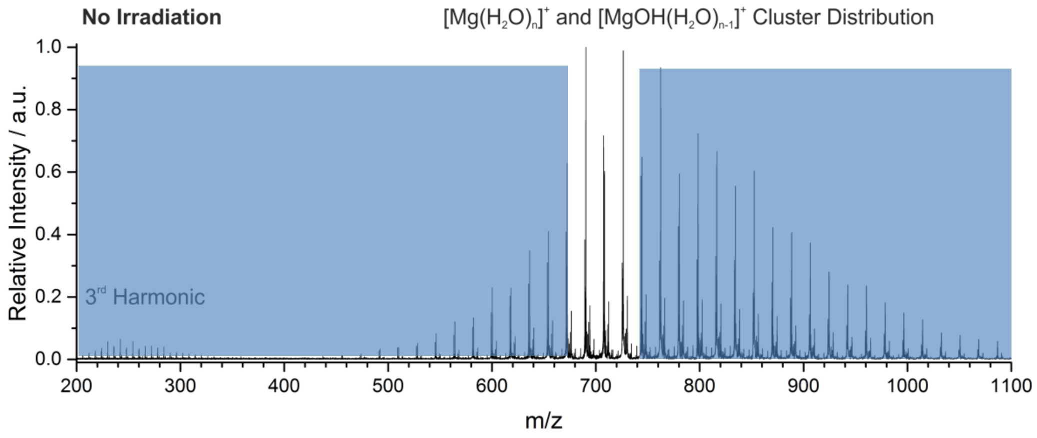

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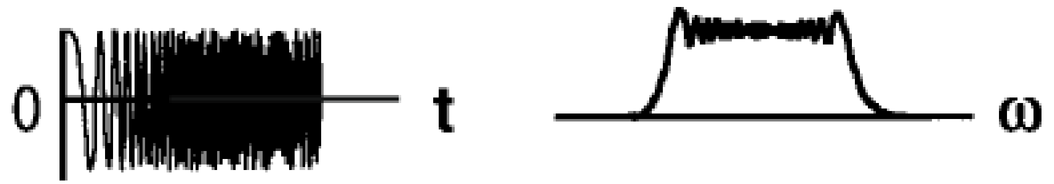
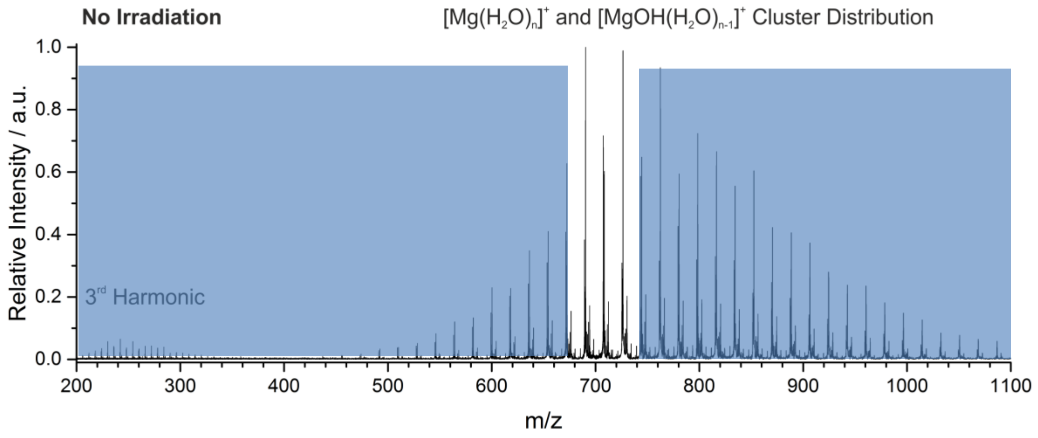
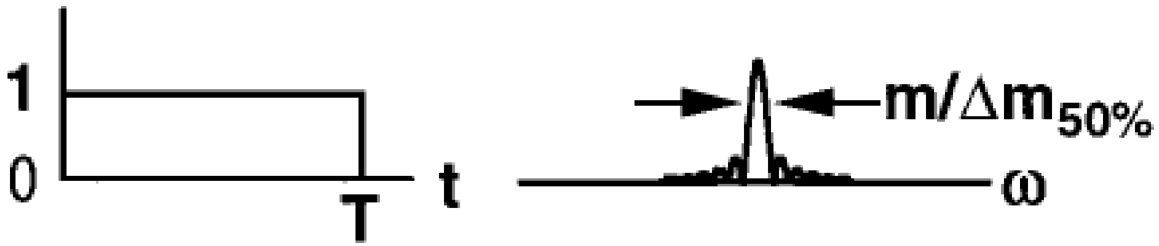
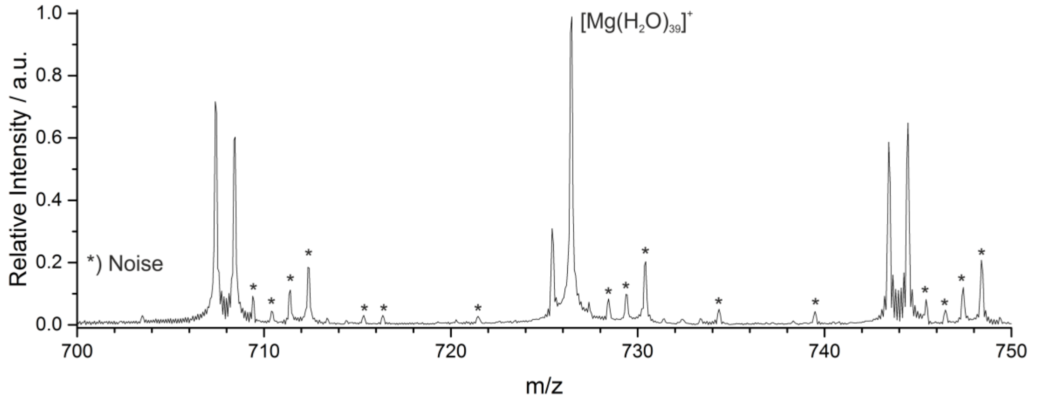




Single Frequency Excitation: Ejection Shots





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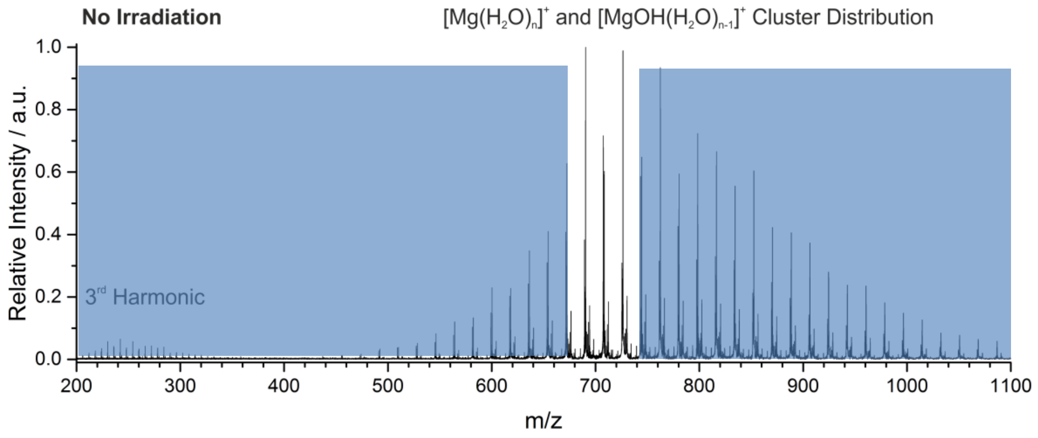

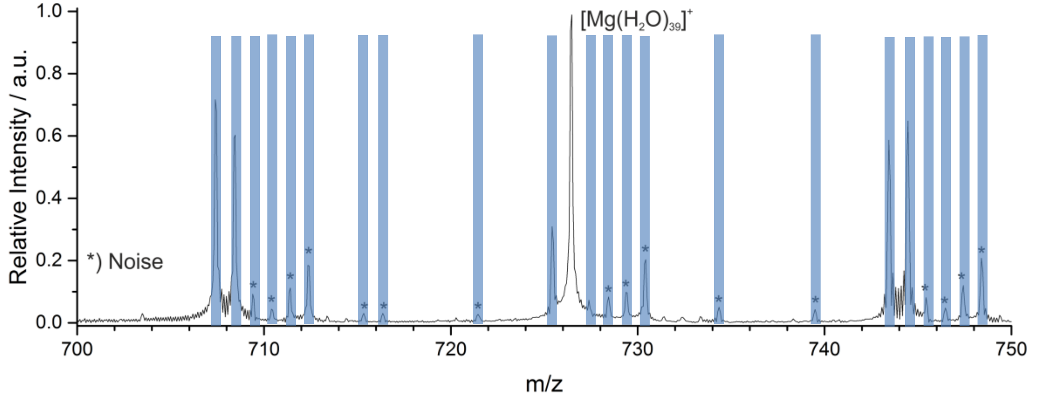

A.G. Marshall, C.L. Hendrickson, G.S. Jackson; Fourier Transform Ion Cyclotron Resonance Mass Spectrometry: A Primer

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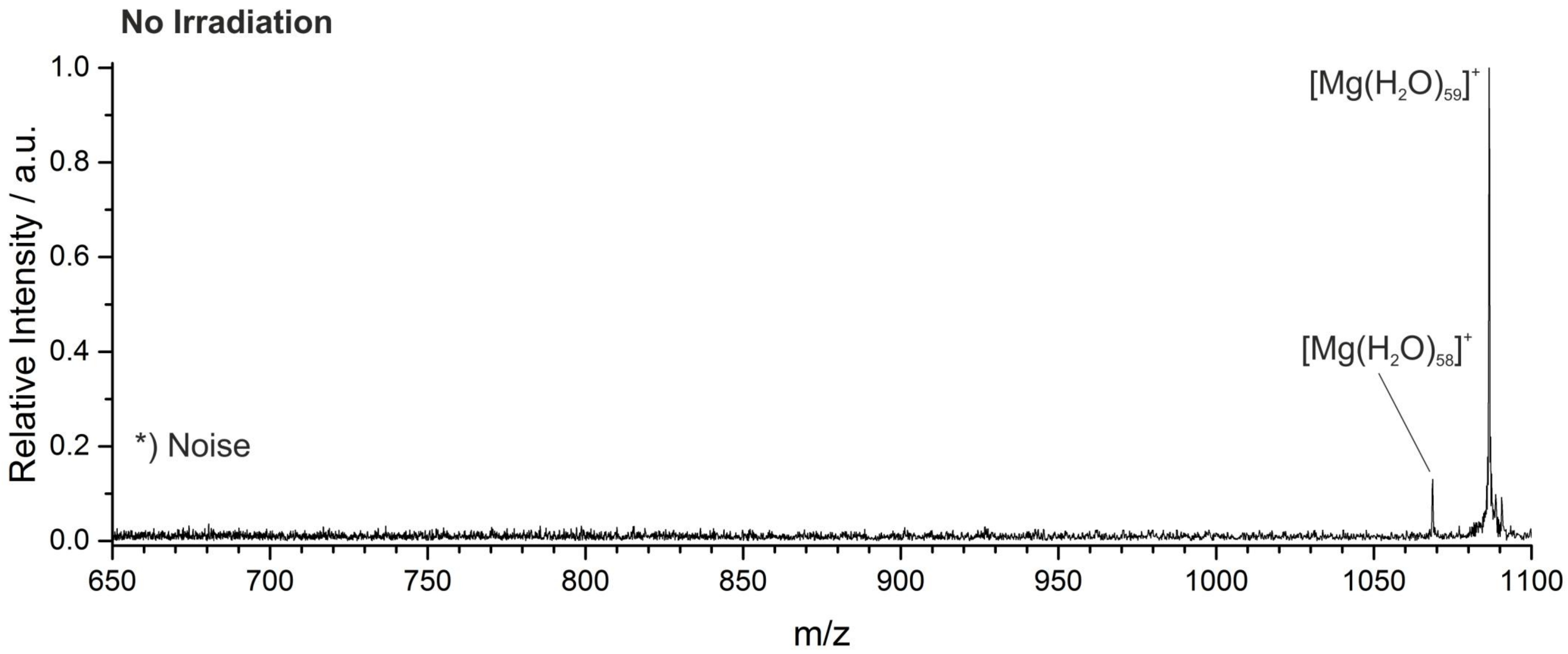
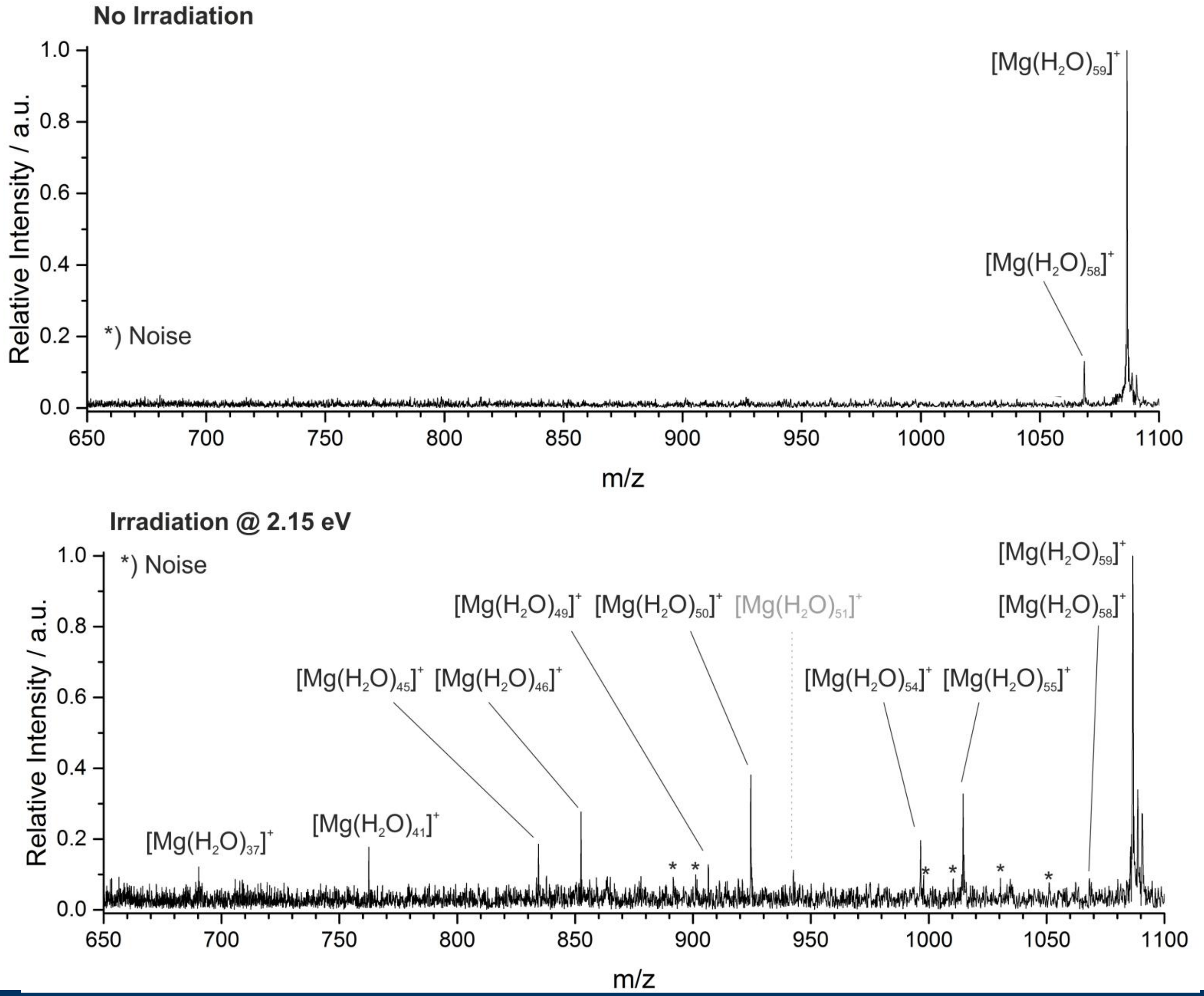
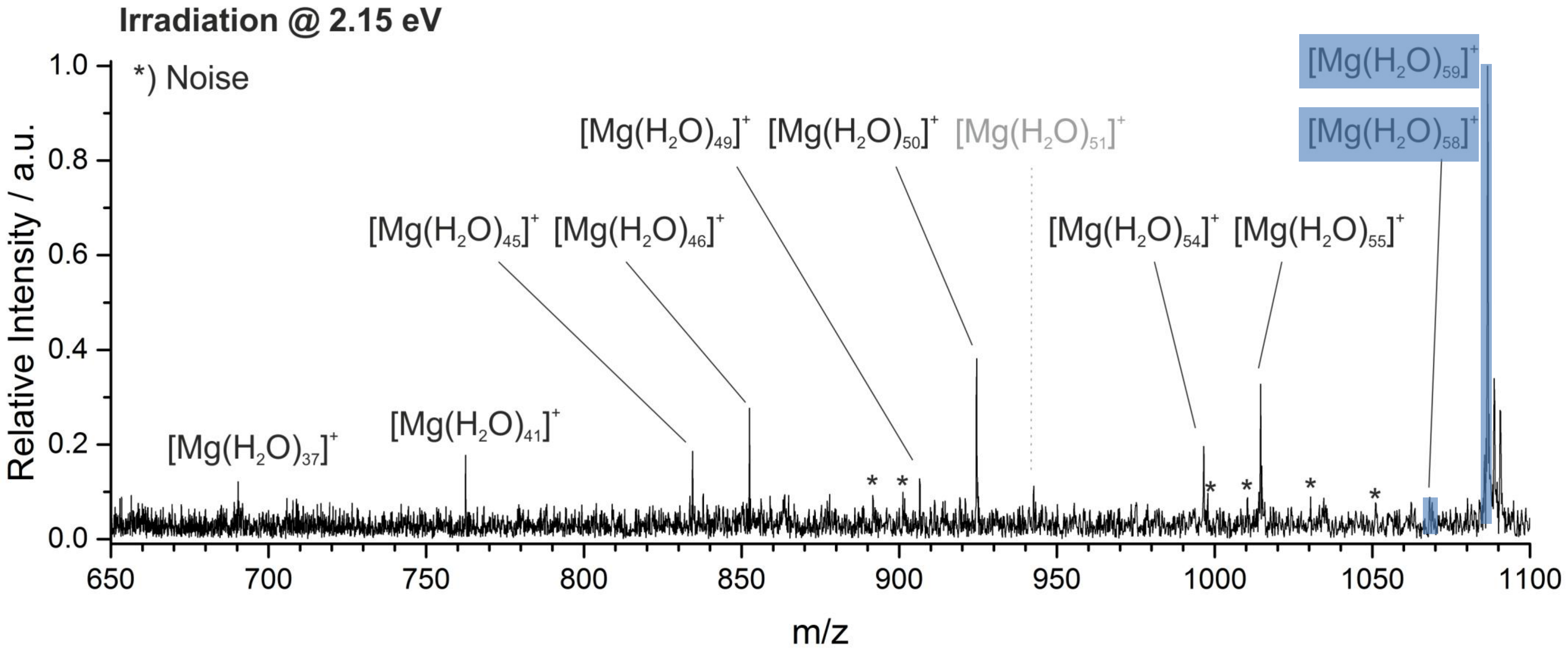


Data Generation

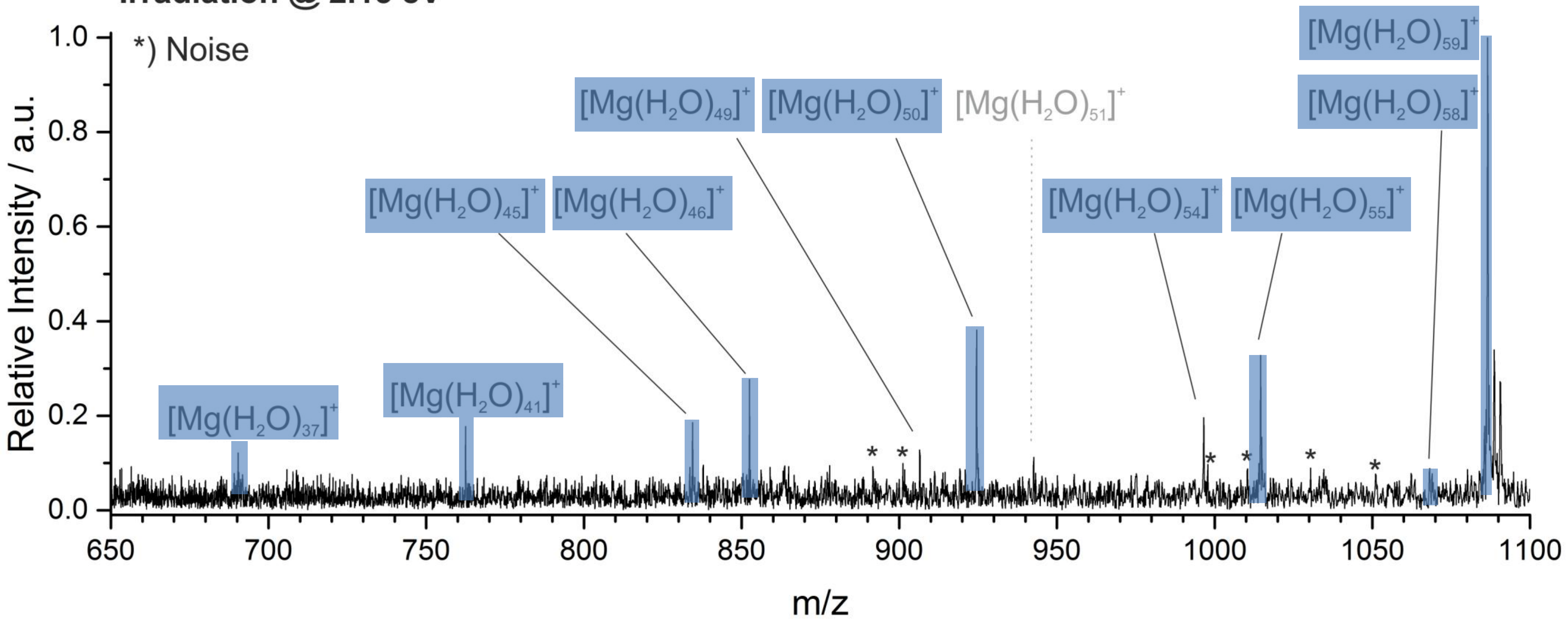


$$I_0 = \sum_{i=0}^{n} I_i \, e^{-\sigma \frac{\lambda p E}{hcA} - k_{BIRD} t}$$



$$I_0 = \sum_{i=0}^{n} I_i \, e^{-\sigma \frac{\lambda p E}{hcA} - k_{BIRD} t}$$

Irradiation @ 2.15 eV



Data Generation

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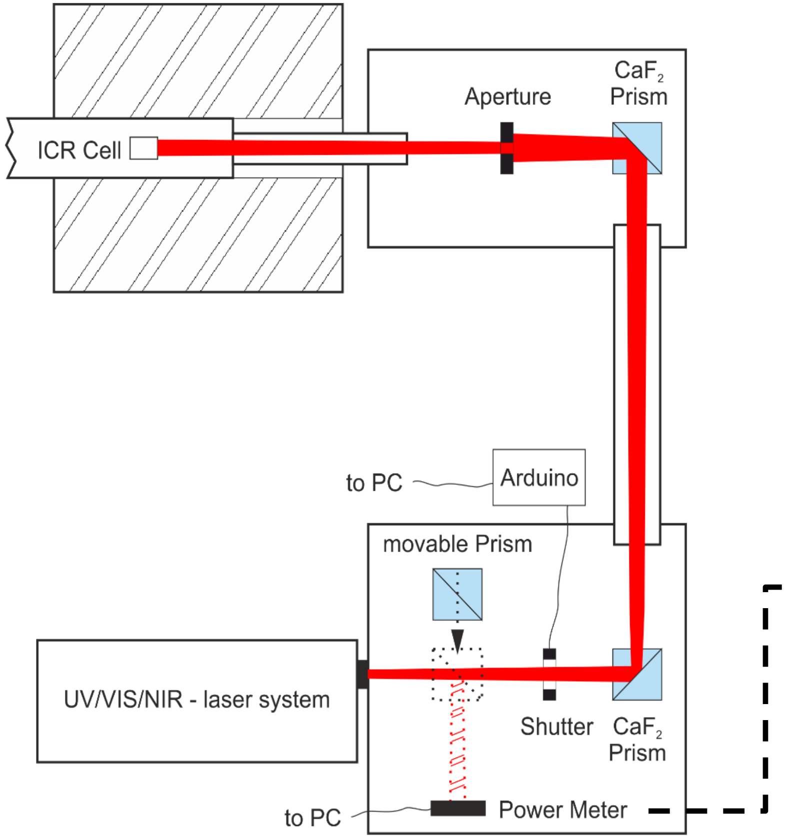
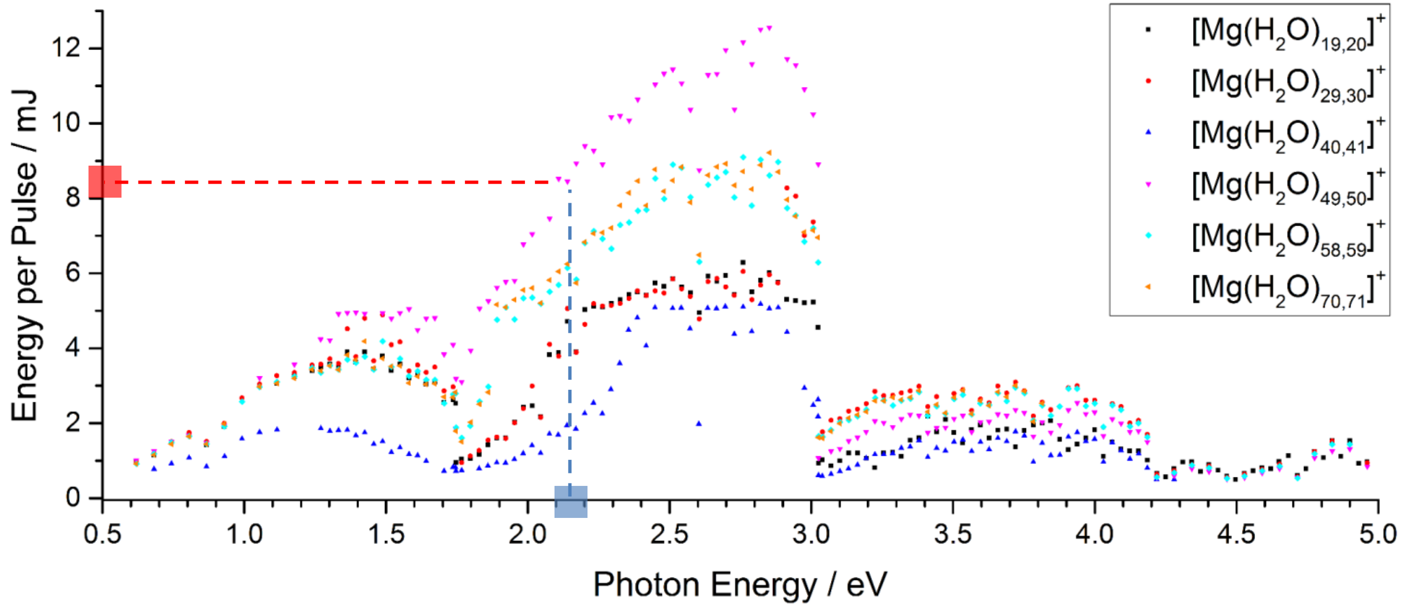
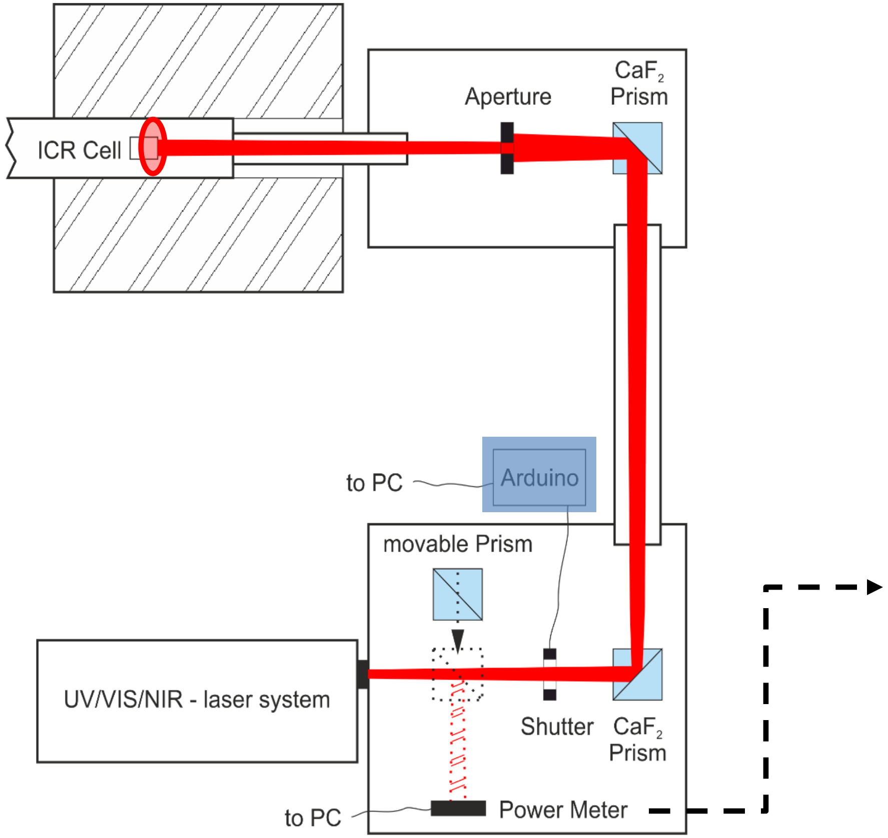
$$I_0 = \sum_{i=0}^{n} I_i \, e^{-\sigma \frac{\lambda p E}{h c A} - k_{BIRD} t}$$

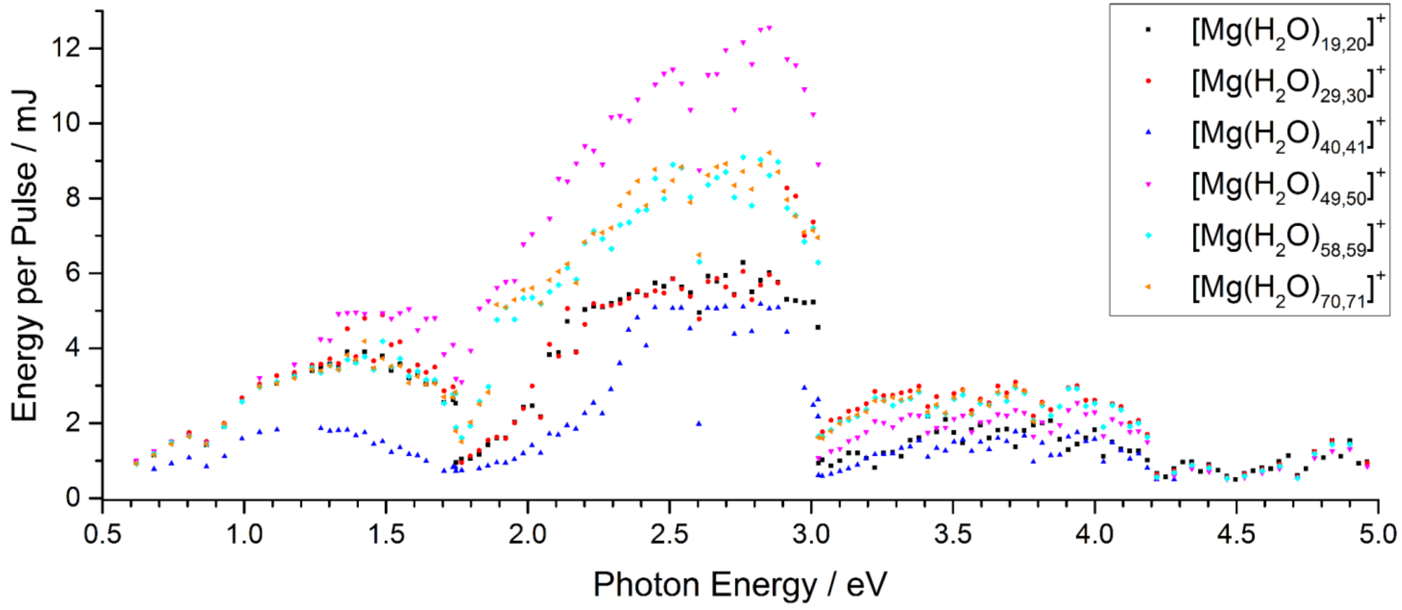


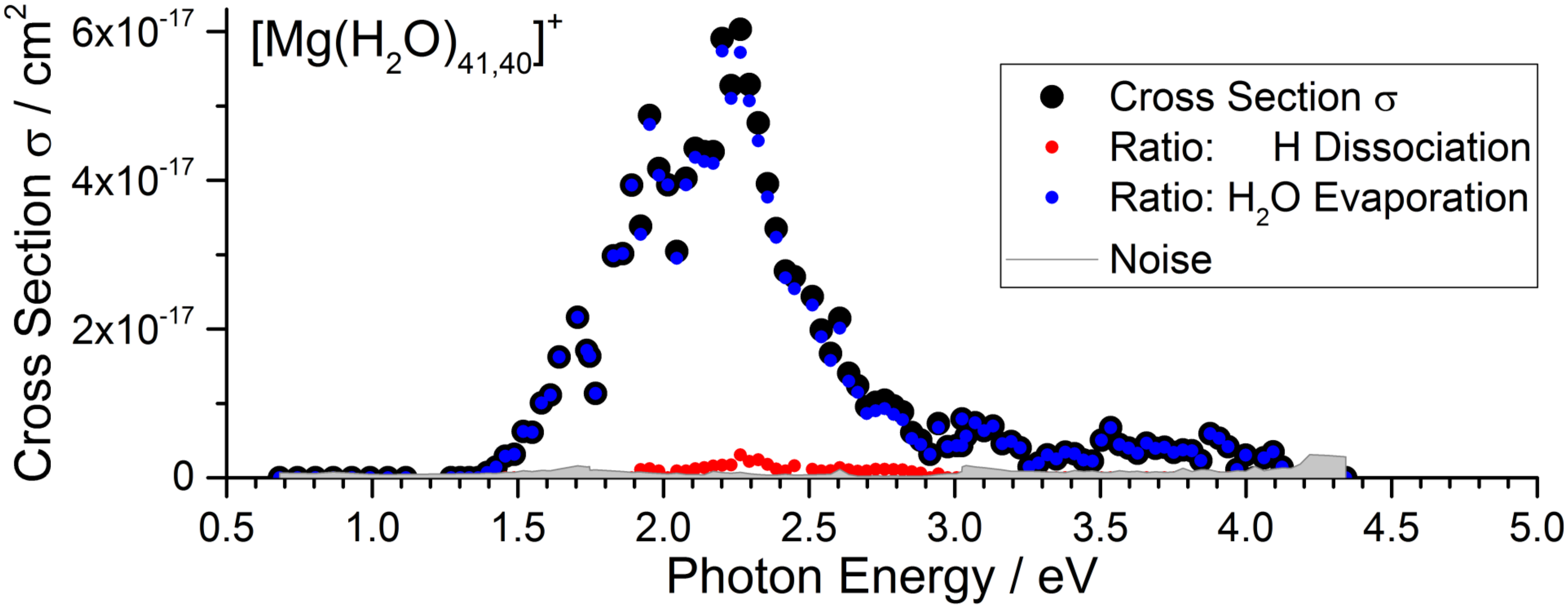


Data Generation

$$I_0 = \sum_{i=0}^{n} I_i \, e^{-\sigma \frac{\lambda p E}{hcA} - k_{BIRD} t}$$






$[Mg(H_2O)_{41,40}]^+$
Cross Section σ / cm²
6x10⁻¹⁷
4x10⁻¹⁷
2x10⁻¹⁷
0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
Photon Energy / eV
Cross Section σ
Ratio: H Dissociation
Ratio: H₂O Evaporation
Noise

Hydrated Magnesium Ions

THE JOURNAL OF CHEMICAL PHYSICS **149**, 044309 (2018)

Photochemistry and spectroscopy of small hydrated magnesium clusters $Mg^+(H_2O)_n$, $n = 1–5$

Milan Ončák,[a] Thomas Taxer, Erik Barwa, Christian van der Linde, and Martin K. Beyer[a]
Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, Technikerstraße 25, 6020 Innsbruck, Austria

(Received 24 April 2018; accepted 11 July 2018; published online 27 July 2018)

Hydrated singly charged magnesium ions $Mg^+(H_2O)_n$, $n \leq 5$, in the gas phase are ideal model systems to study photochemical hydrogen evolution since atomic hydrogen is formed over a wide range of wavelengths, with a strong cluster size dependence. Mass selected clusters are stored in the cell of an Fourier transform ion cyclotron resonance mass spectrometer at a temperature of 130 K for several seconds, which allows thermal equilibration via blackbody radiation. Tunable laser light is used for photodissociation. Strong transitions to D_{1-3} states (correlating with the $3s$-$3p_{x,y,z}$ transitions of Mg^+) are observed for all cluster sizes, as well as a second absorption band at 4–5 eV for n = 3-5. Due to the lifted degeneracy of the $3p_{x,y,z}$ energy levels of Mg^+, the absorptions are broad and red shifted with increasing coordination number of the Mg^+ center, from 4.5 eV for n = 1 to 1.8 eV for n = 5. In all cases, H atom formation is the dominant photochemical reaction channel. Quantum chemical calculations using the full range of methods for excited state calculations reproduce the experimental spectra and explain all observed features. In particular, they show that H atom formation occurs in excited states, where the potential energy surface becomes repulsive along the O···H coordinate at relatively small distances. The loss of H_2O, although thermochemically favorable, is a minor channel because, at least for the clusters n = 1-3, the conical intersection through which the system could relax to the electronic ground state is too high in energy. In some absorption bands, sequential absorption of multiple photons is required for photodissociation. For n = 1, these multiphoton spectra can be modeled on the basis of quantum chemical calculations. https://doi.org/10.1063/1.5037401

Faraday Discussions

ROYAL SOCIETY OF CHEMISTRY

Cite this: *Faraday Discuss.*, 2019, **217**, 584

PAPER

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Electronic spectroscopy and nanocalorimetry of hydrated magnesium ions $[Mg(H_2O)_n]^+$, $n = 20–70$: spontaneous formation of a hydrated electron?†

Thomas Taxer, Milan Ončák, * Erik Barwa, Christian van der Linde and Martin K. Beyer *

Received 23rd November 2018, Accepted 7th December 2018

DOI: 10.1039/c8fd00204e

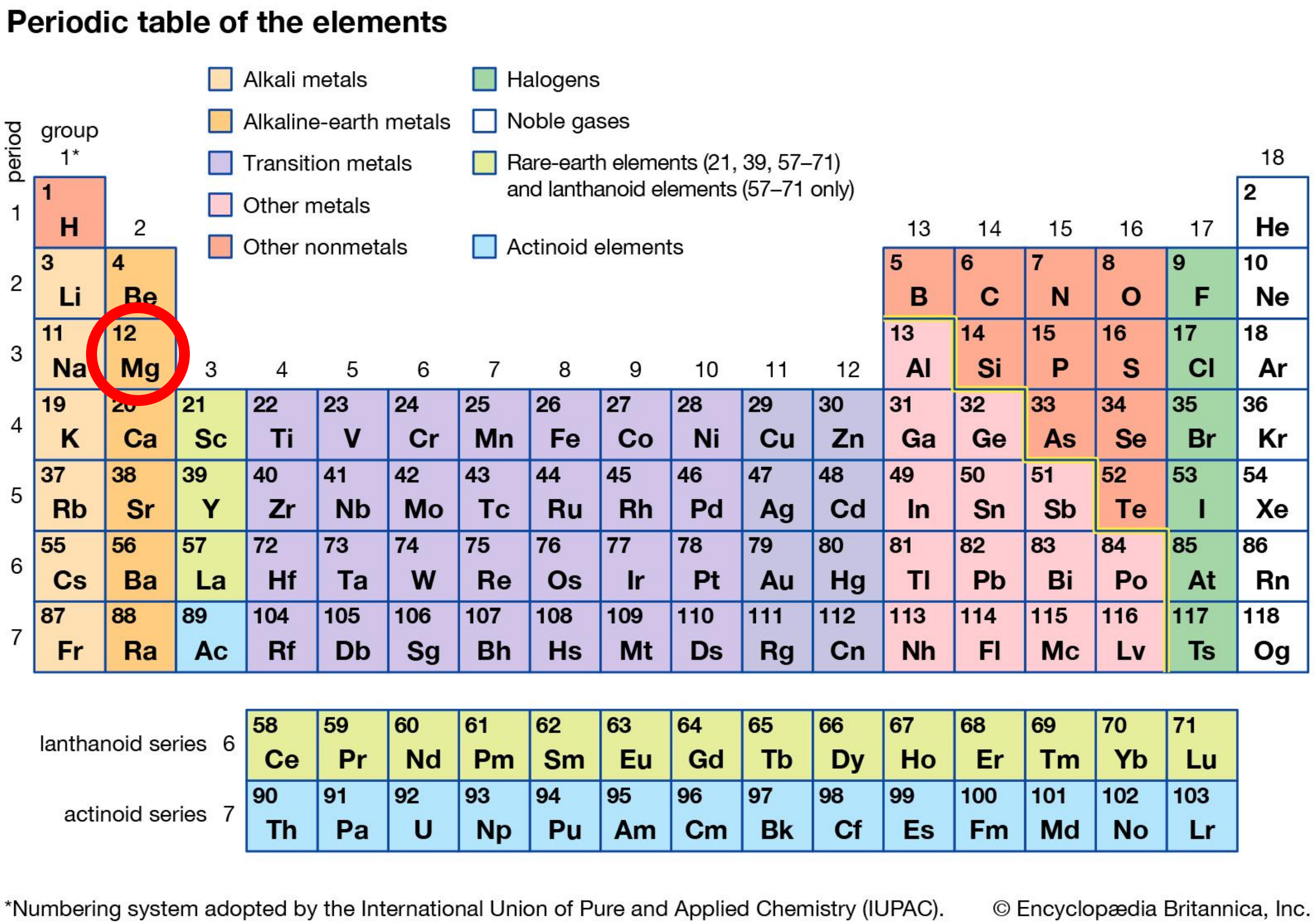
Hydrated singly charged magnesium ions $[Mg(H_2O)_n]^+$ are thought to consist of an Mg^{2+} ion and a hydrated electron for n > 15. This idea is based on mass spectra, which exhibit a transition from $[MgOH(H_2O)_{n-1}]^+$ to $[Mg(H_2O)_n]^+$ around n = 15–22, black-body infrared radiative dissociation, and quantum chemical calculations. Here, we present photodissociation spectra of size-selected $[Mg(H_2O)_n]^+$ in the range of n = 20–70 measured for photon energies of 1.0–5.0 eV. The spectra exhibit a broad absorption from 1.4 to 3.2 eV, with two local maxima around 1.7–1.8 eV and 2.1–2.5 eV, depending on cluster size. The spectra shift slowly from n = 20 to n = 50, but no significant change is observed for n = 50–70. Quantum chemical modeling of the spectra yields several candidates for the observed absorptions, including five- and six-fold coordinated Mg^{2+} with a hydrated electron in its immediate vicinity, as well as a solvent-separated Mg^{2+}/e^- pair. The photochemical behavior resembles that of the hydrated electron, with barrierless interconversion into the ground state following the excitation.

Hydrated Magnesium Ions

Wikipedia

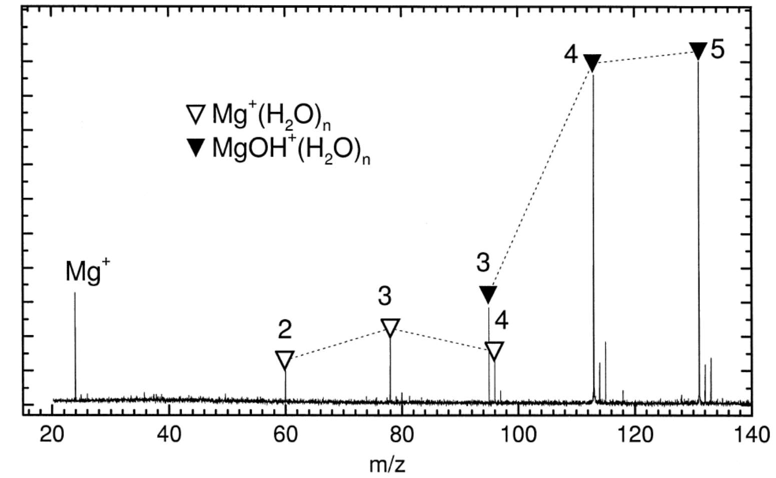
Electronic Configuration of Mg^+

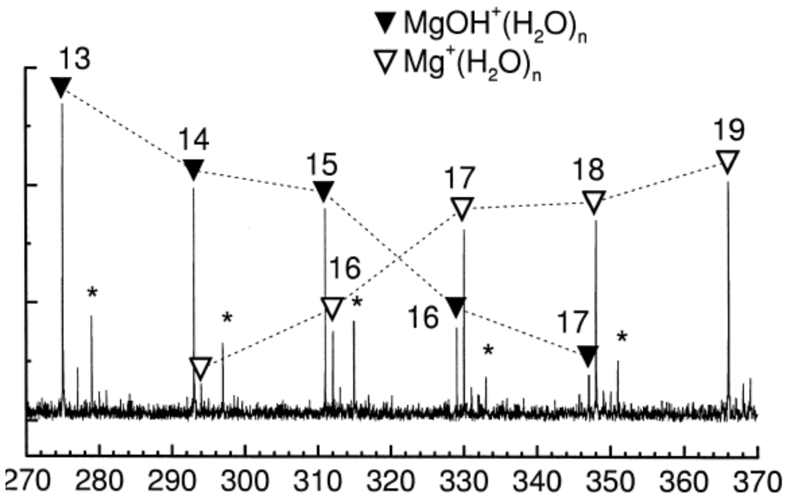
$1s^2 2s^2 2p^6 \underline{3s^1}$



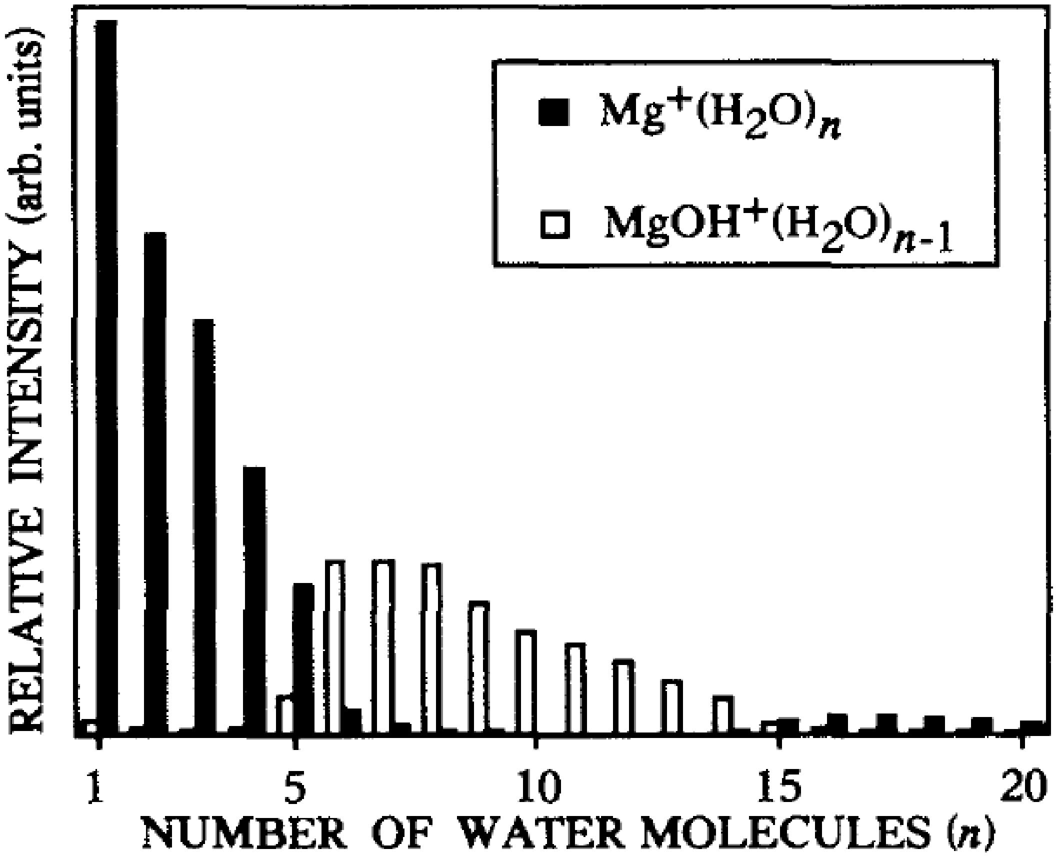
Introduction

C. Berg et al. / Chemical Physics 239 (**1998**) 379–392

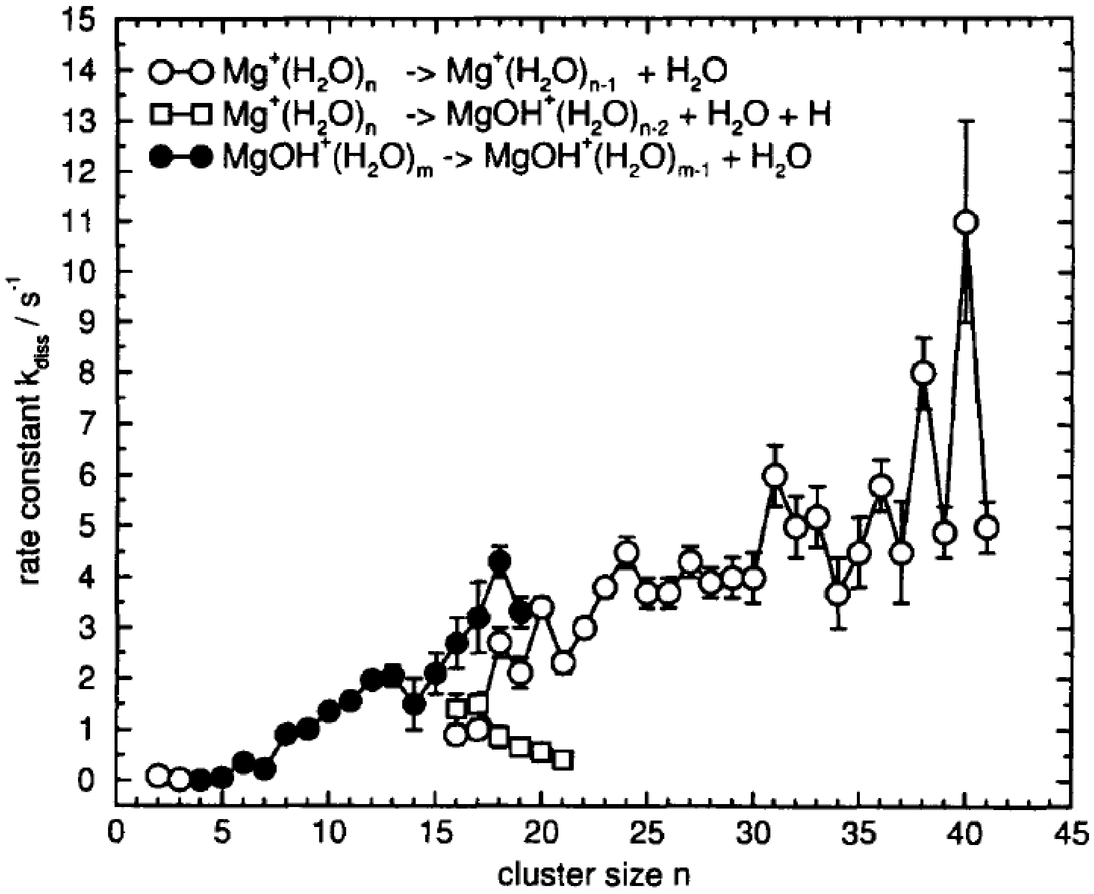


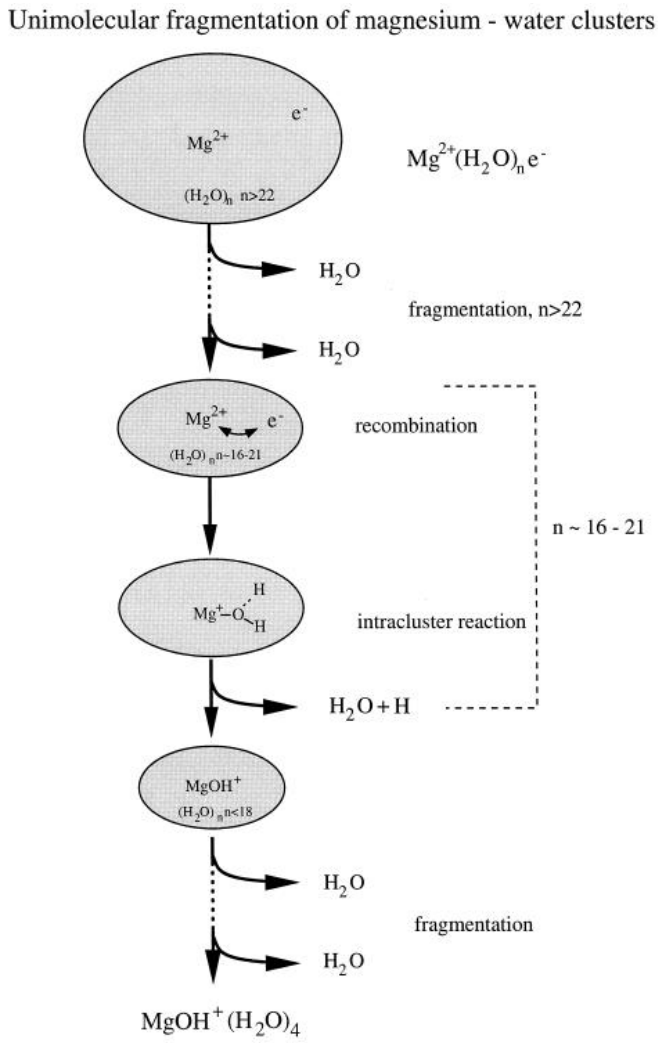


Misaizu et al. / J. Chern. Phys. 100 (**1994**) 1161



Hydrated Magnesium Ions $[Mg(H_2O)_n]^+$





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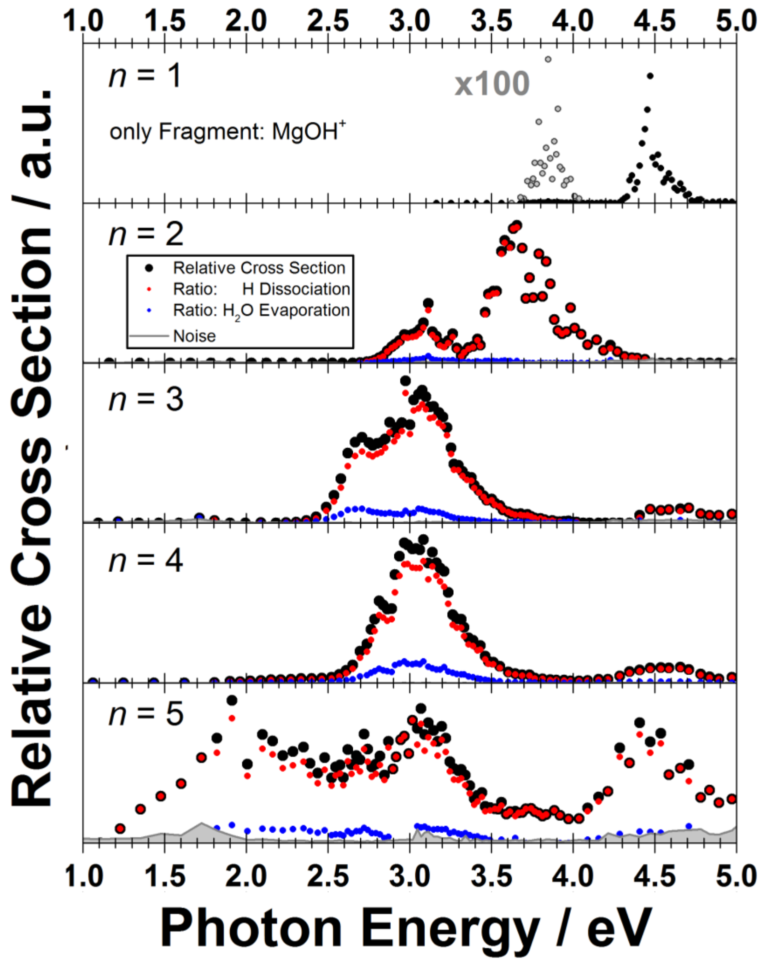
Short Recap of Results for small Clusters



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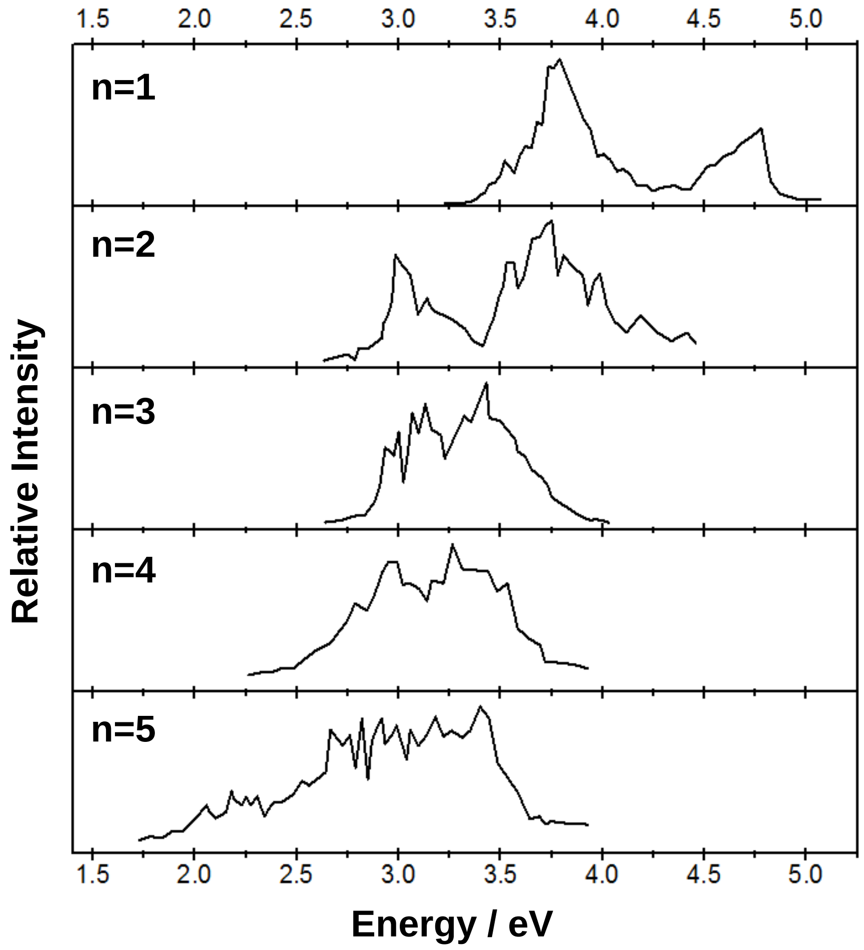
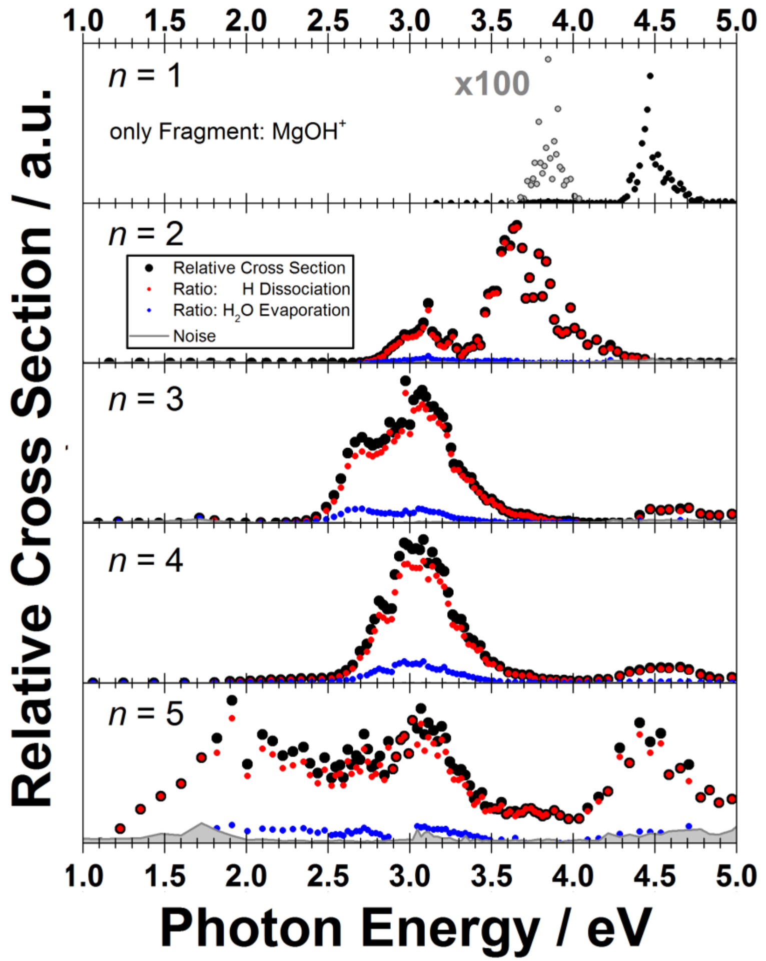


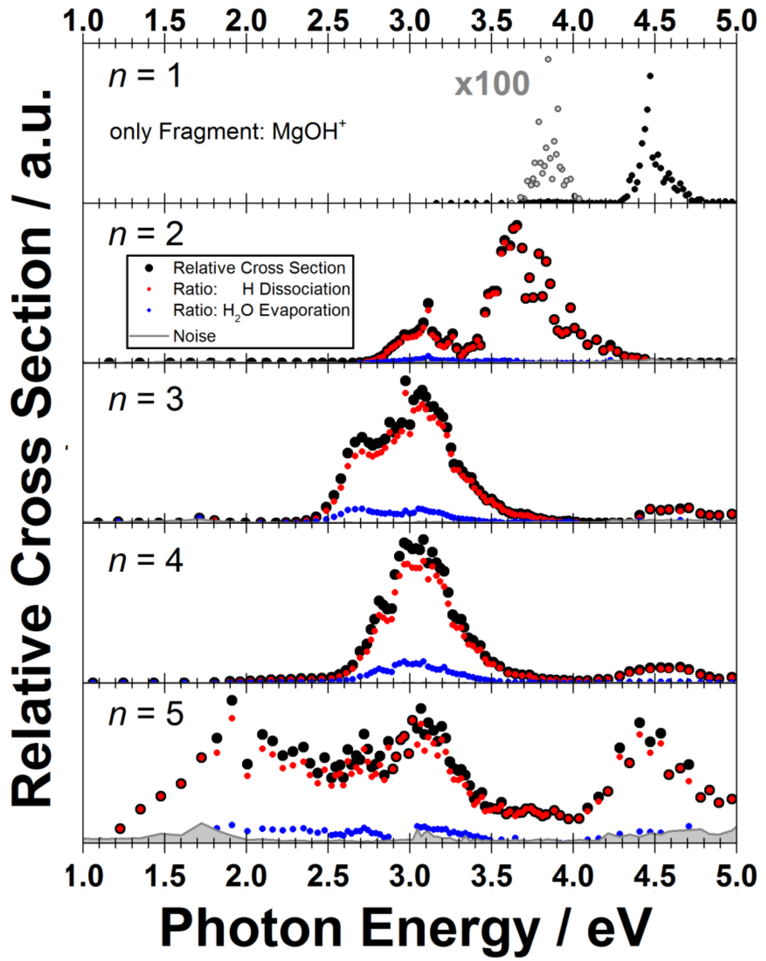
Short Recap of Results for small Clusters



Two Fragmentation Channels:

$[Mg(H_2O)_n]^+ \rightarrow [MgOH(H_2O)_{n-m-1}]^+ + (H_2O)_m + H$

Short Recap of Results for small Clusters

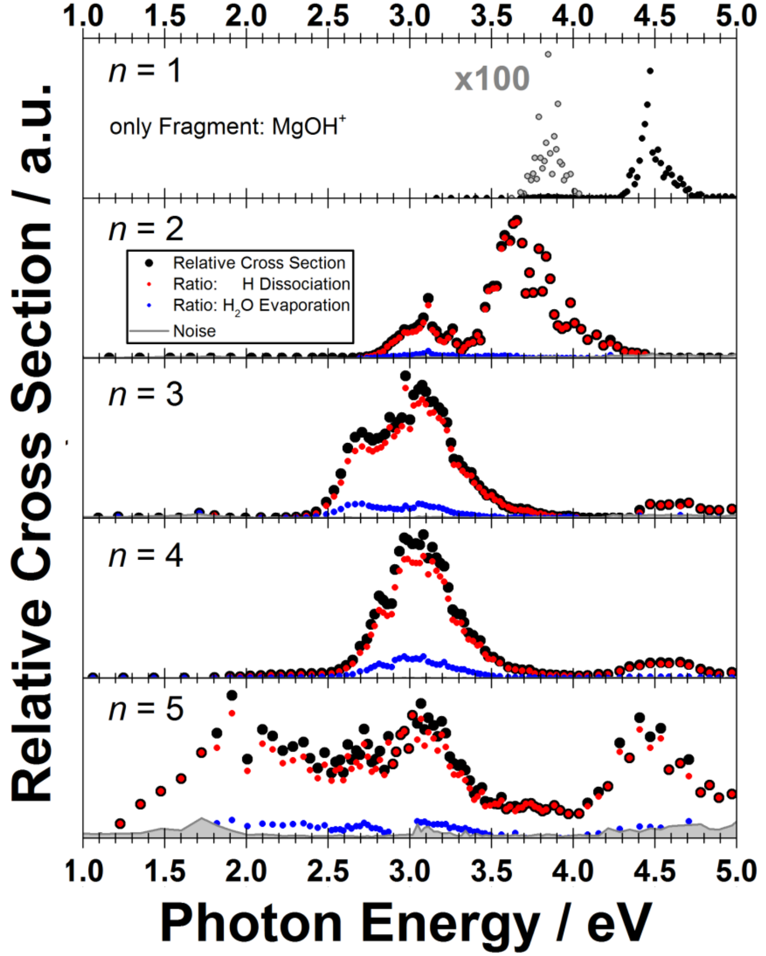


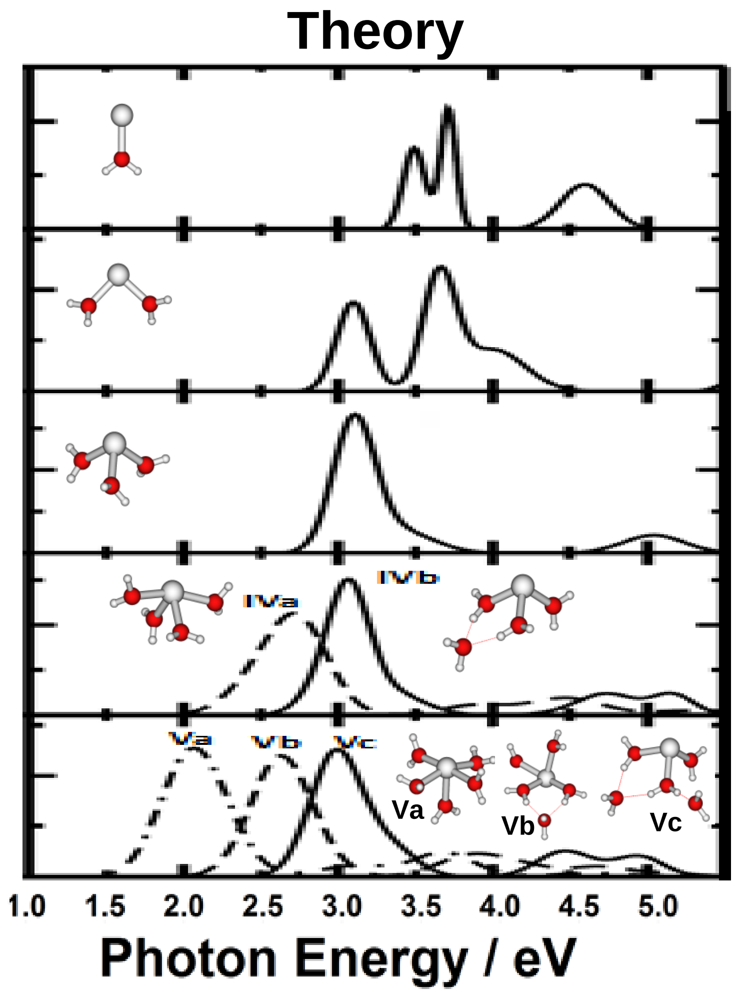
Two Fragmentation Channels:

$[Mg\,(H_2O)_n]^+ \rightarrow [MgOH(H_2O)_{n-m-1}]^+ + (H_2O)_m + H$

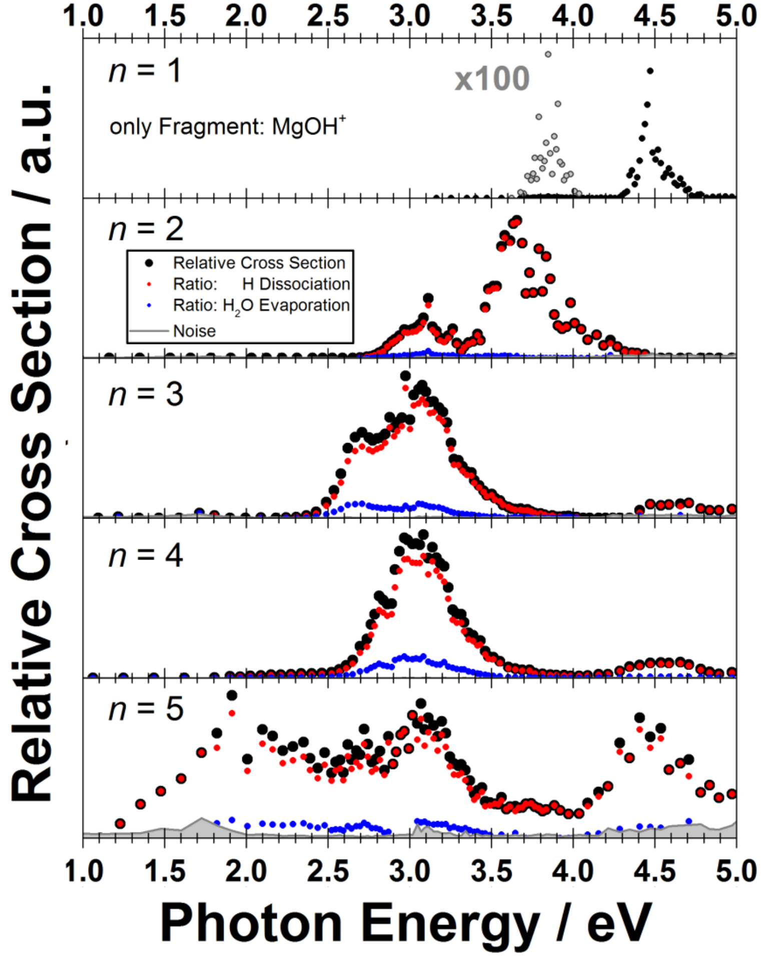
$[Mg\,(H_2O)_n]^+ \rightarrow [Mg(H_2O)_{n-m}]^+ + (H_2O)_m$

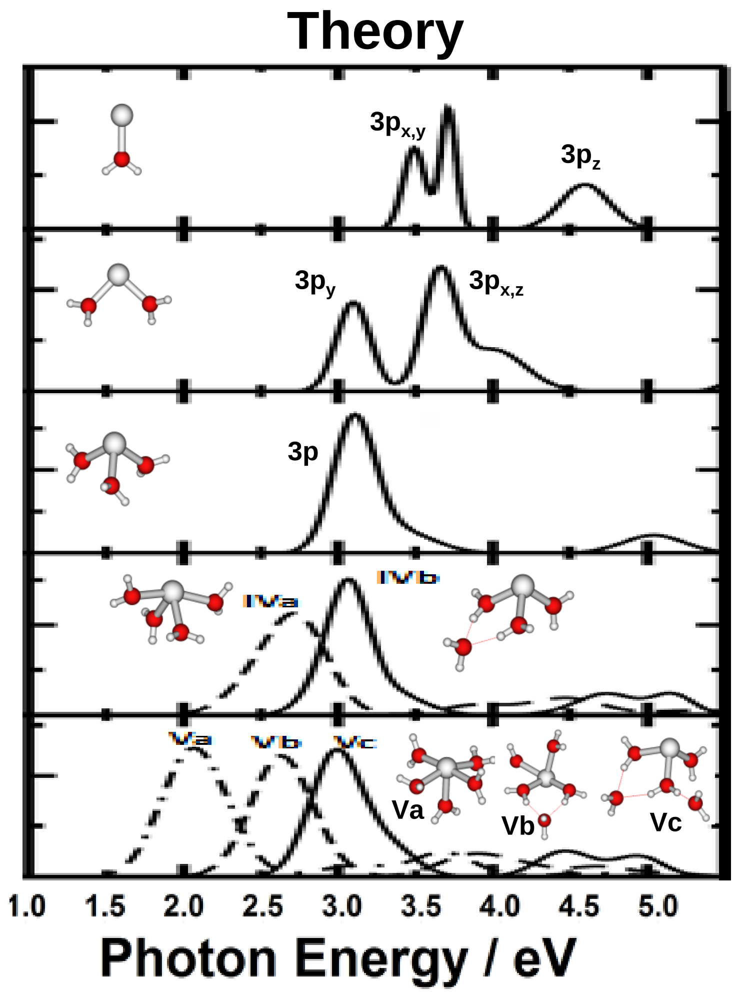
Short Recap of Results for small Clusters

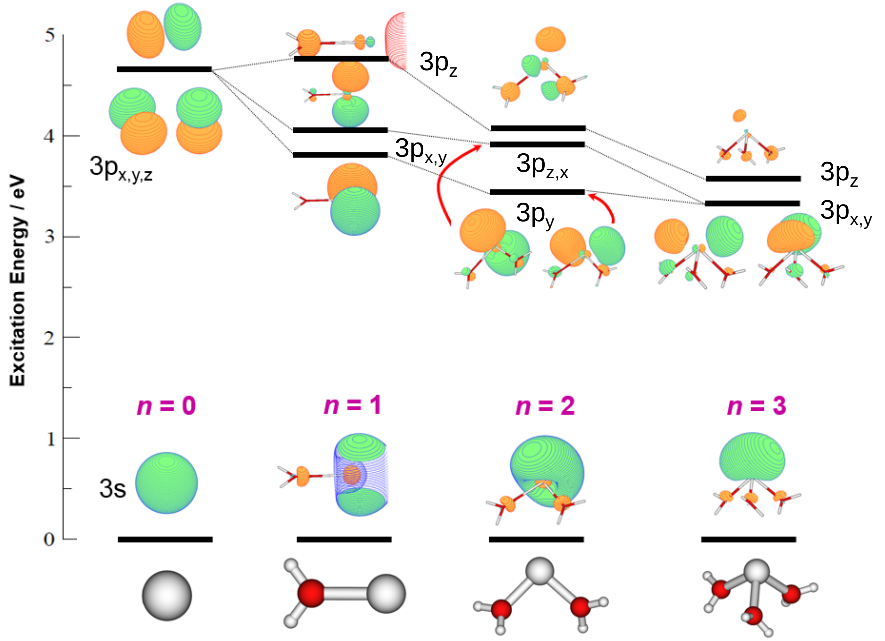




Short Recap of Results for small Clusters

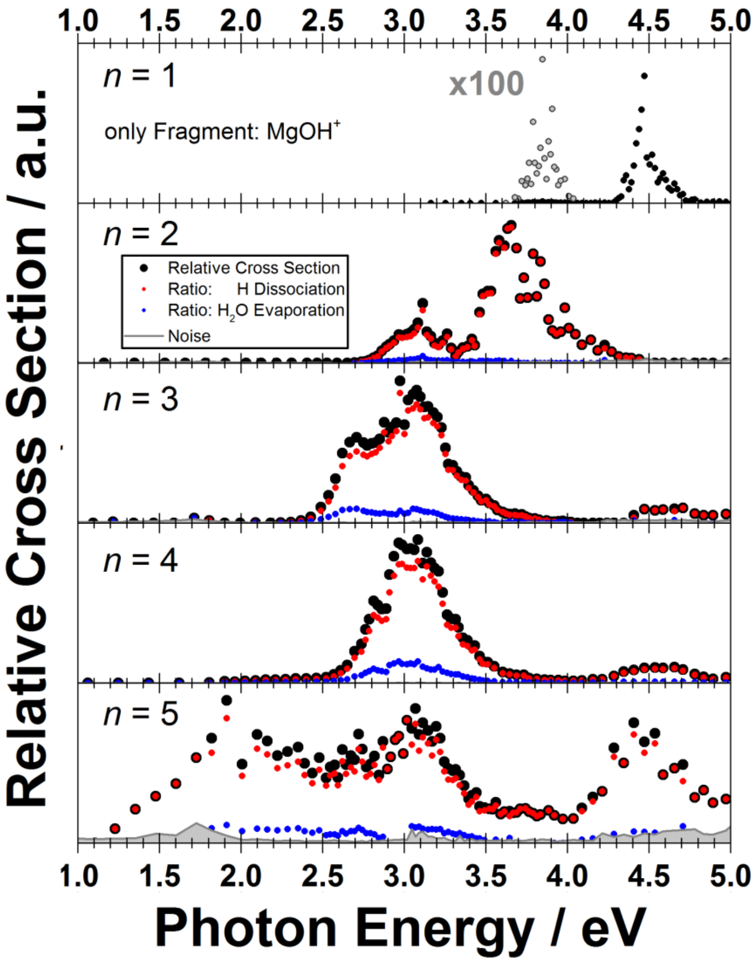


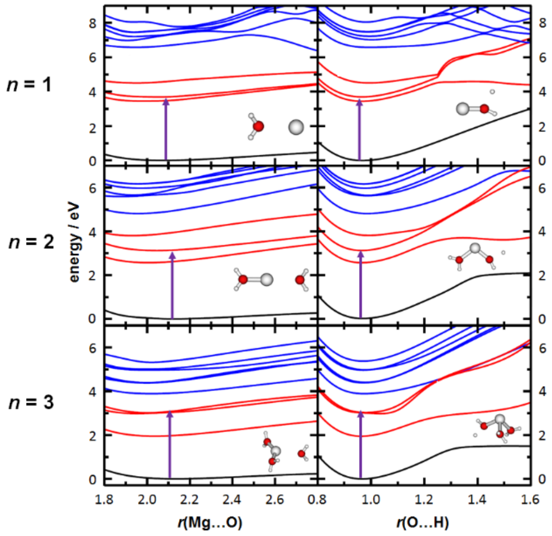




Excitation Energies: TD-BHandHLYP/def2-TZVP
Orbitals: CASSCF/6-31+g*

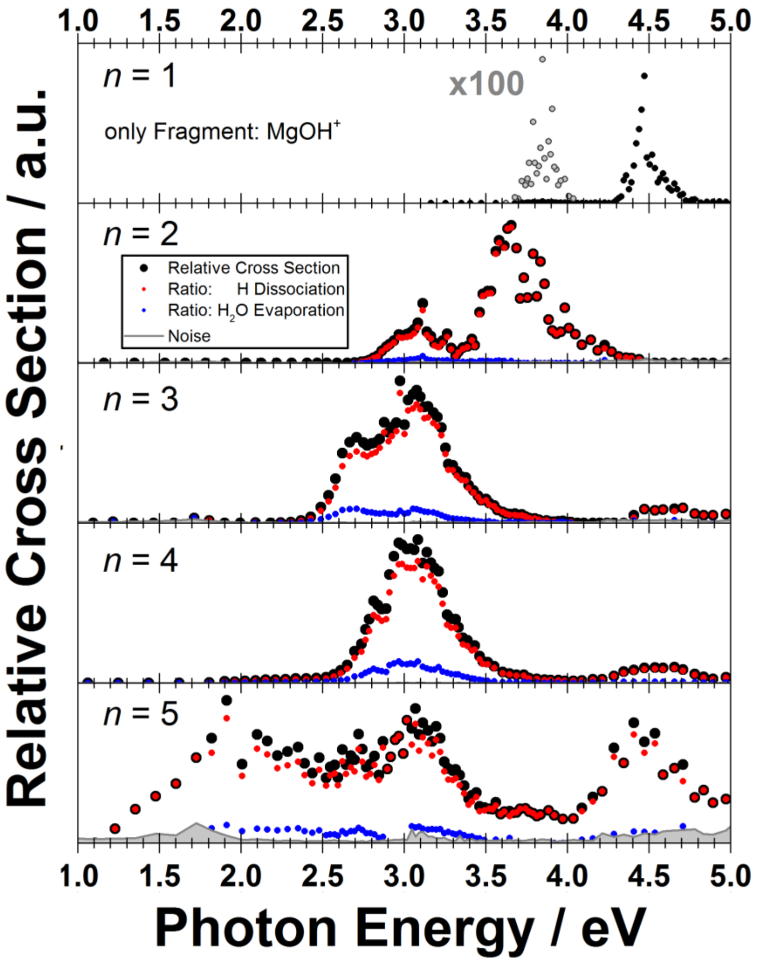
Short Recap of Results for small Clusters

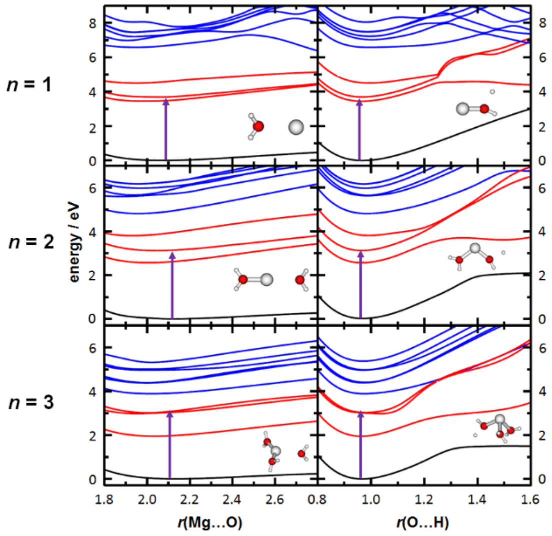




H Dissociation: in the Excited State (1γ/2γ, 2γ)

Short Recap of Results for small Clusters



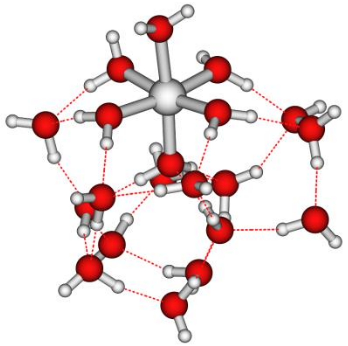


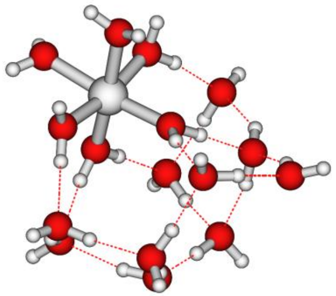
H Dissociation: in the Excited State (1γ/2γ, 2γ)

H_2O evaporation: in higher lying Excited States (2γ)

in the Ground State after Fluorescence

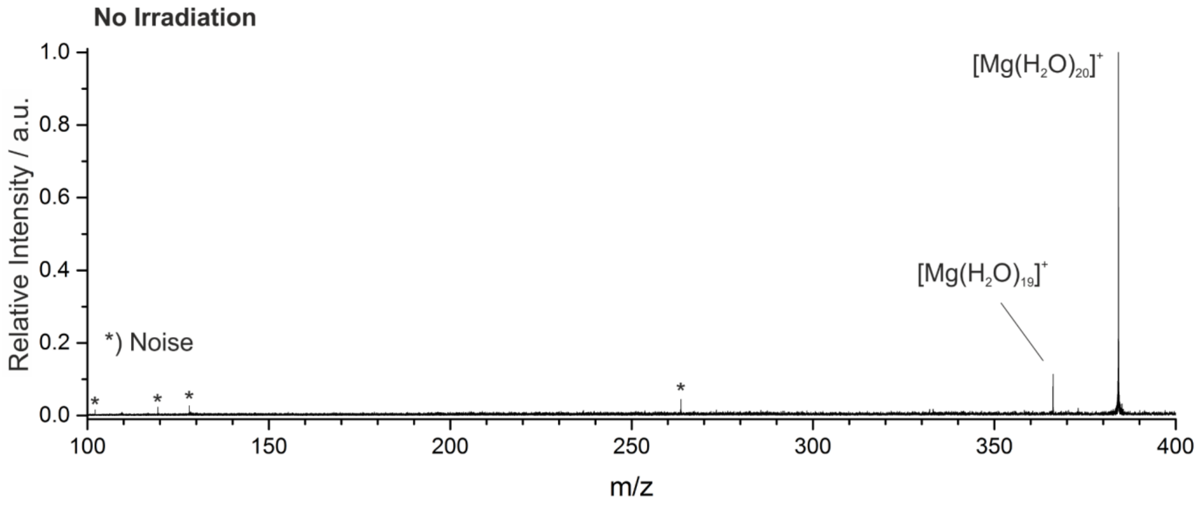
Experimental Results for large Clusters (n = 20, 30, 40, 50, 60, 70)





Hydrated Magnesium Ions $[Mg(H_2O)_n]^+$

Precursor Ions: $[Mg(H_2O)_{19,20}]^+$



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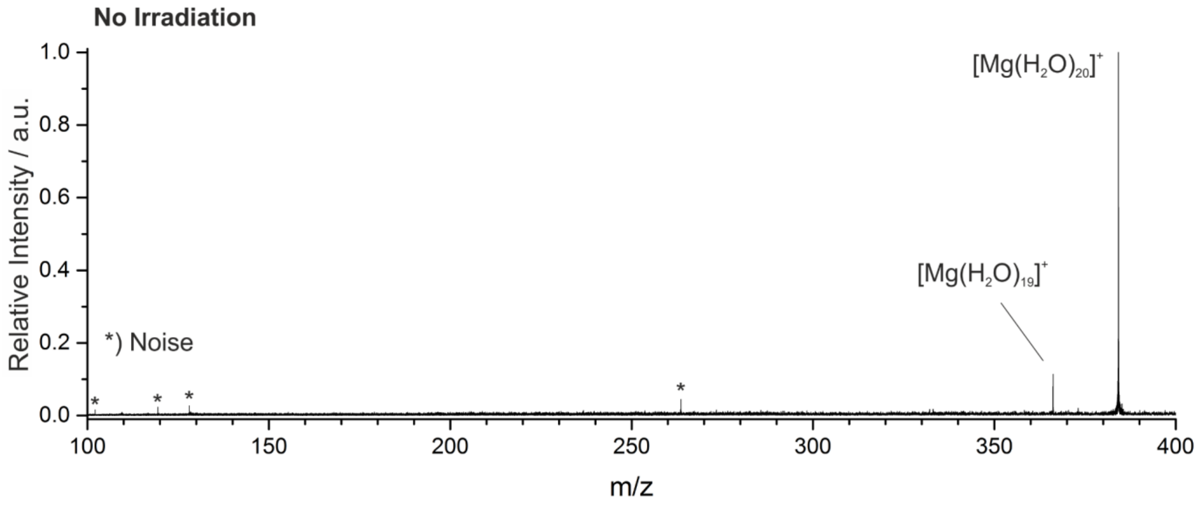

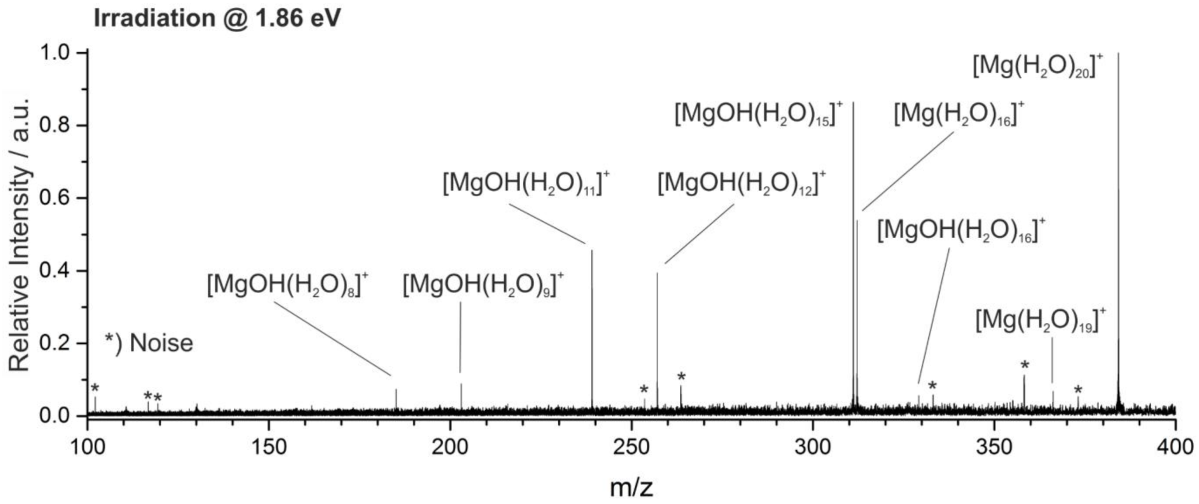

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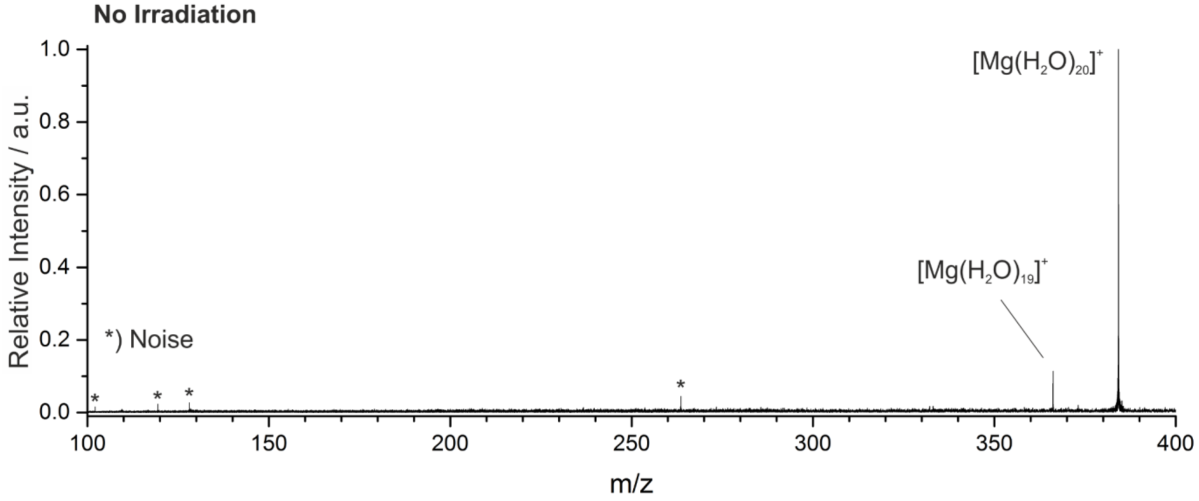

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$$[Mg(H_2O)_n]^+ \rightarrow [MgOH(H_2O)_{n-m-1}]^+ + (H_2O)_m + H$$

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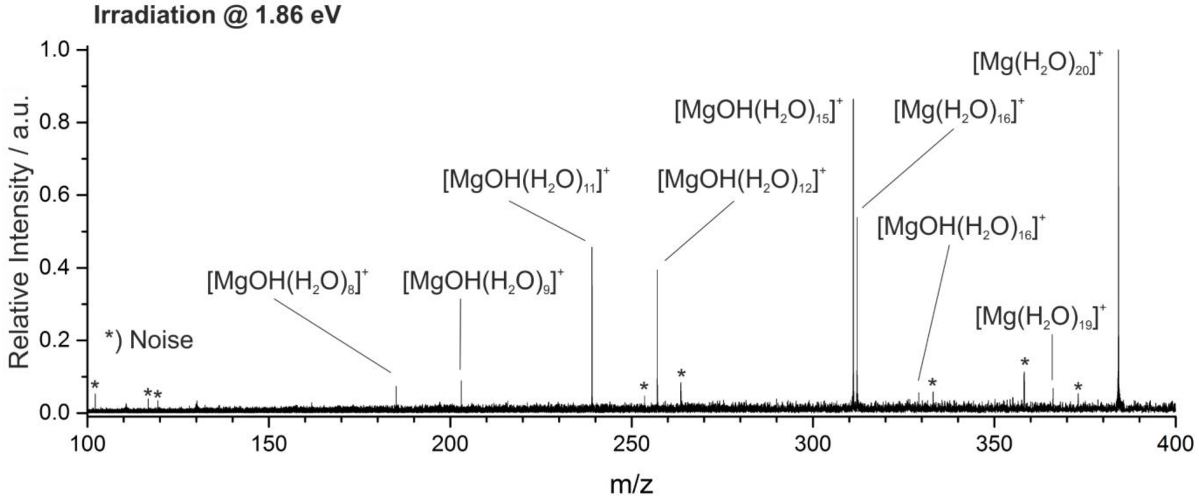
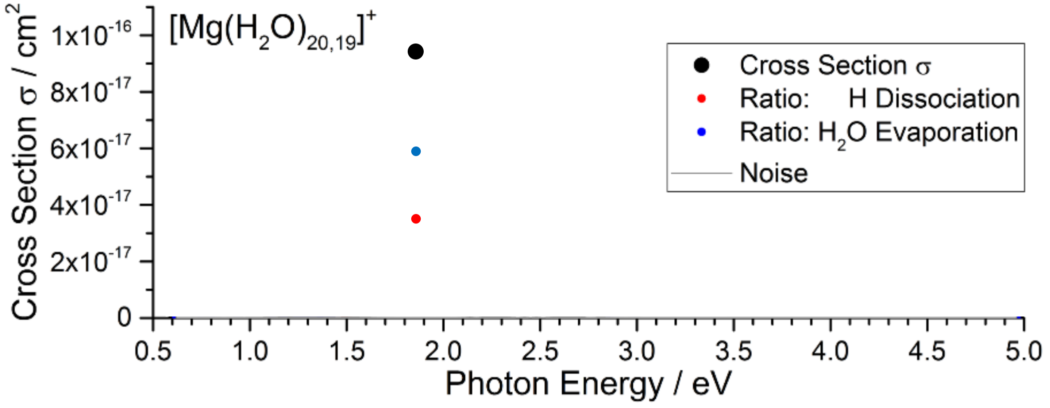
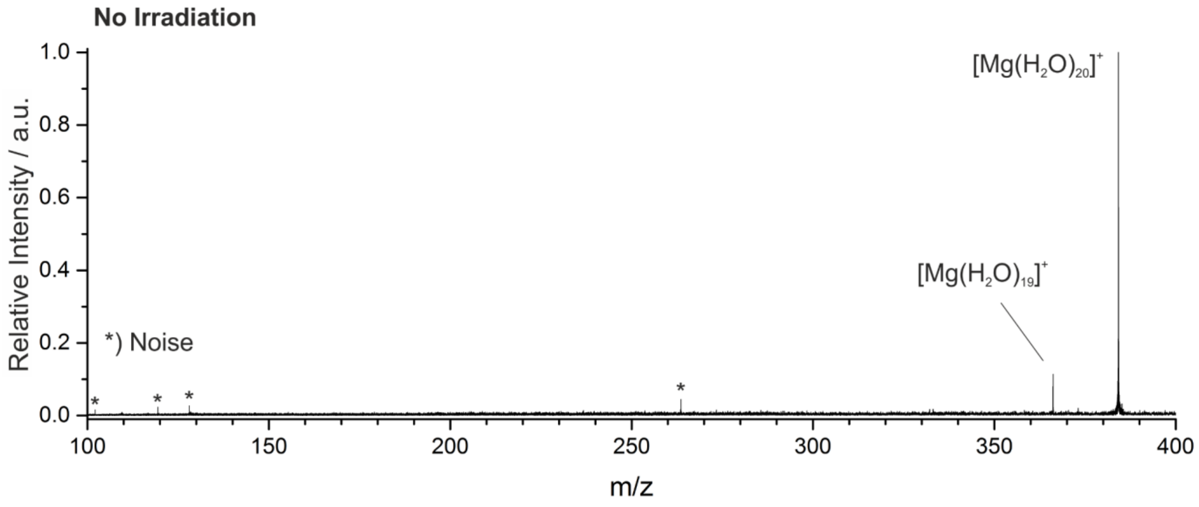


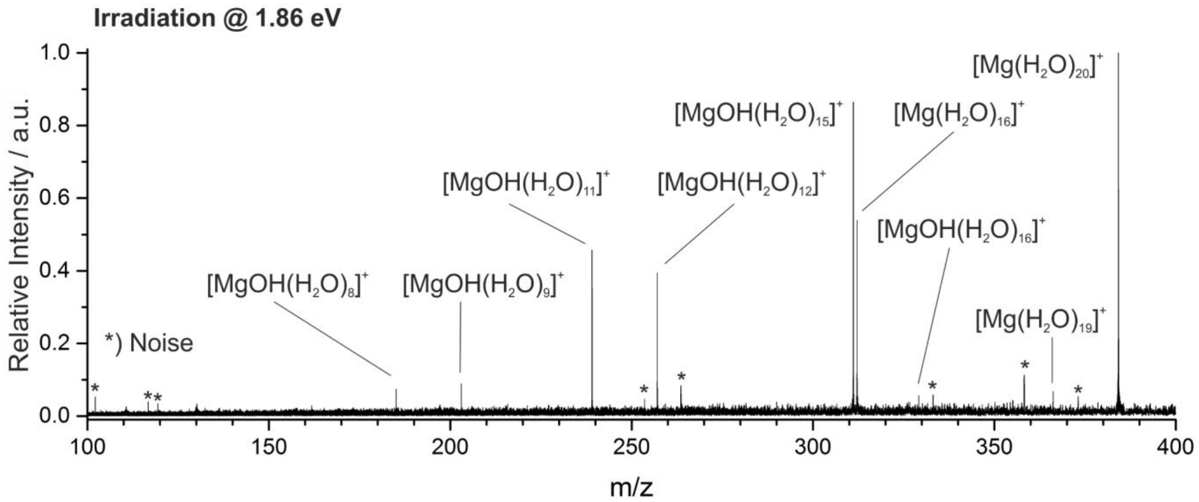
Photochemistry and Spectroscopy of Hydrated Metal Ions $[M(H_2O)_n]^+$

Hydrated Magnesium Ions $[Mg(H_2O)_n]^+$



Precursor Ions: $[Mg\,(H_2O)_{19,20}]^+$





Hydrated Magnesium Ions $[Mg(H_2O)_n]^+$

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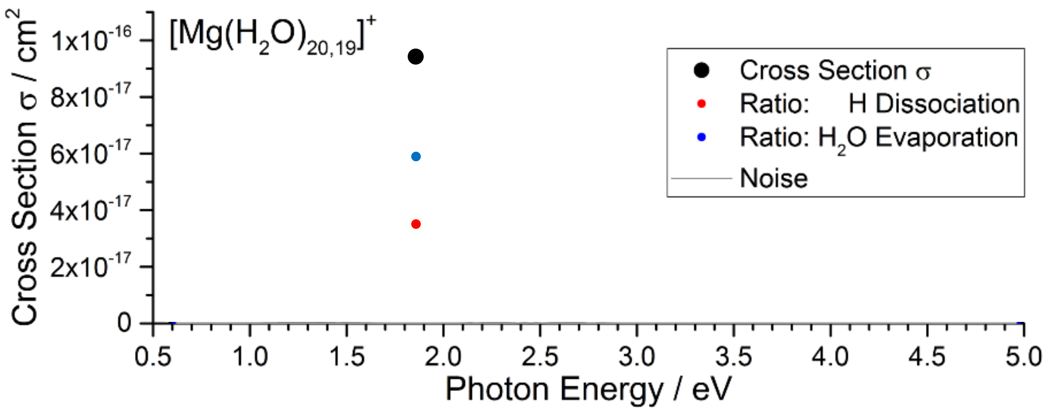
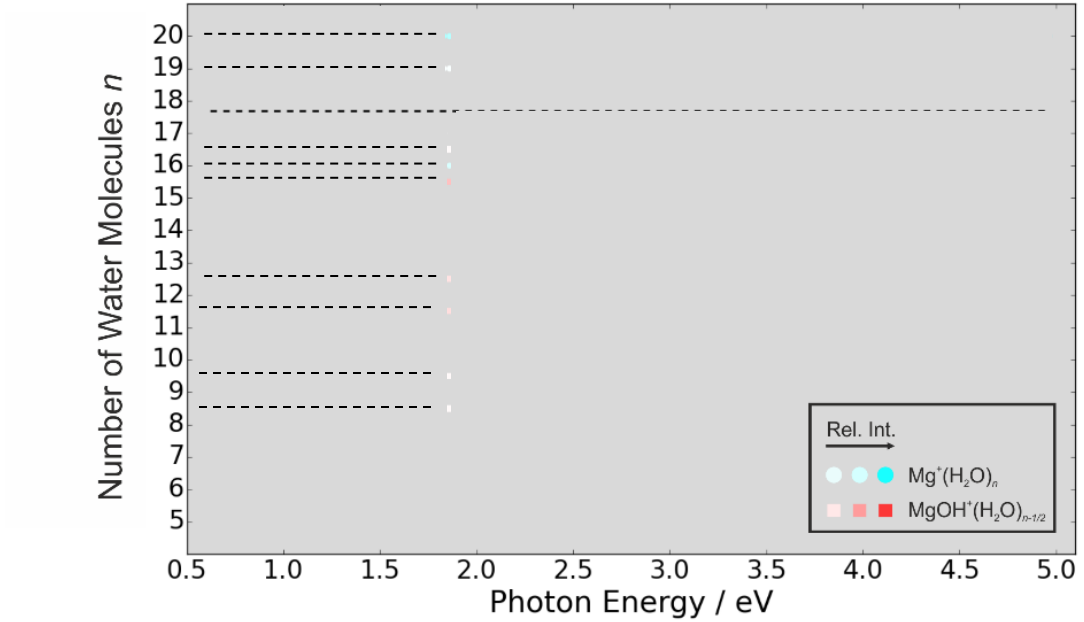
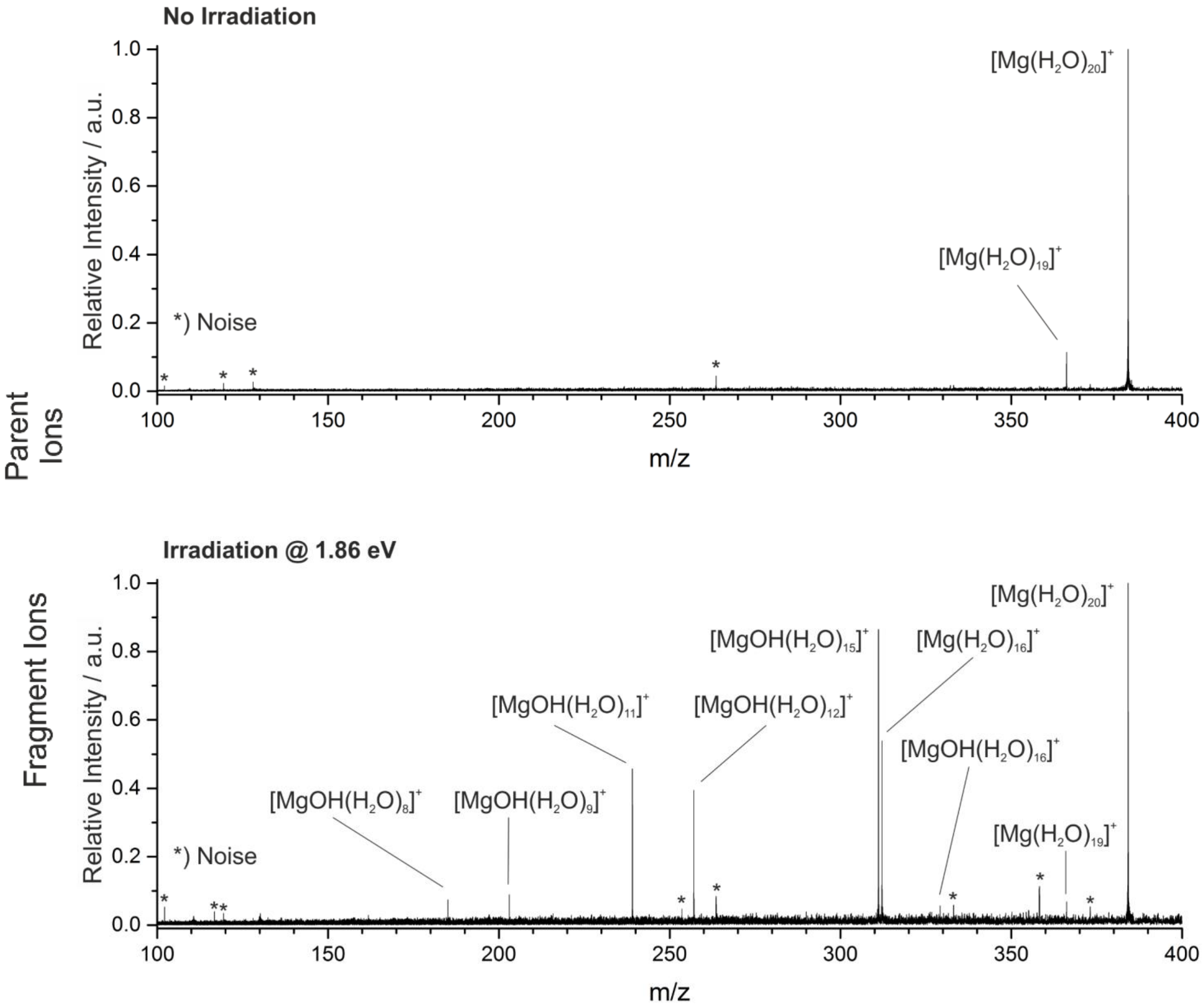
Precursor Ions: $[Mg(H_2O)_{19,20}]^+$







Photochemistry and Spectroscopy of Hydrated Metal Ions $[M(H_2O)_n]^+$

Hydrated Magnesium Ions $[Mg(H_2O)_n]^+$

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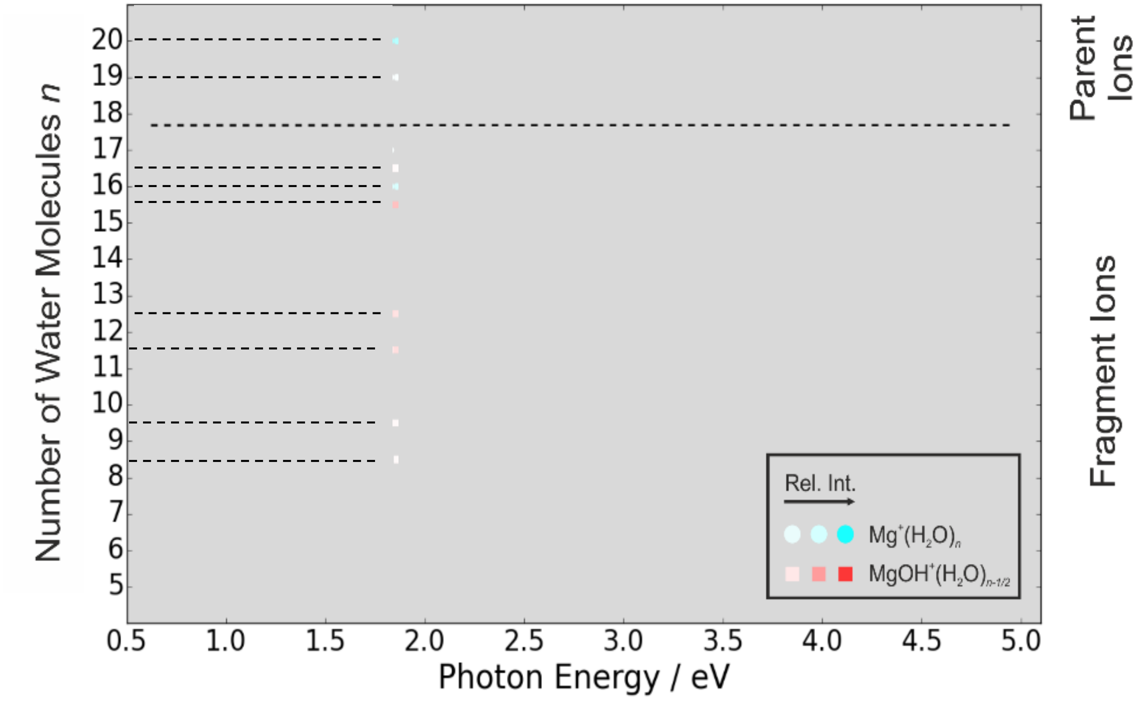

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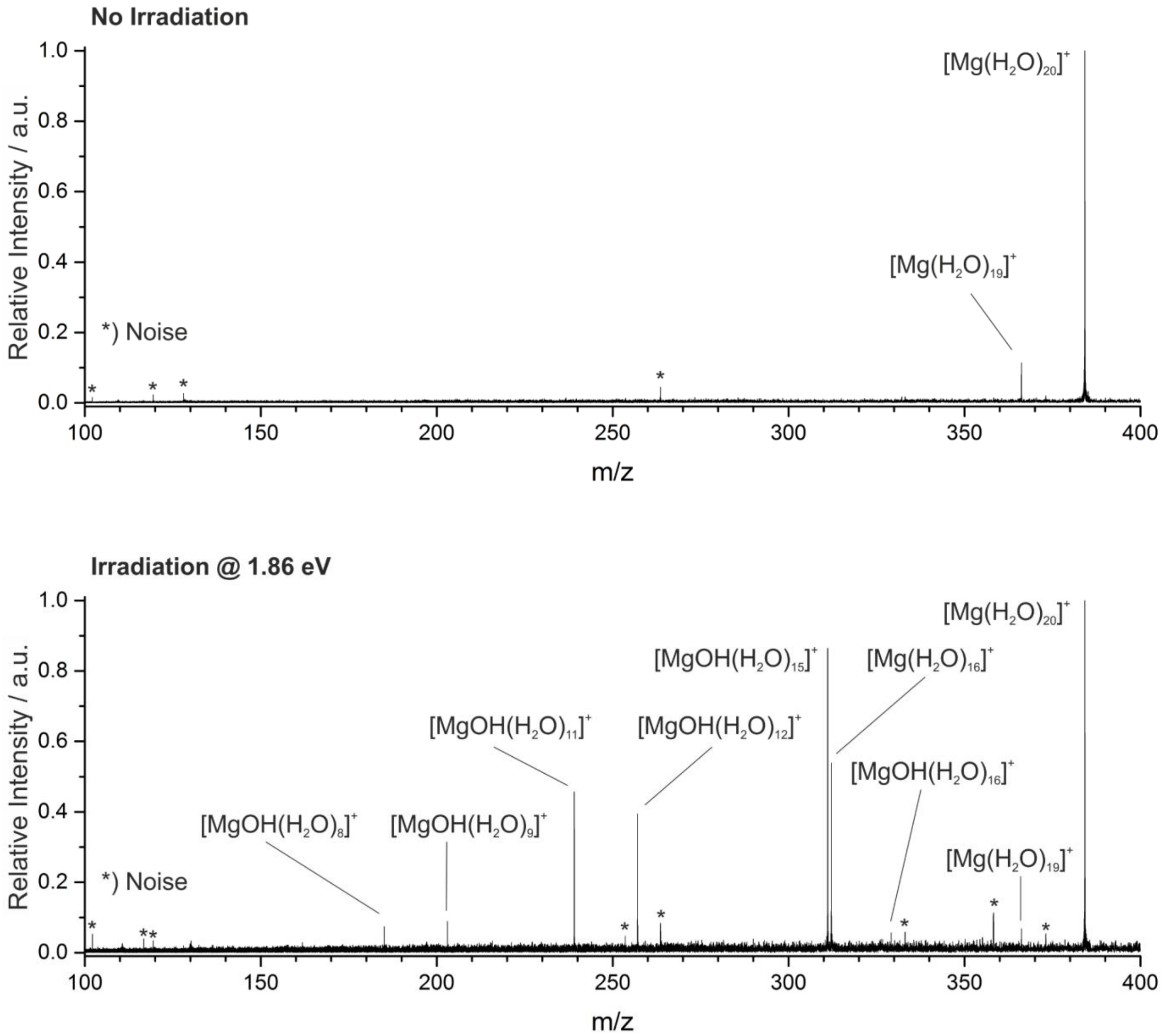

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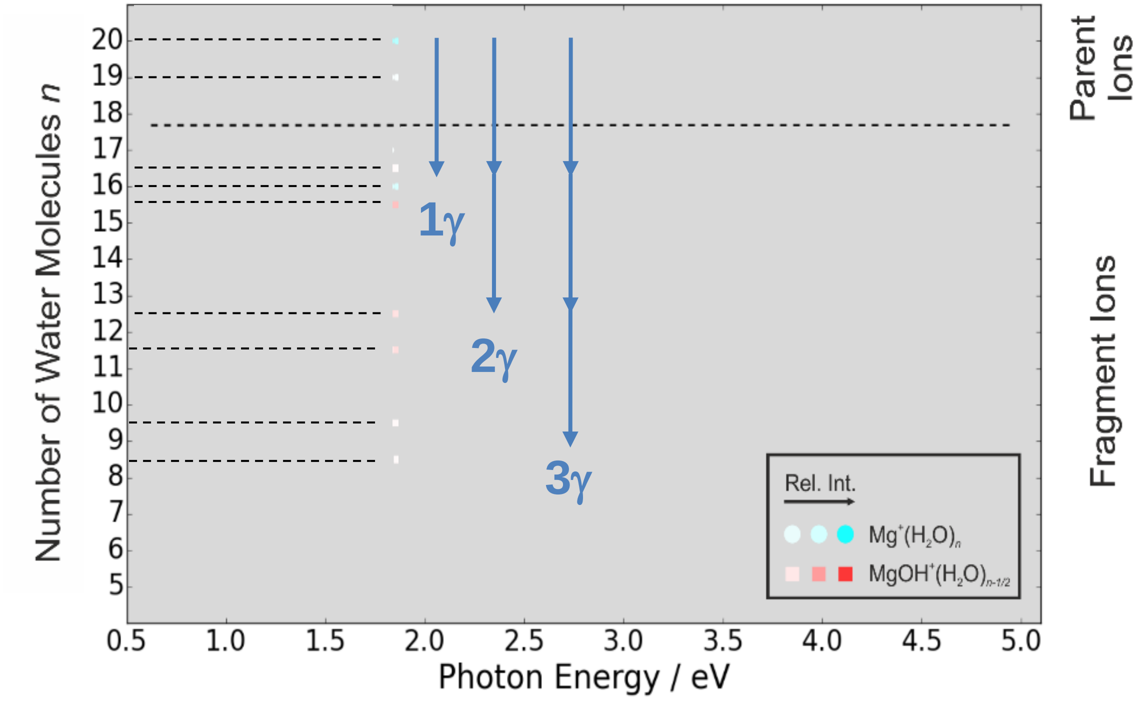

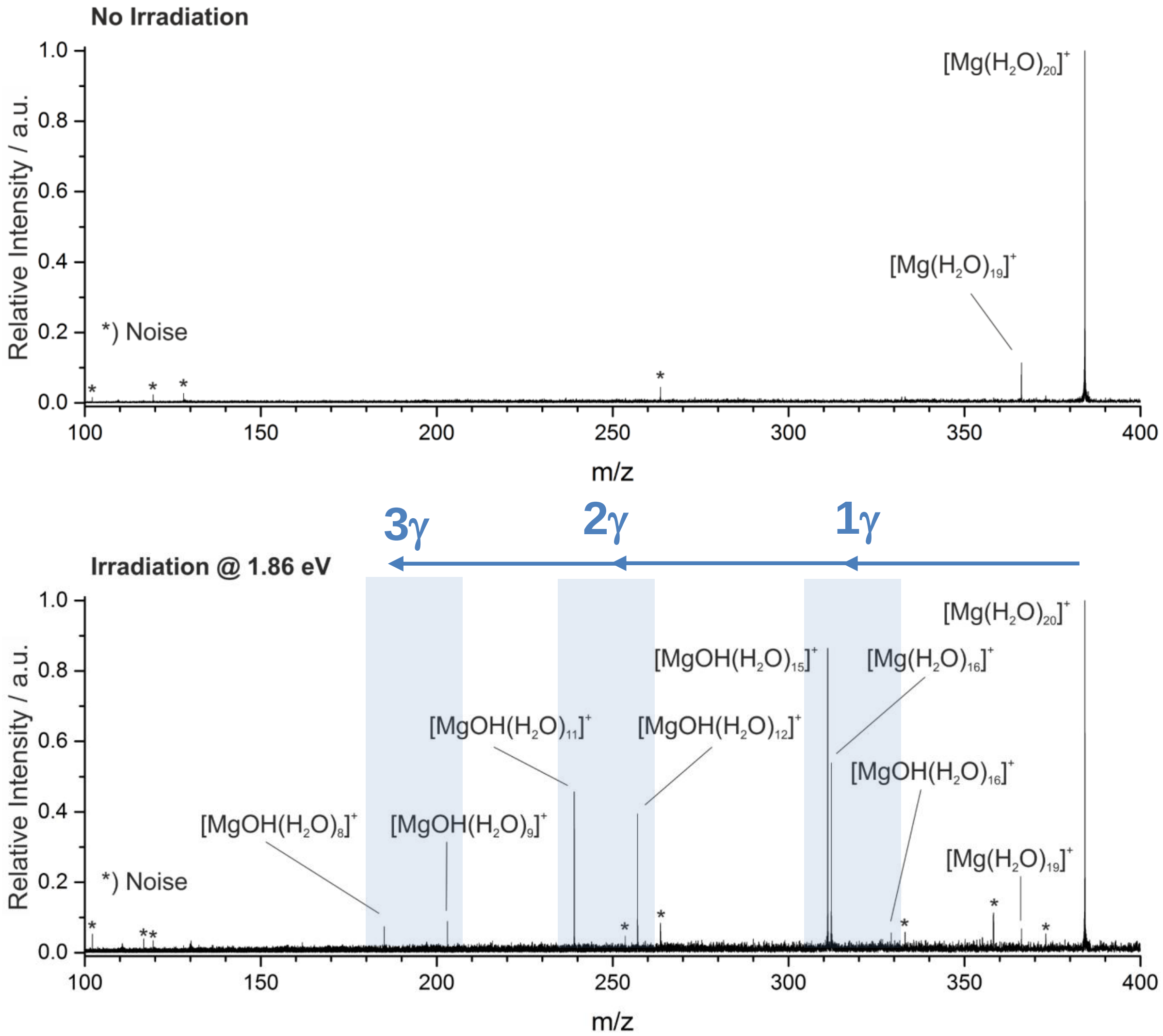

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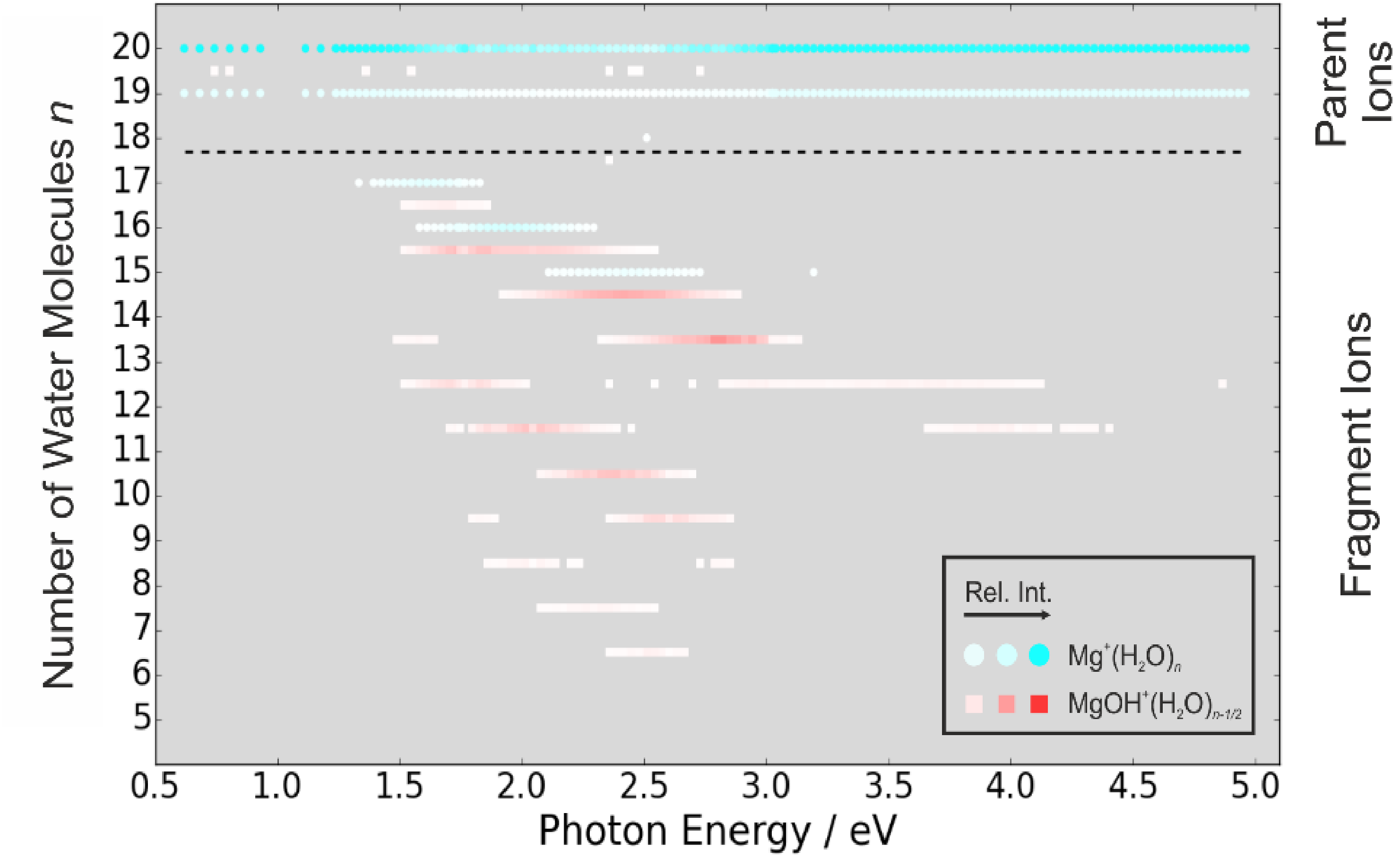

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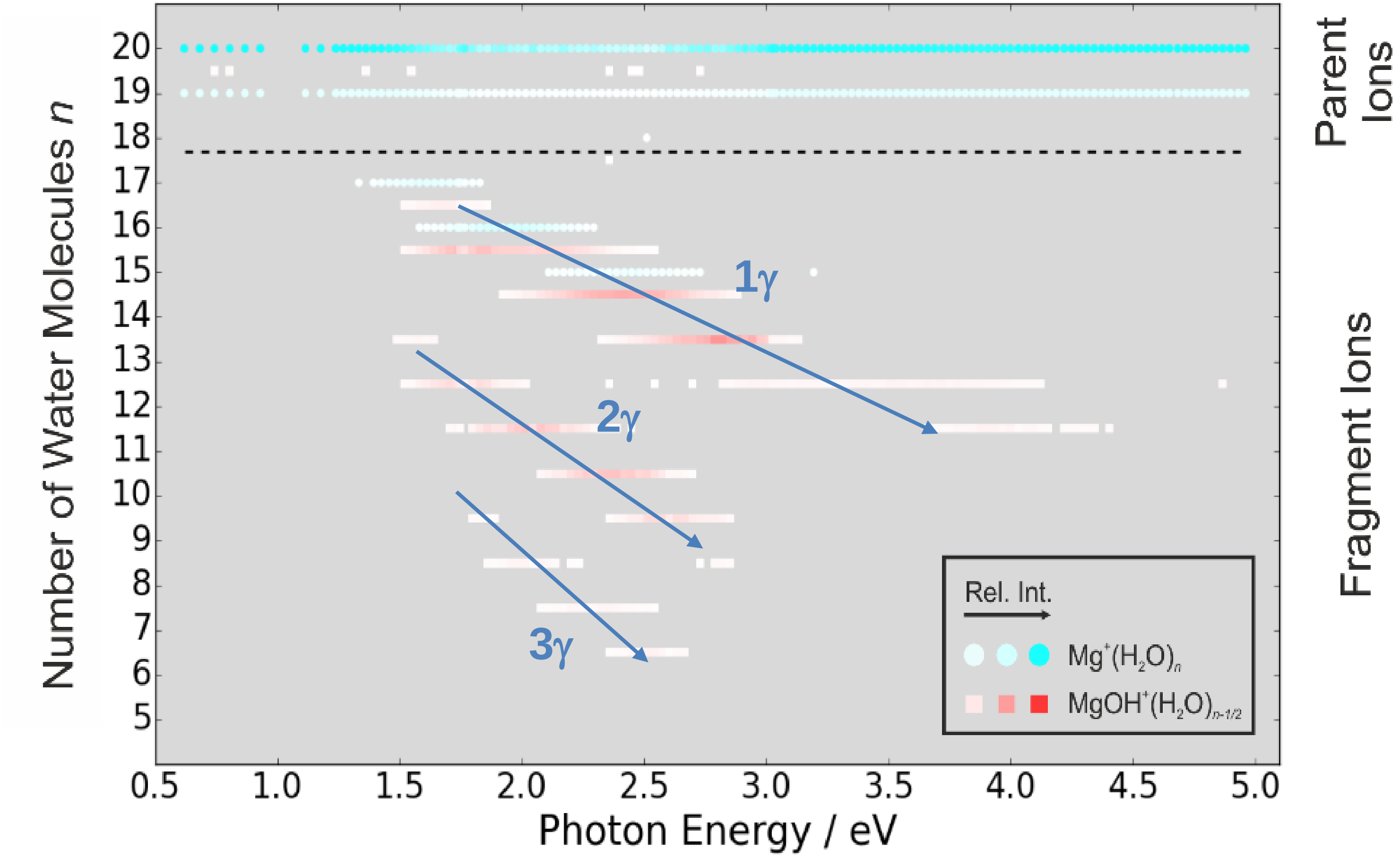
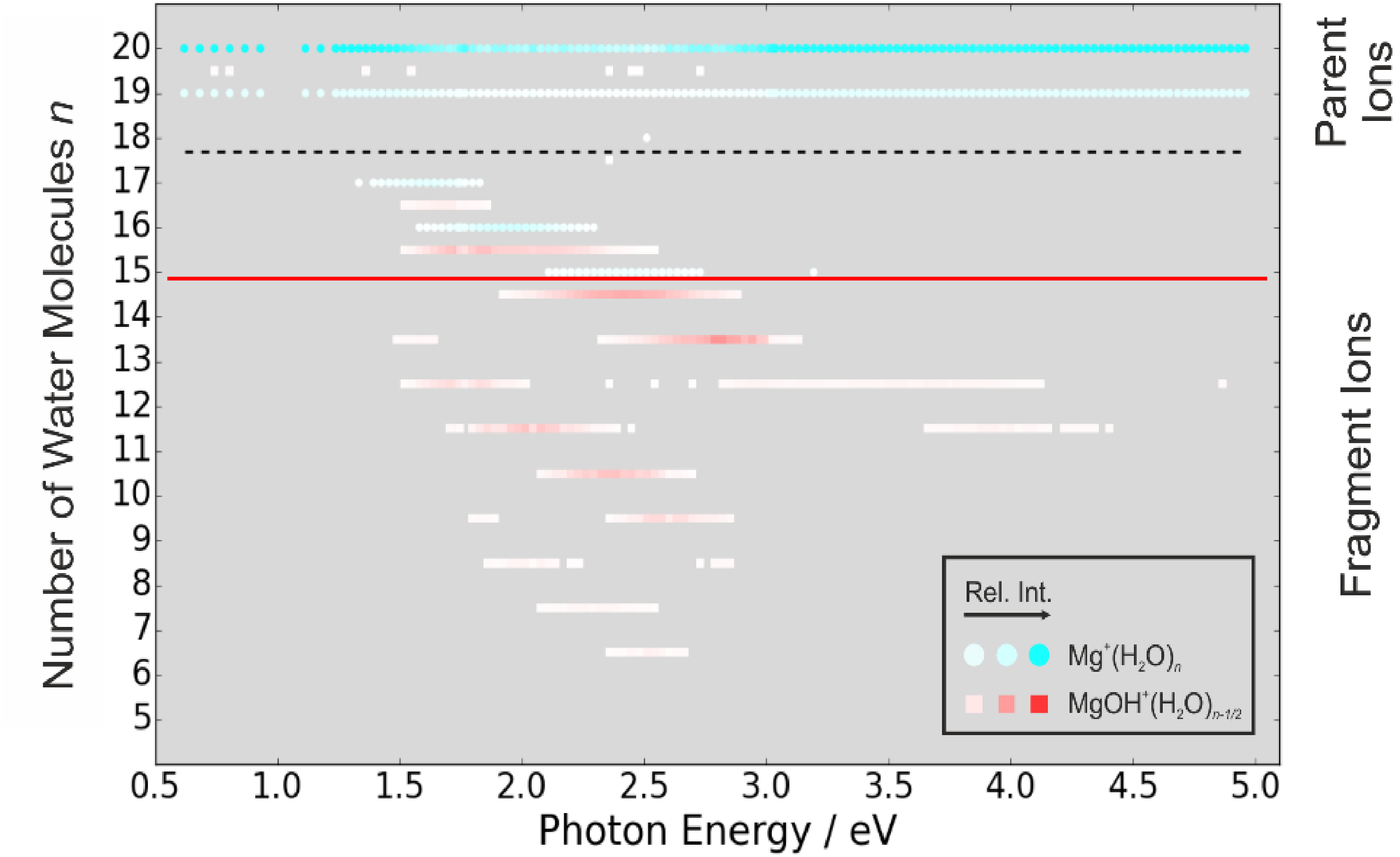


Increasing loss of Water Molecules with increasing Photon Energy.

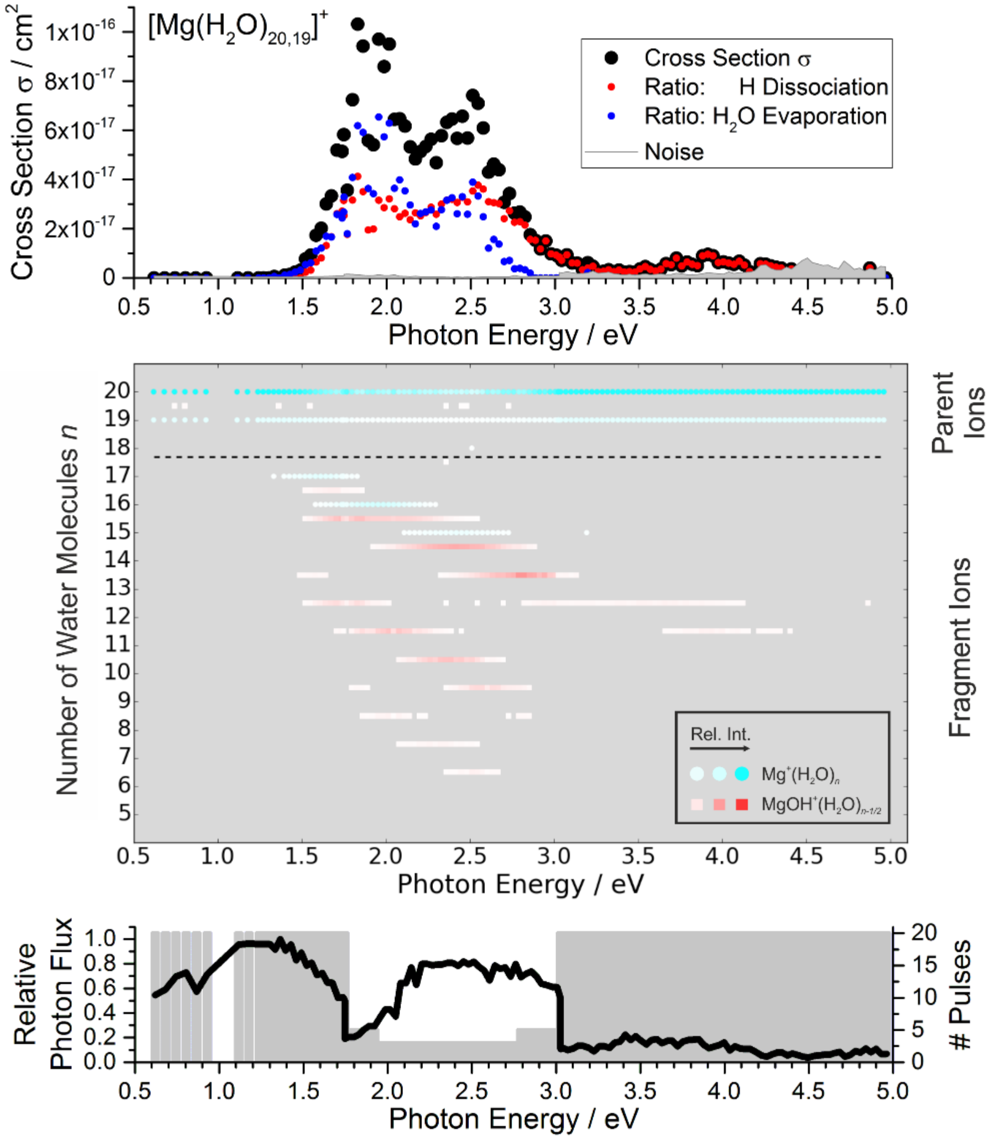
Precursor Ions: $[Mg(H_2O)_{19,20}]^+$



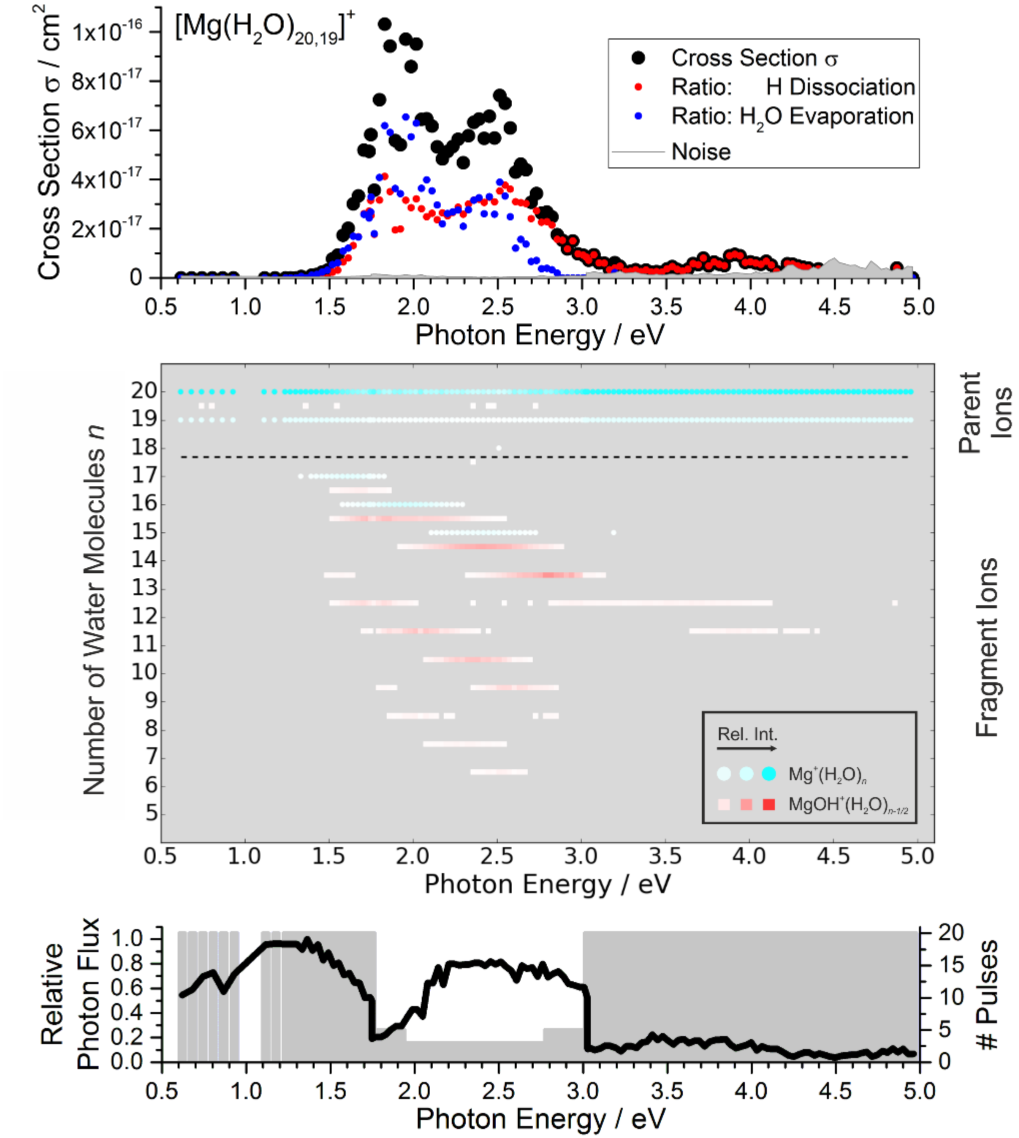
For n ≤ 14 Water Molecules:

only $[MgOH(H_2O)_n]^+$ Fragment Ions are observed.

Hydrated Magnesium Ions $[Mg(H_2O)_n]^+$



Hydrated Magnesium Ions $[Mg(H_2O)_n]^+$



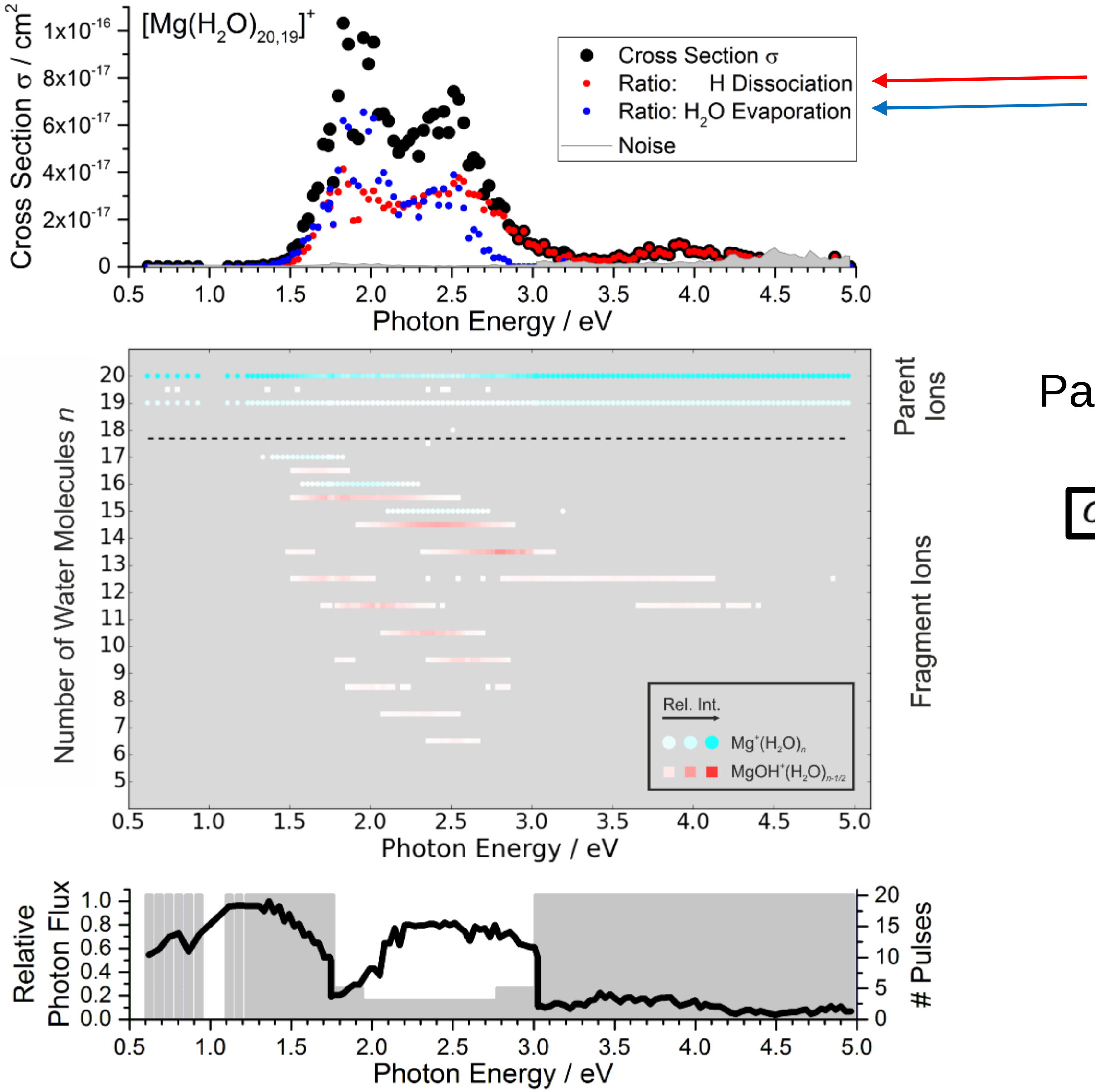
Partial Cross Sections:

$$\sigma = \sigma_{H2O} + \sigma_H$$

$$\frac{\sigma_{H2O}}{\sigma_H} = \frac{I_{H2O}}{I_H}$$

Photochemistry and Spectroscopy of Hydrated Metal Ions $[M(H_2O)_n]^+$

Hydrated Magnesium Ions $[Mg(H_2O)_n]^+$



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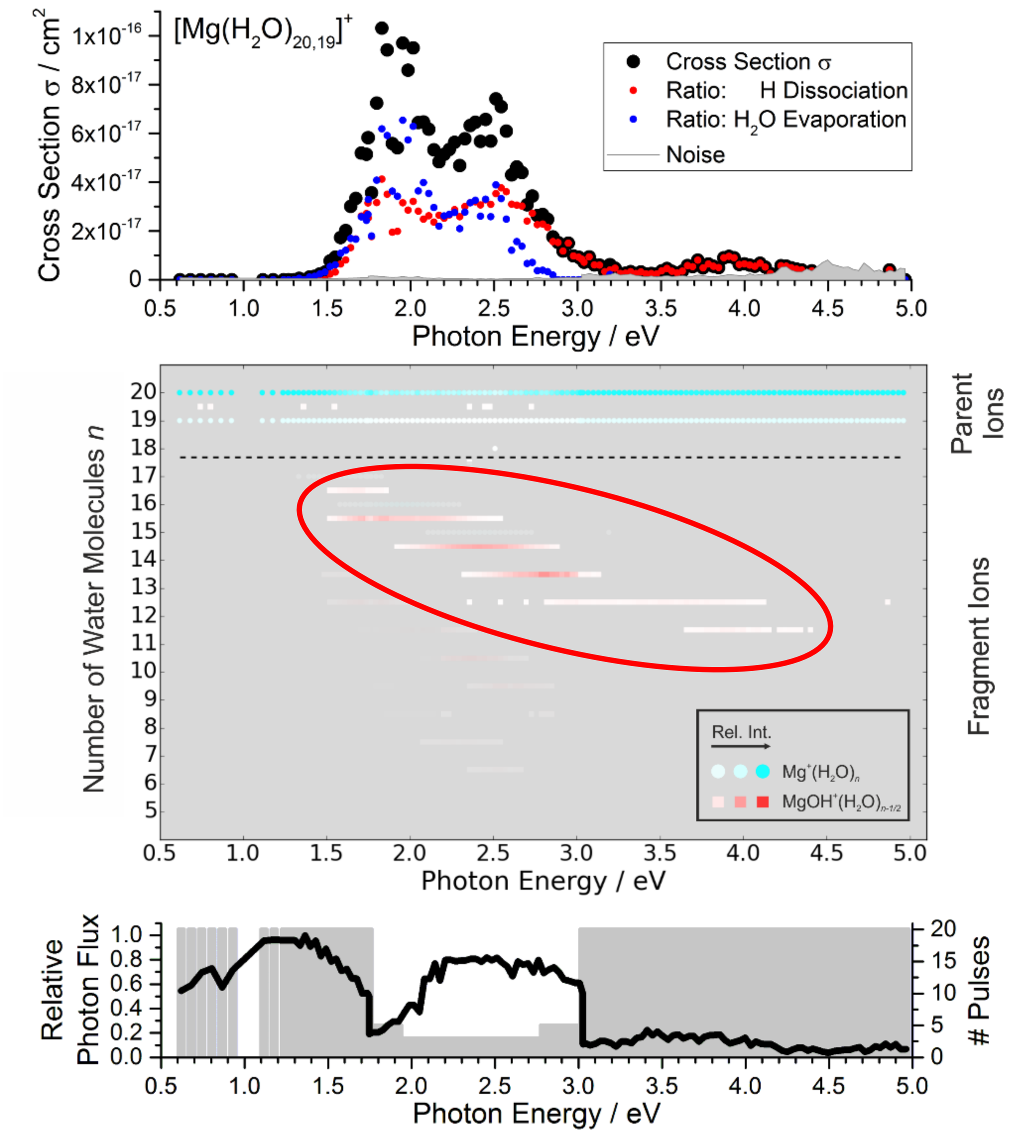

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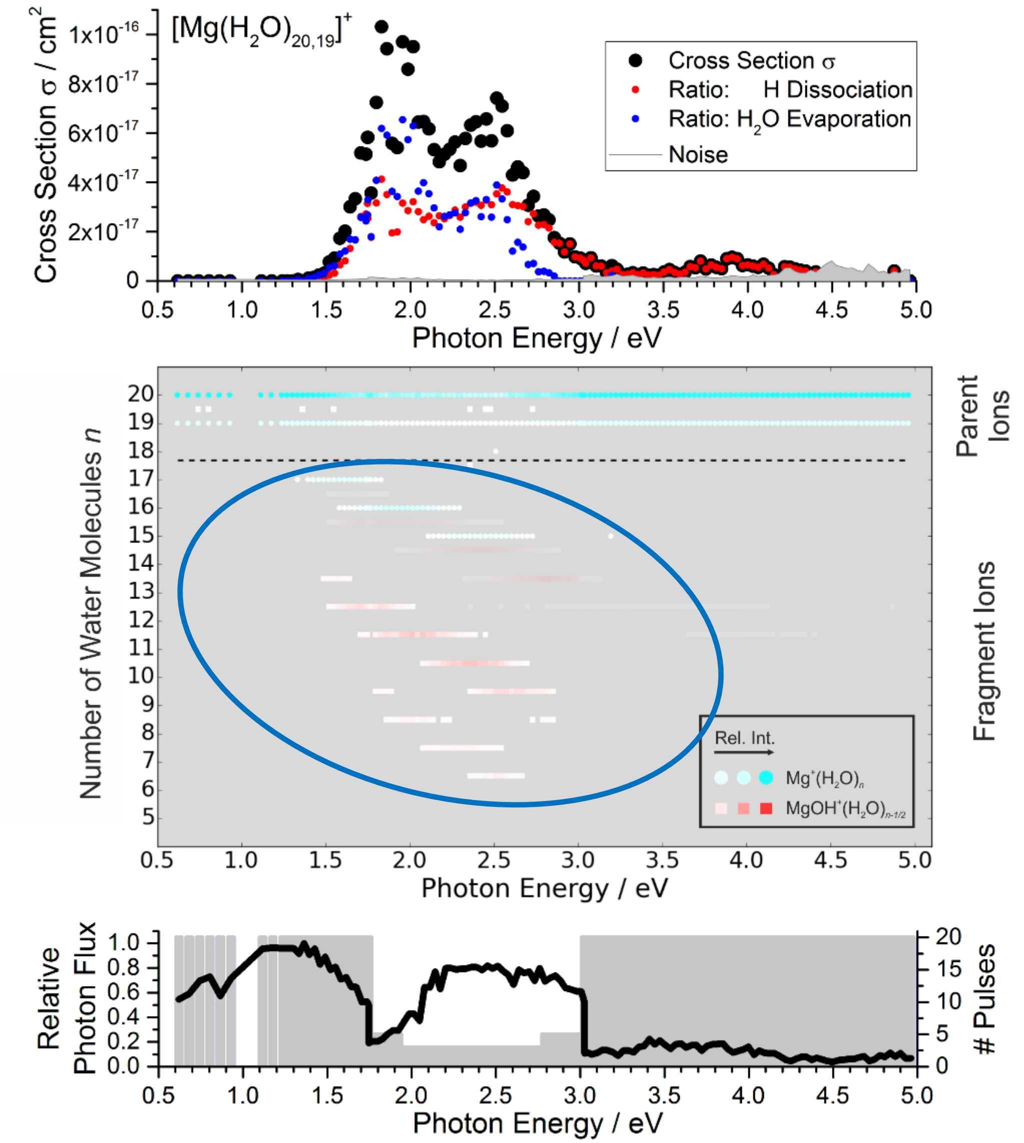
Hydrated Magnesium Ions $[Mg(H_2O)_n]^+$



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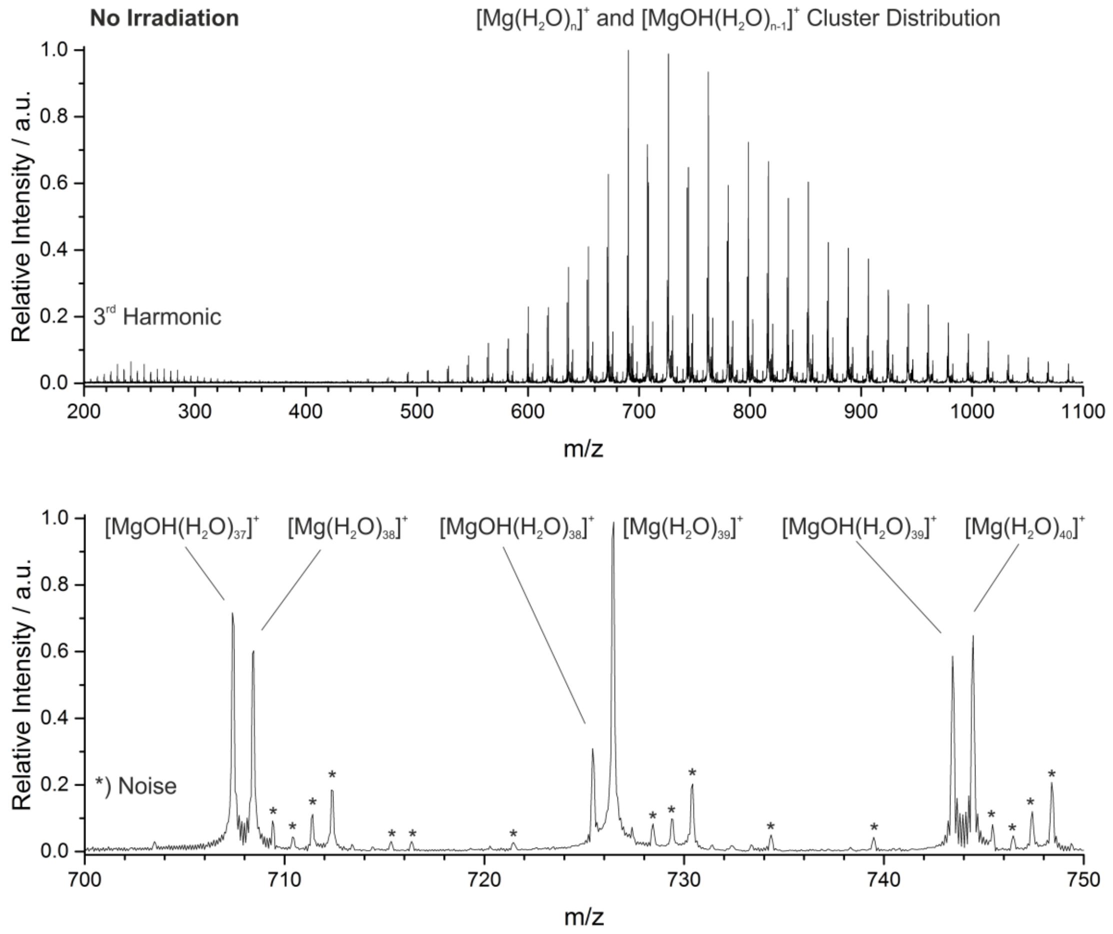
Proof that hyd. Magnesium Hydroxide Ions do not absorb in the relevant Wavelength Range



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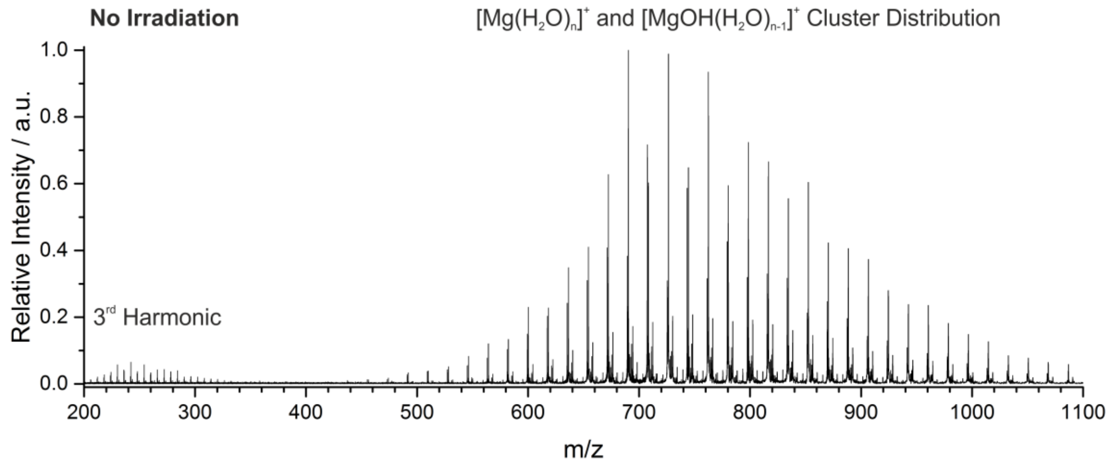
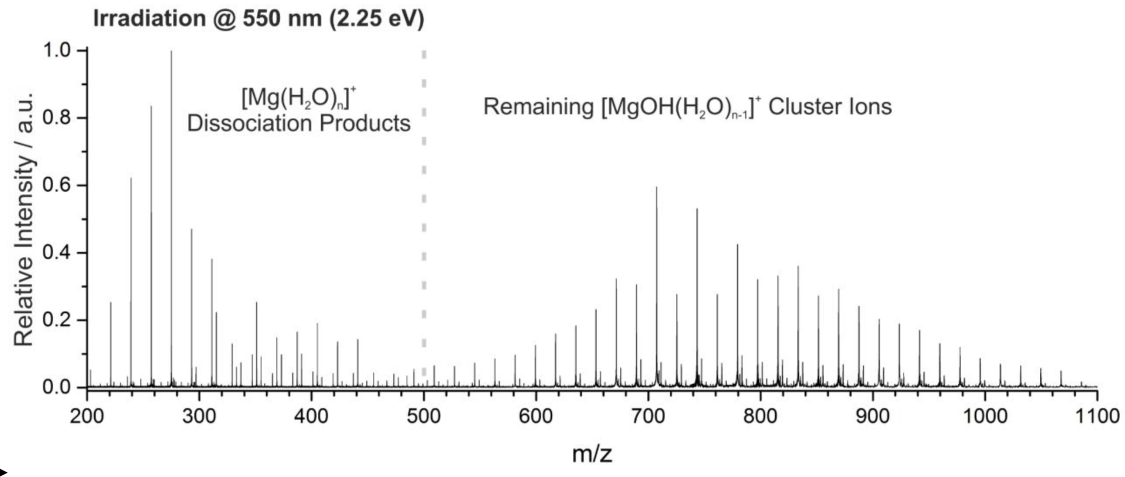
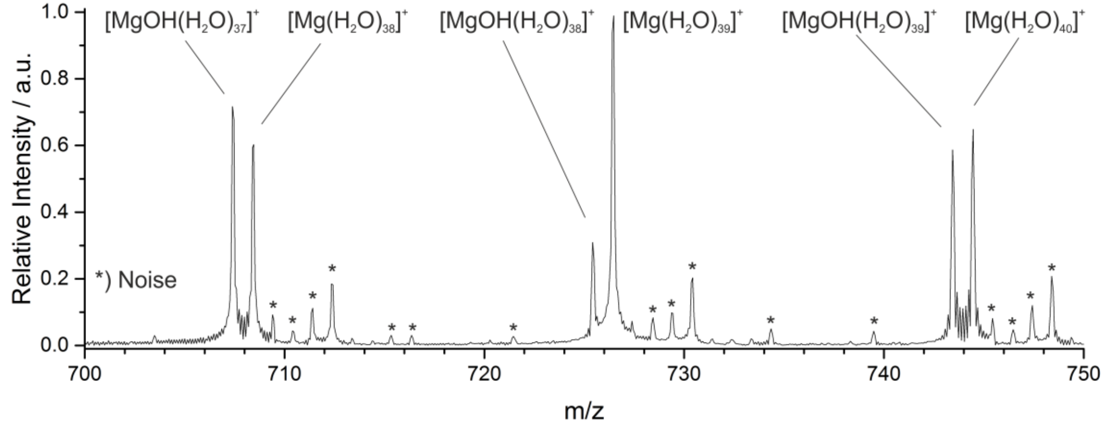
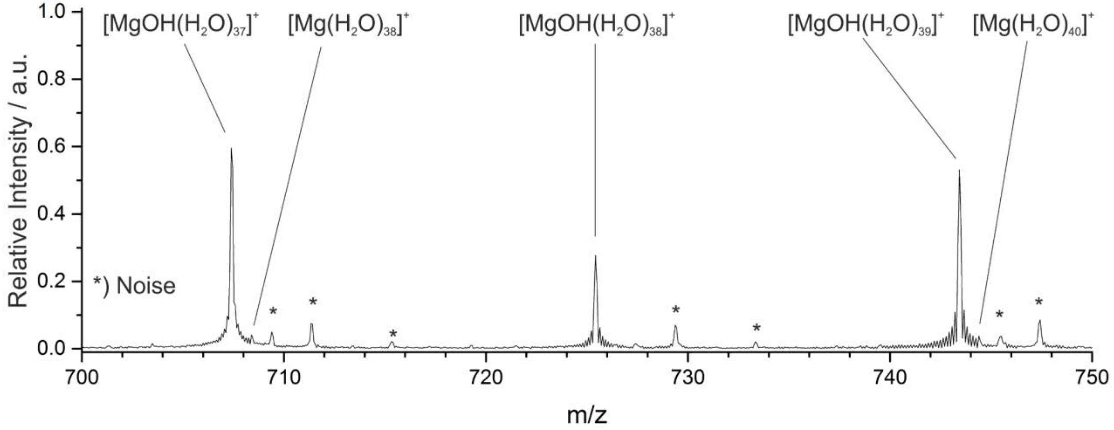
Proof that hyd. Magnesium Hydroxide Ions do not absorb in the relevant Wavelength Range









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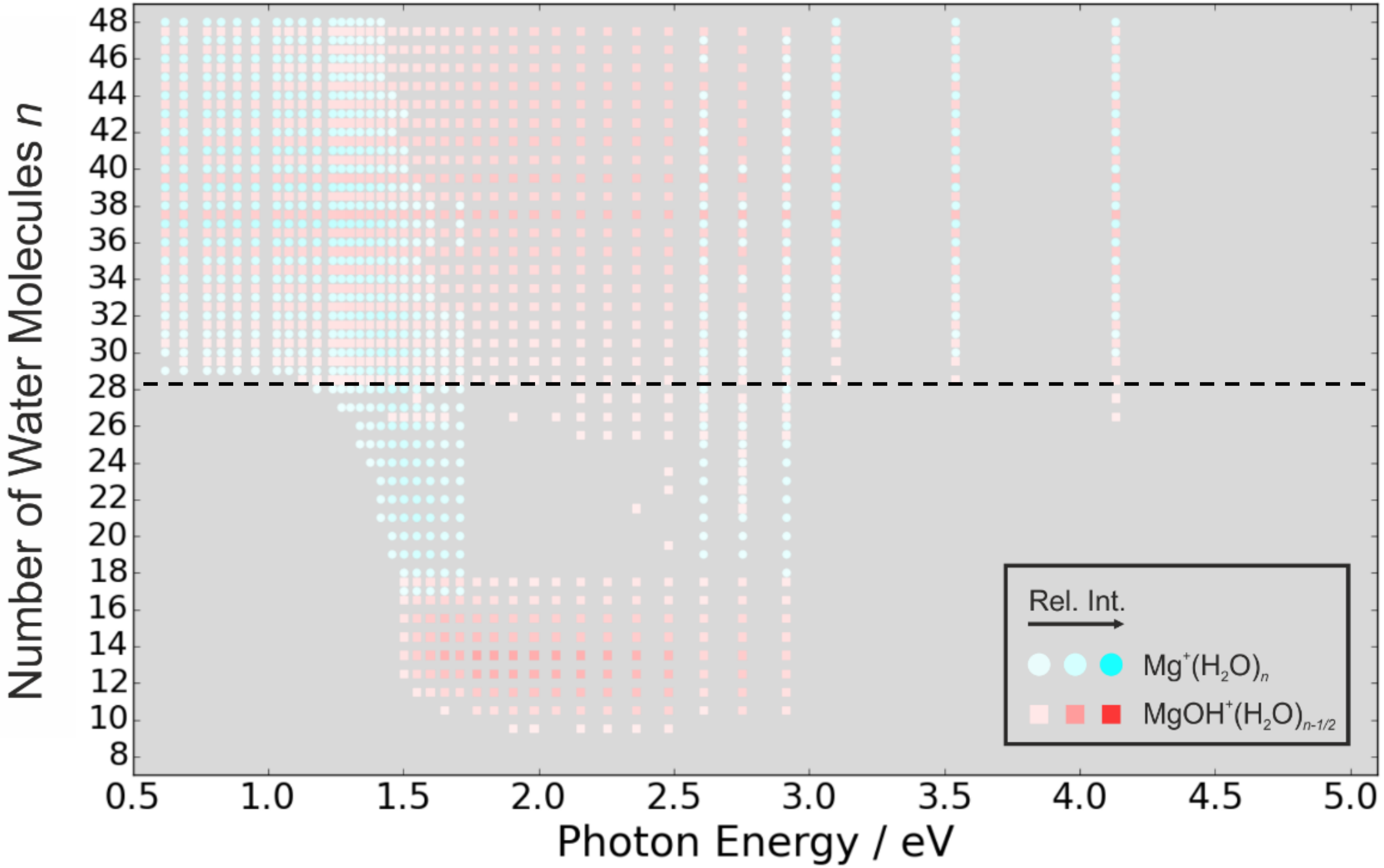
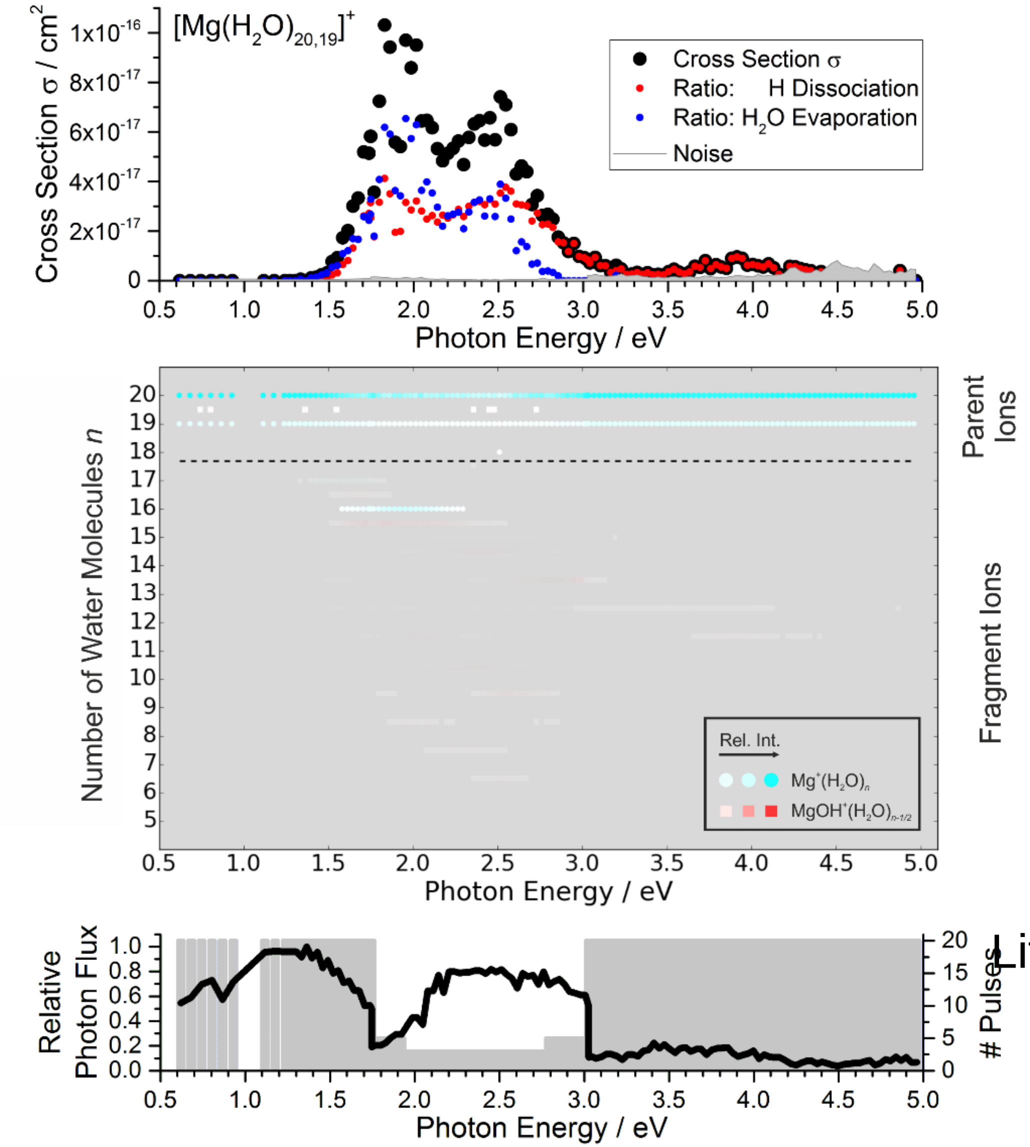
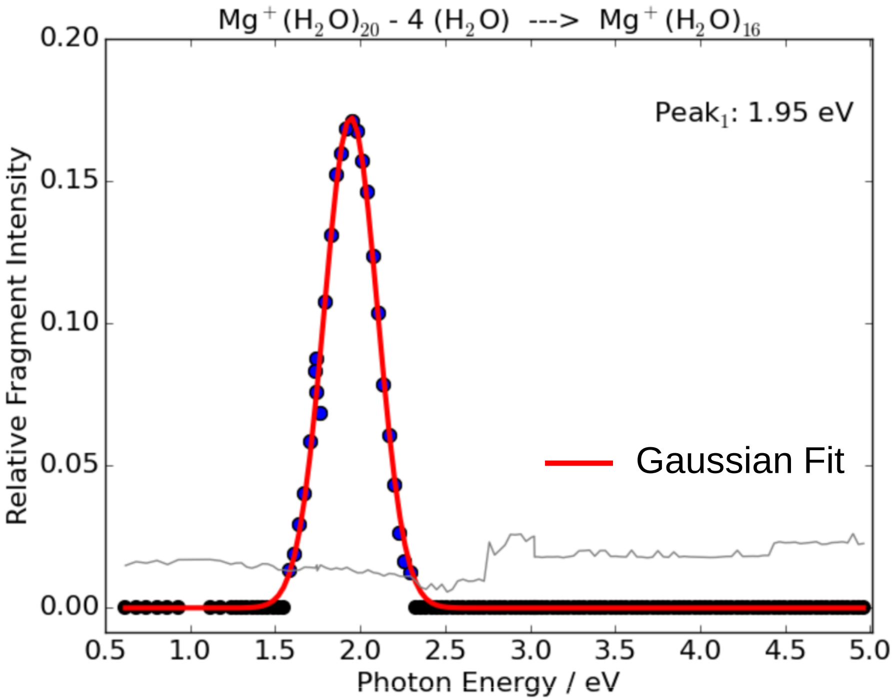


Hydrated Magnesium Ions $[Mg(H_2O)_n]^+$





$1.95\ eV / 4\ H_2O \approx 0.49\ eV / H_2O$

Literature Value of H_2O Binding Energy (for $n > 40$): ~0.447 eV

Photochemistry and Spectroscopy of Hydrated Metal Ions $[M(H_2O)_n]^+$

Hydrated Magnesium Ions $[Mg(H_2O)_n]^+$

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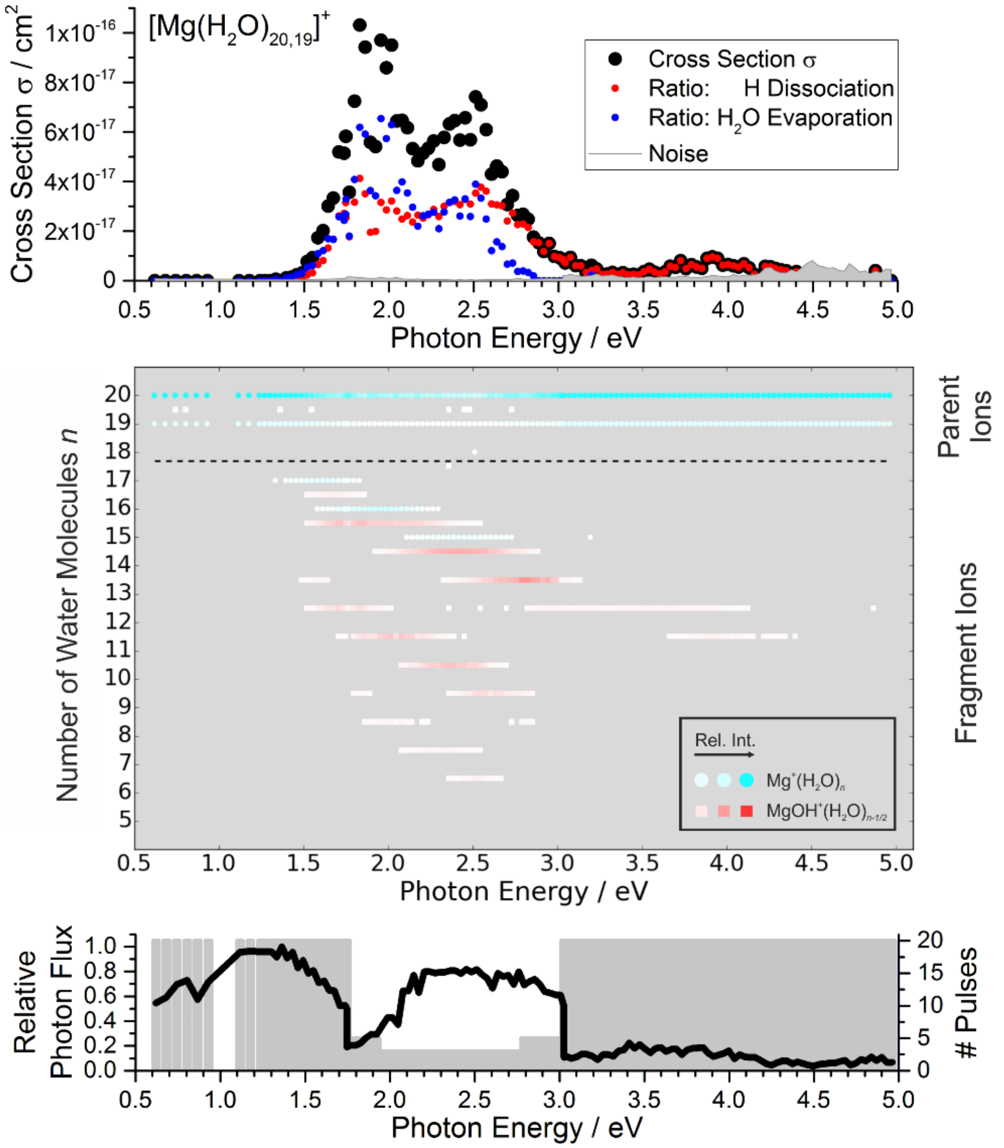

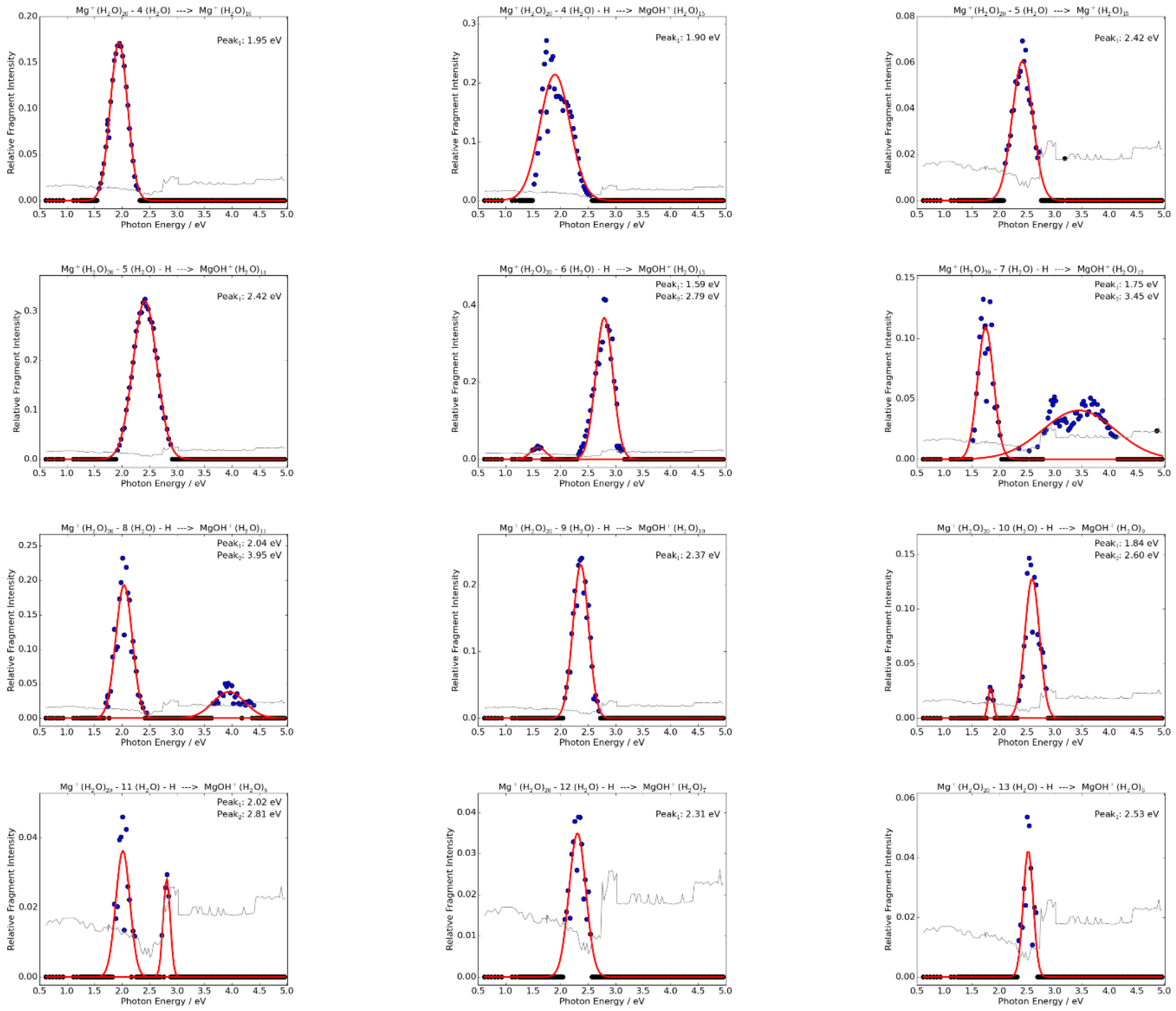

Photochemistry and Spectroscopy of Hydrated Metal Ions $[M(H_2O)_n]^+$

Hydrated Magnesium Ions $[Mg(H_2O)_n]^+$

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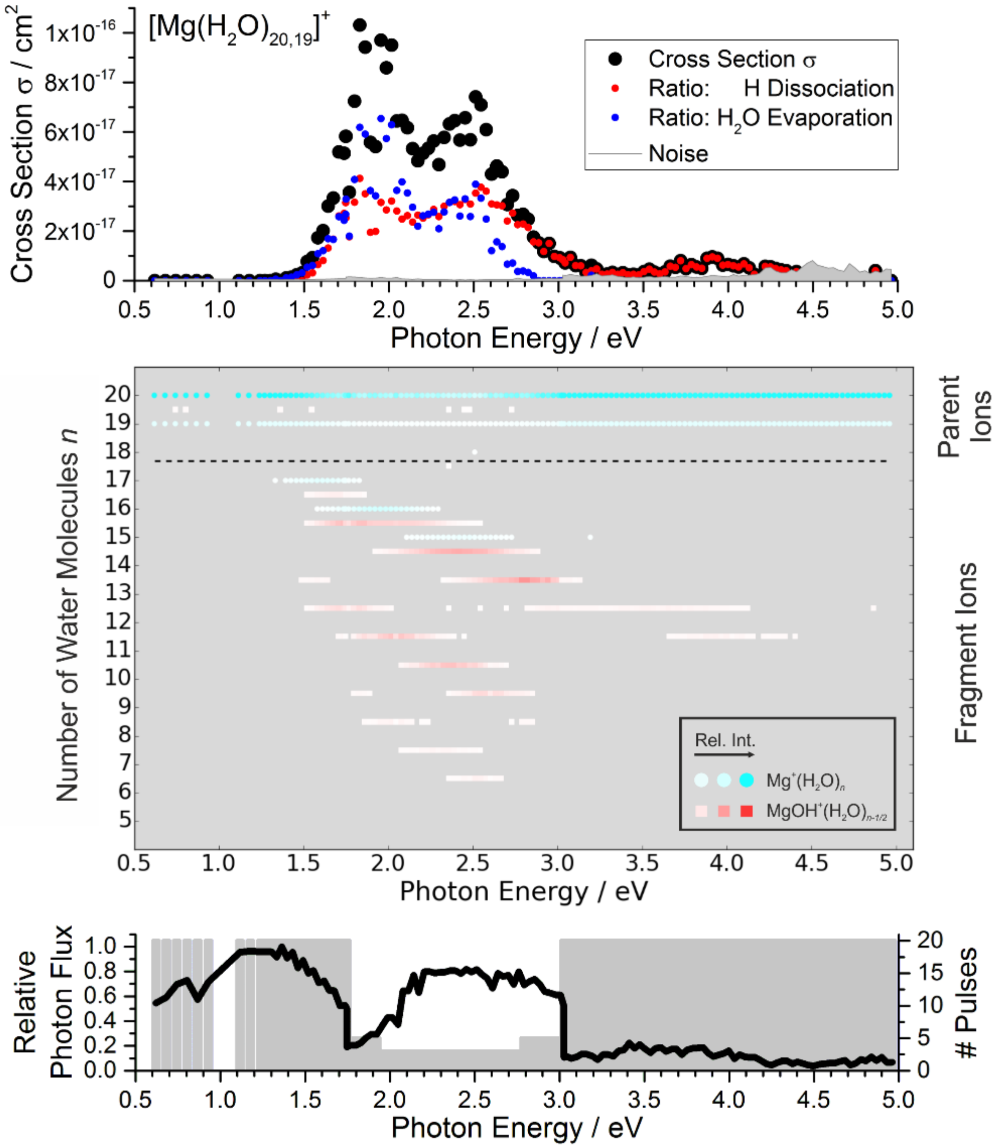
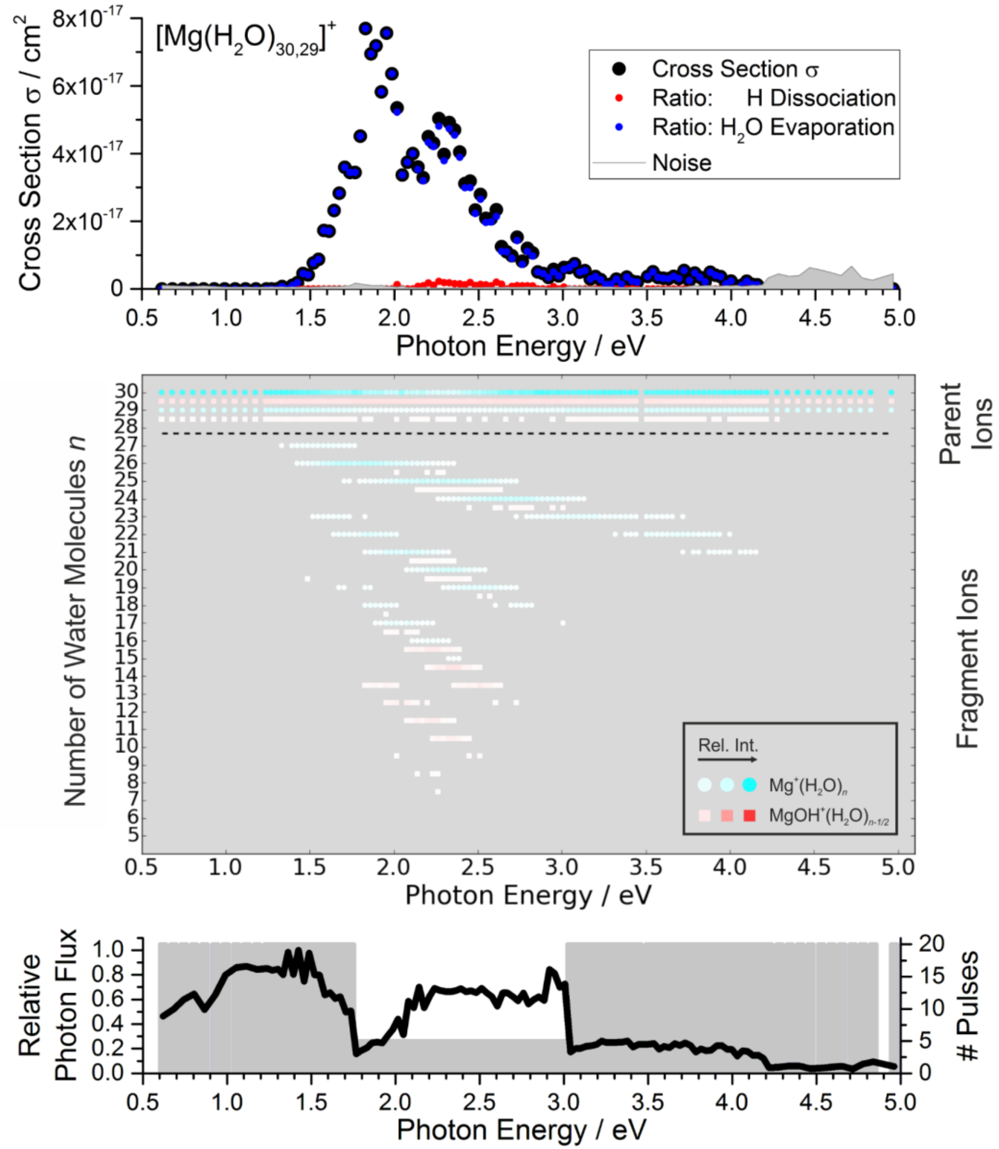
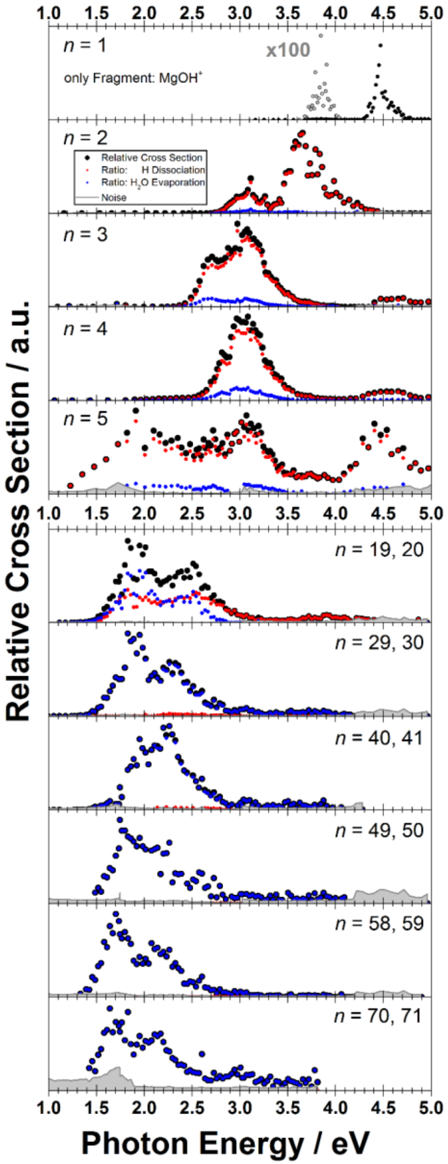


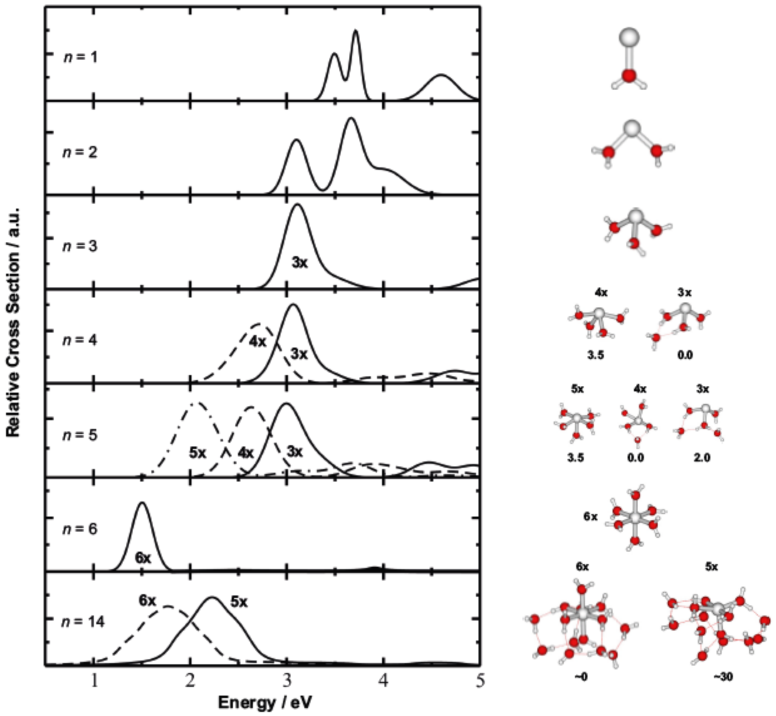


Theoretical Results and Interpretation

Photochemistry and Spectroscopy of Hydrated Metal Ions $[M(H_2O)_n]^+$

Hydrated Magnesium Ions $[Mg(H_2O)_n]^+$

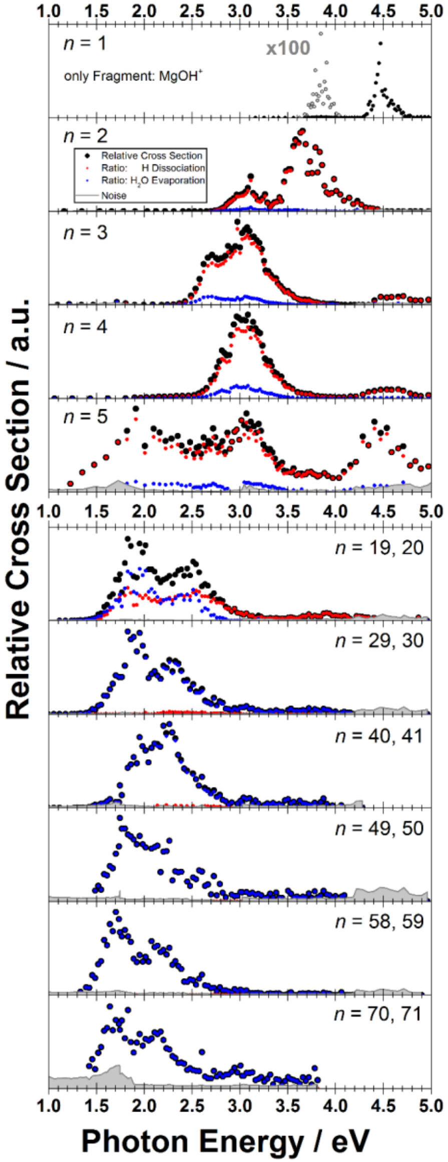


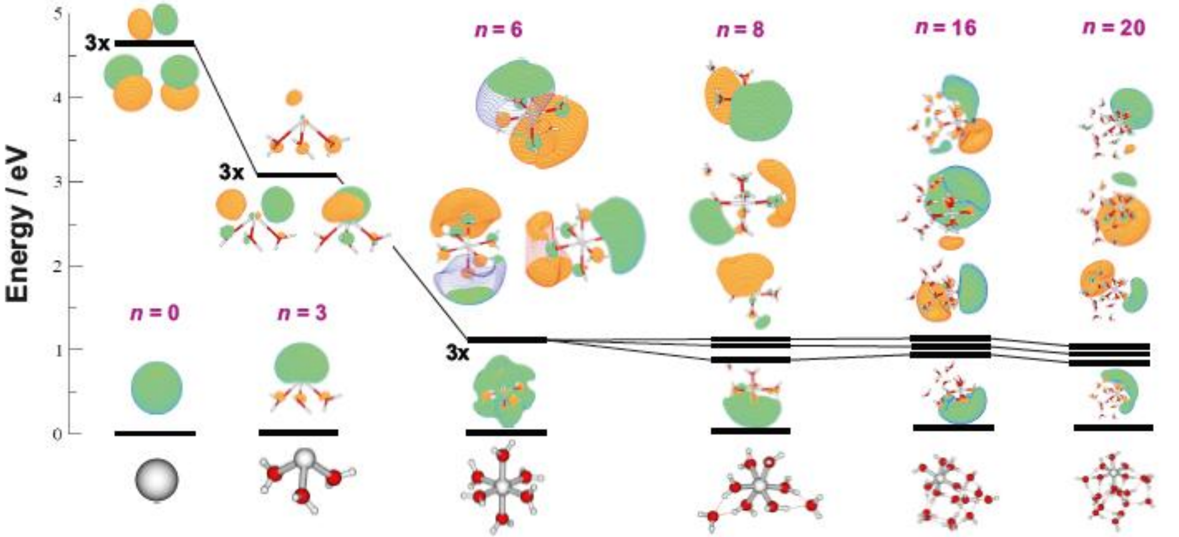


n = 1-5: Excitation energies and oscillator strengths calculated at the CC2/aug-co-pVTZ level of theory,
Frequencies and forces in the excited states calculated at the CAM-B3LYP/aug-co-pVTZ level.

n = 6,14: CC2/def2TZVP//B3LYP/6-31++g**, artificially broadened

Hydrated Magnesium Ions $[Mg(H_2O)_n]^+$





Excitation energies: TD-BHandHLYP/6-31++g**, orbitals: CASSCF/6-31++g**

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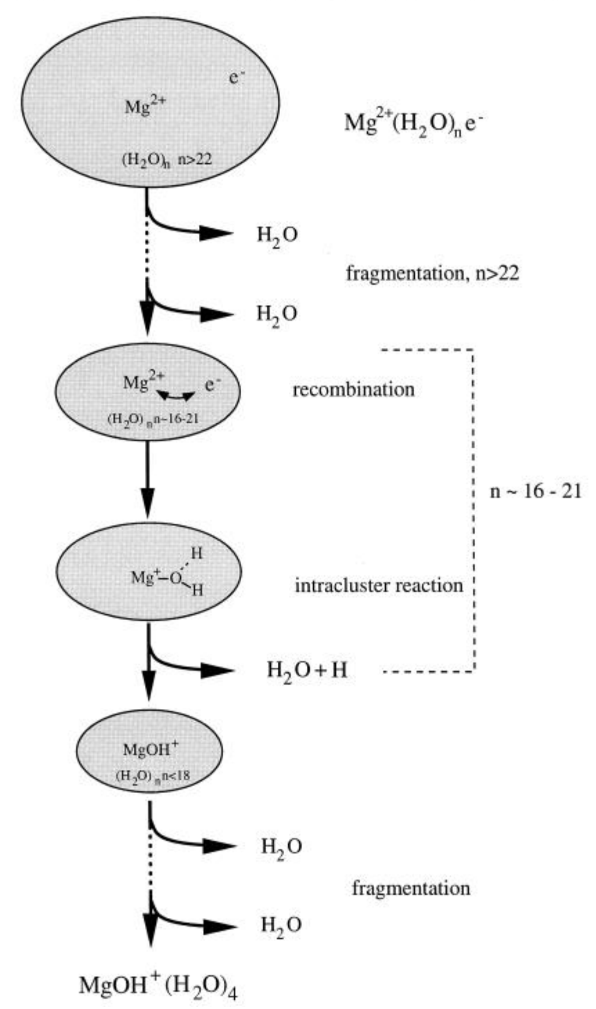
Hydrated Magnesium Ions $[Mg(H_2O)_n]^+$

C. Berg et al. / Chemical Physics 239 (**1998**) 379–392

Unimolecular fragmentation of magnesium - water clusters



Hydrated Electron $Mg^{2+}(H_2O)_n^-$ for $n \geq 20$?

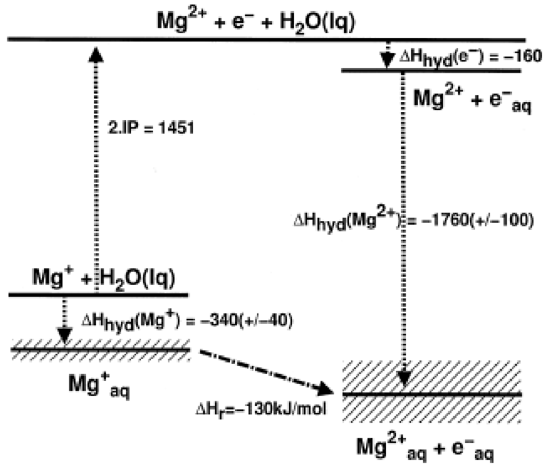
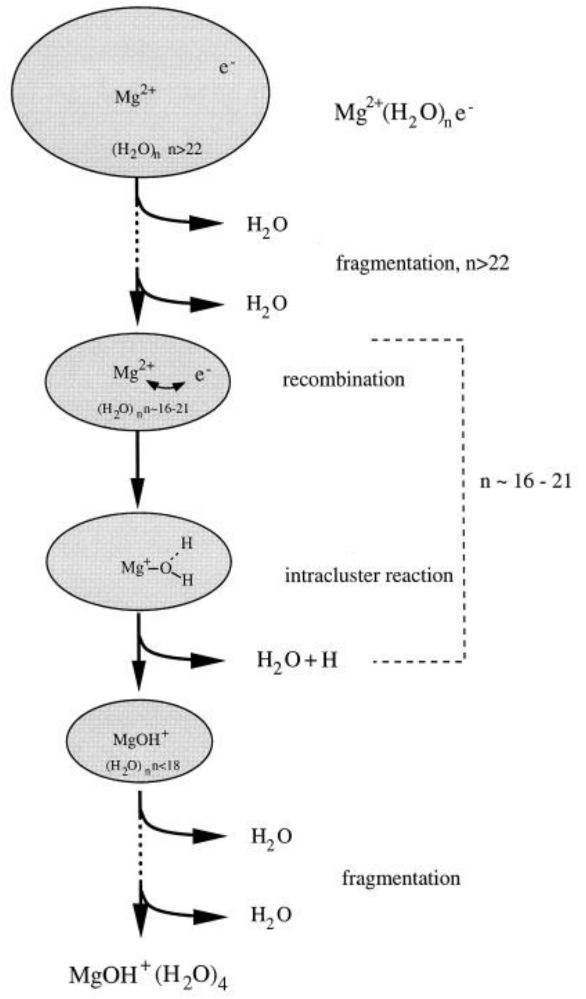


Fig. 6. Energetics of Mg^+ hydration. Electron detachment and separate hydration of Mg^{2+}_{aq} and e^-_{aq} is favoured by ~130 kJ/mol.

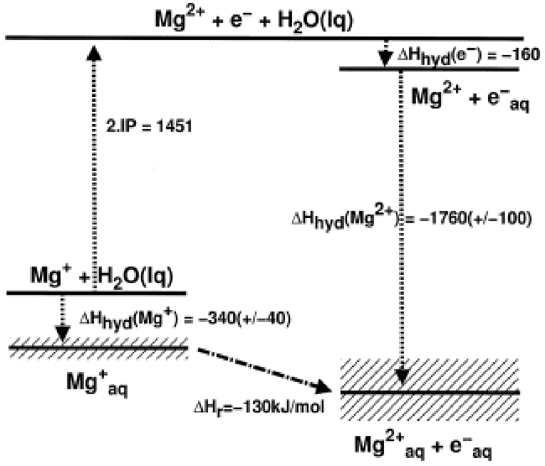
Hydrated Magnesium Ions $[Mg(H_2O)_n]^+$

C. Berg et al. / Chemical Physics 239 (**1998**) 379–392

Unimolecular fragmentation of magnesium - water clusters



Hydrated Electron <u>$Mg^{2+}(H_2O)_n^-$</u> for $n \geq 20$?



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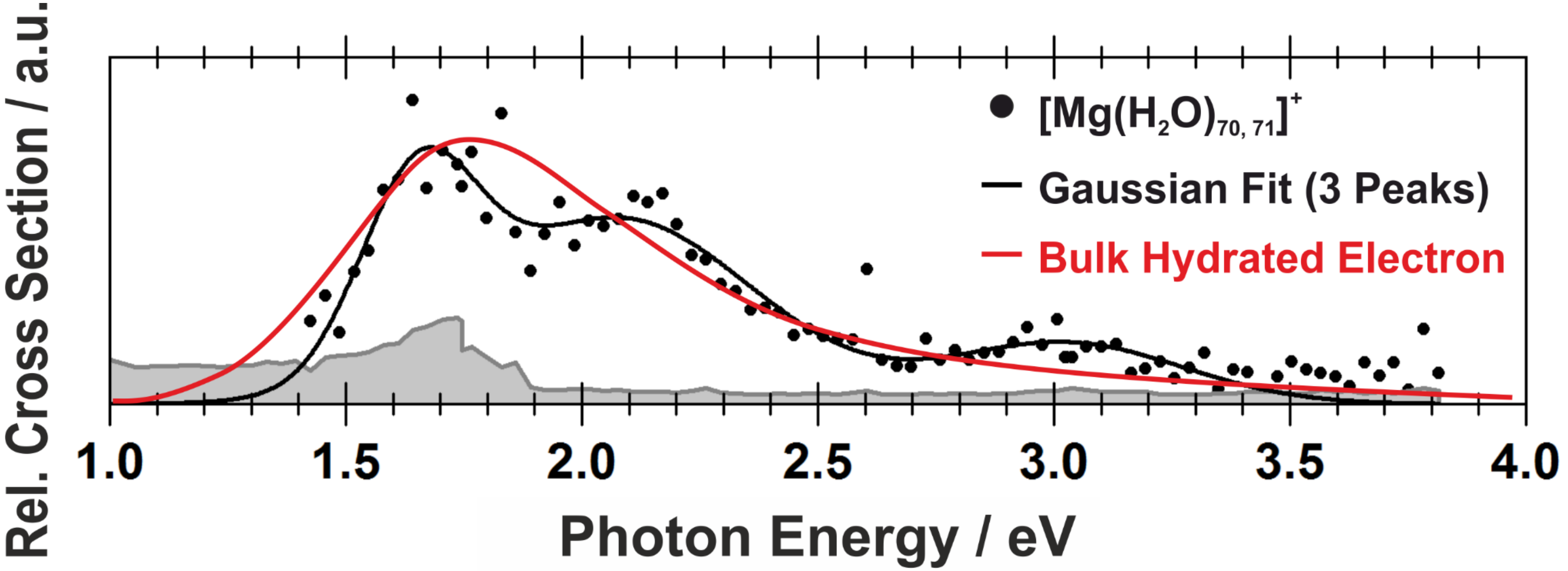

Water Molecule Binding Energy

# photons	1					
n	20	30	40	50	60	70
lost H_2O	E per H_2O / eV					
3	0,53	0,52	0,53	0,52	0,52	
4	0,49	0,45	0,49	0,45	0,46	0,45
5	0,48	0,46	0,49	0,46	0,48	0,45
6		0,45	0,47	0,46	0,47	0,44
7		0,45	0,48	0,44	0,45	0,43
8		0,46	0,47	0,45		0,44
9		0,44		0,44		
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23						
24						
avg.	0,50	0,46	0,49	0,46	0,48	0,44

# photons	2					
n	20	30	40	50	60	70
lost H_2O	E per H_2O / eV					
3						
4						
5						
6						
7		0,47	0,51		0,48	
8		0,47	0,48	0,46	0,47	0,46
9		0,46	0,47	0,45	0,47	0,46
10		0,46	0,47	0,46	0,46	0,45
11		0,45	0,47	0,46	0,47	0,45
12			0,46	0,46	0,46	
13					0,46	
14						
15						
16						
17						
18						
19						
20						
21						
22						
23						
24						
avg.		0,46	0,48	0,46	0,47	0,46

# photons	3					
n	20	30	40	50	60	70
lost H_2O	E per H_2O / eV					
3						
4						
5						
6						
7						
8						
9						
10						
11		0,49			0,47	
12		0,47	0,49	0,46	0,47	0,46
13		0,47	0,48	0,47	0,46	0,46
14		0,48	0,47	0,48	0,49	0,46
15		0,47	0,47	0,47	0,46	0,45
16			0,47	0,48		
17						
18						
19						
20						
21						
22						
23						
24						
avg.		0,48	0,47	0,47	0,47	0,46

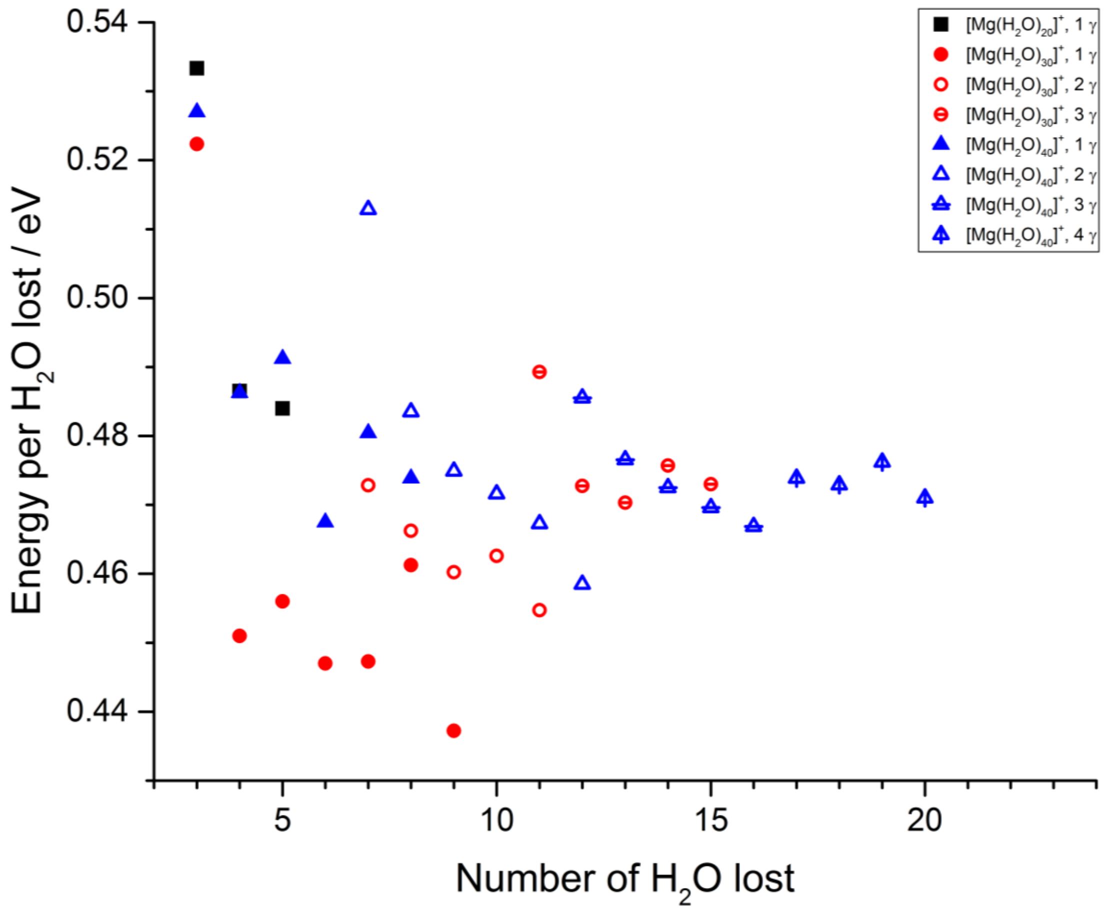
# photons	4					
n	20	30	40	50	60	70
lost H_2O	E per H_2O / eV					
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15				0,47		
16				0,47		
17			0,47		0,46	0,45
18			0,47	0,48		0,47
19			0,48	0,48		0,47
20			0,47			
21						
22						
23						
24						
avg.			0,47	0,48	0,46	0,46

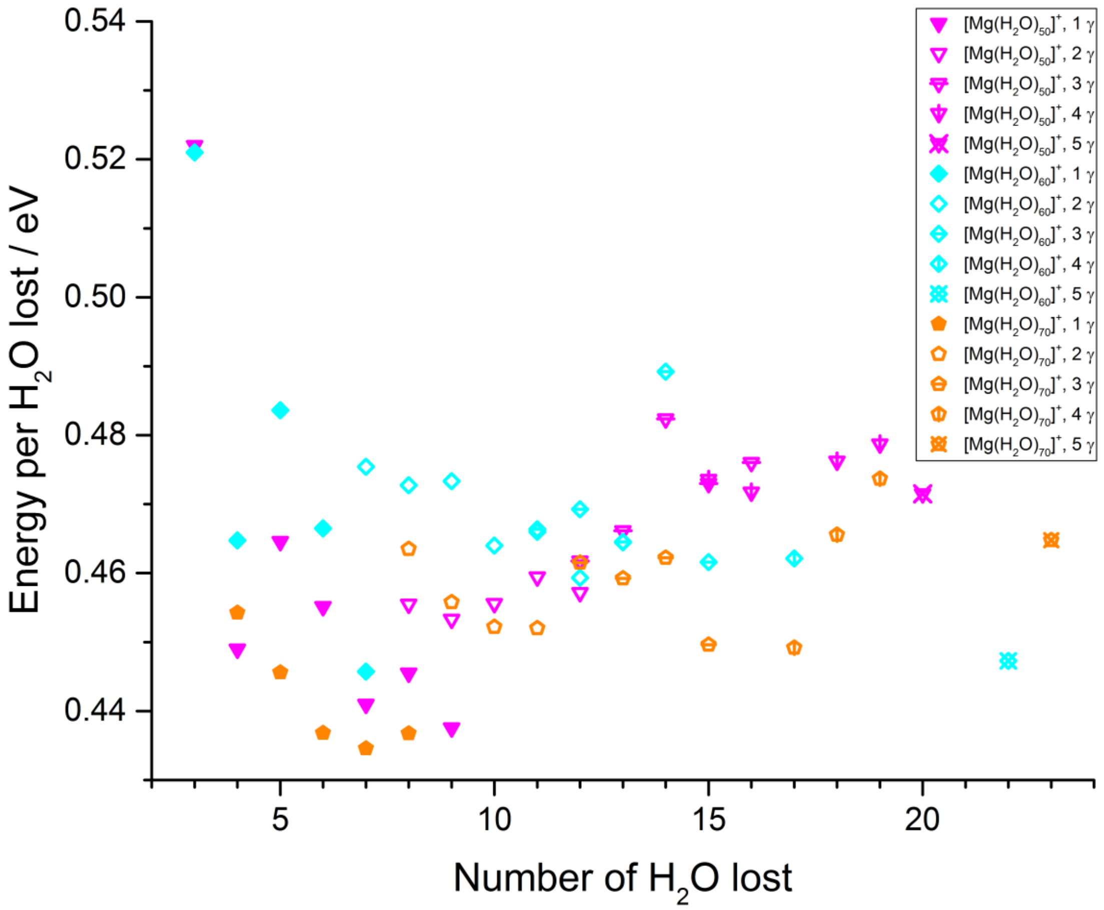
# photons	5					
n	20	30	40	50	60	70
lost H_2O	E per H_2O / eV					
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20				0,47		
21						
22					0,45	
23						0,46
24						
avg.				0,47	0,45	0,46

# photons	1	2	3	4
n	avg.			
lost H_2O	E per H2O / eV			
3	0,53			
4	0,47			
5	0,47			
6	0,45			
7	0,45	0,49		
8	0,45	0,47		
9	0,44	0,46		
10		0,46		
11		0,46	0,48	
12		0,46	0,47	
13		0,46	0,47	
14			0,48	
15			0,47	0,47
16			0,47	0,47
17				0,46
18				0,47
19				0,48
20				0,47
21				
22				
23				
24				
avg.	0,47	0,47	0,47	0,47

Water Molecule Binding Energy

Average: 0.468(19) eV per H_2O / Literature: 0.447(4) eV (for n > 40)

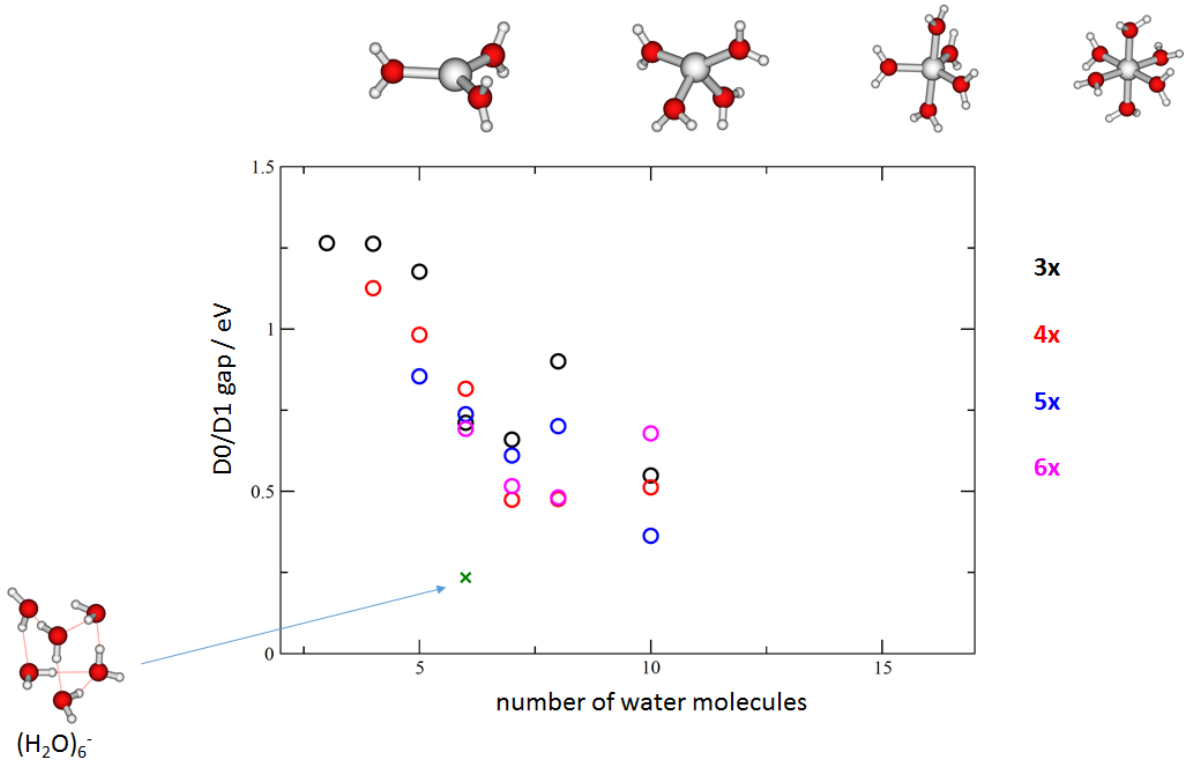




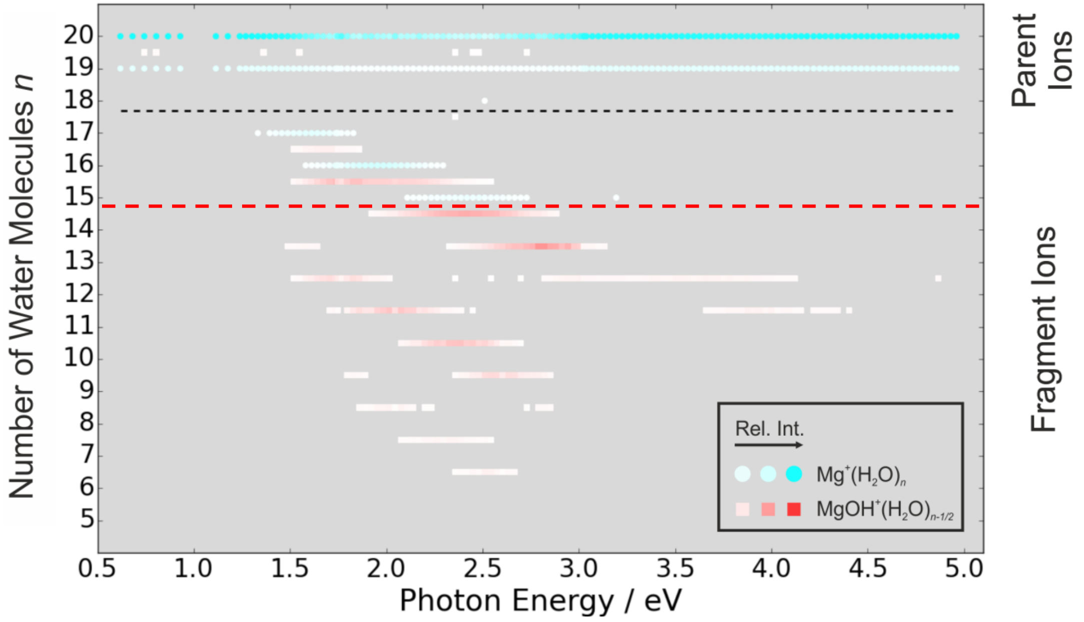
Photochemistry of Water Evaporation

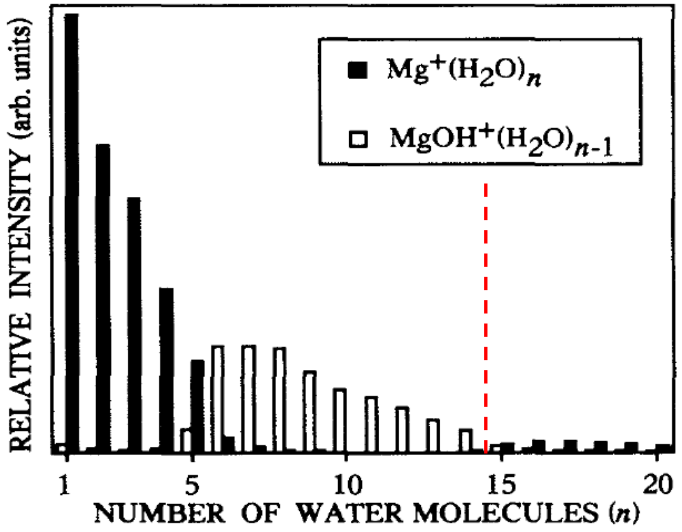
Average: 0.468(19) eV per H_2O / Literature: 0.447(4) eV (for $n > 40$)

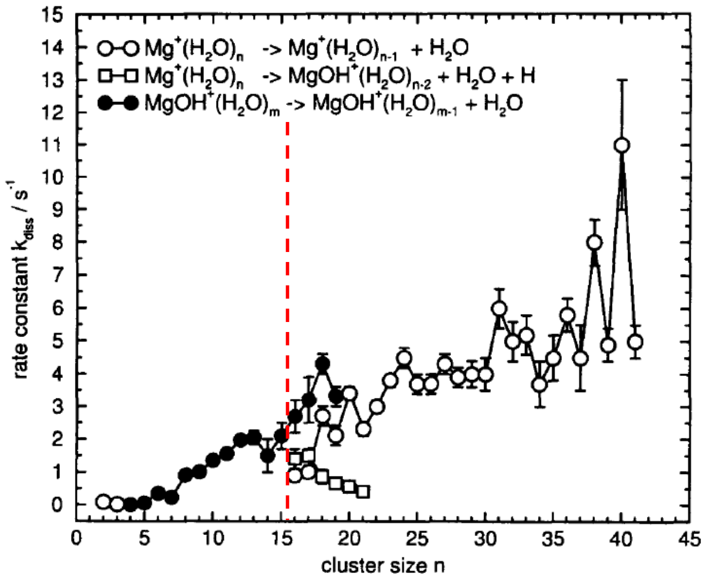
→ Dissociation in the electronic Ground State: fast IC, no Fluorescence



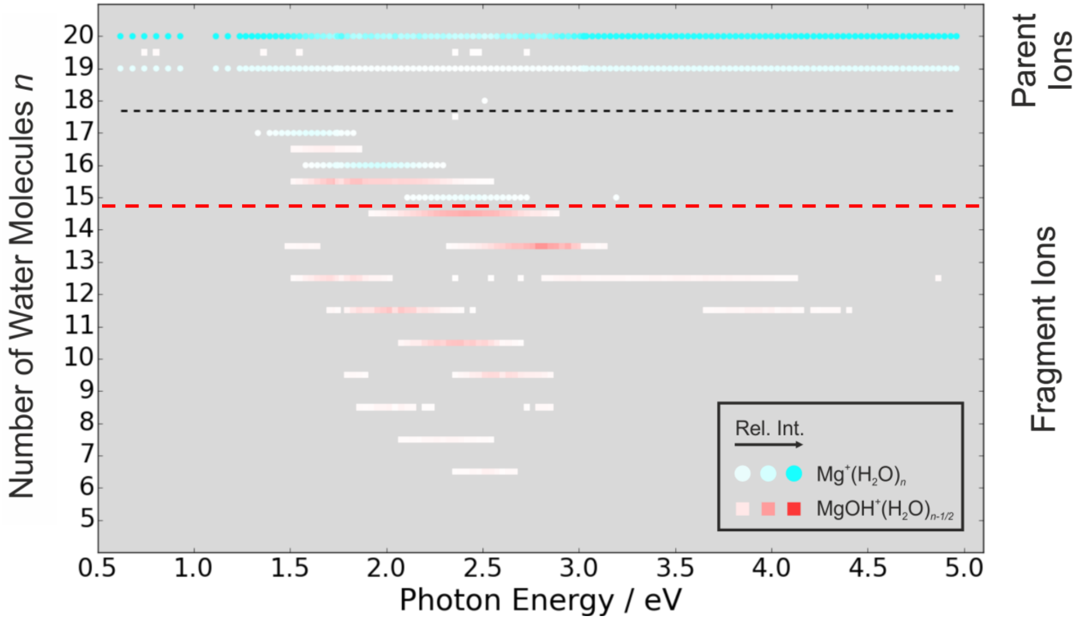
Photochemistry of Hydrogen Dissociation

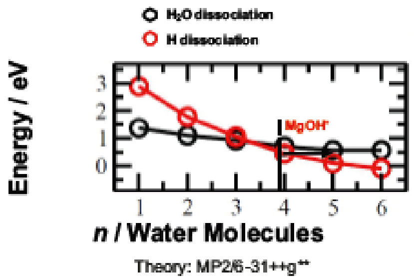


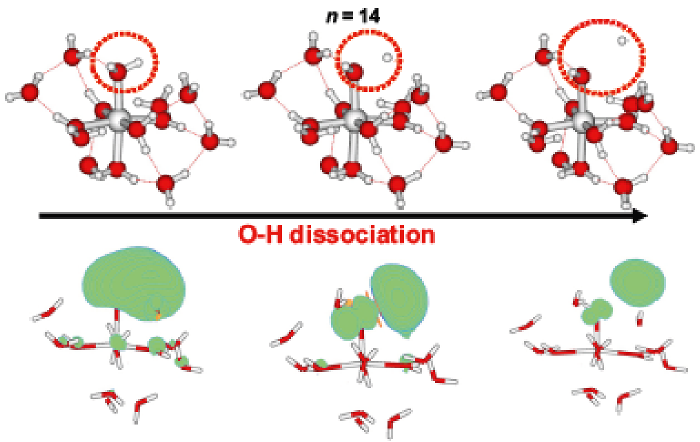


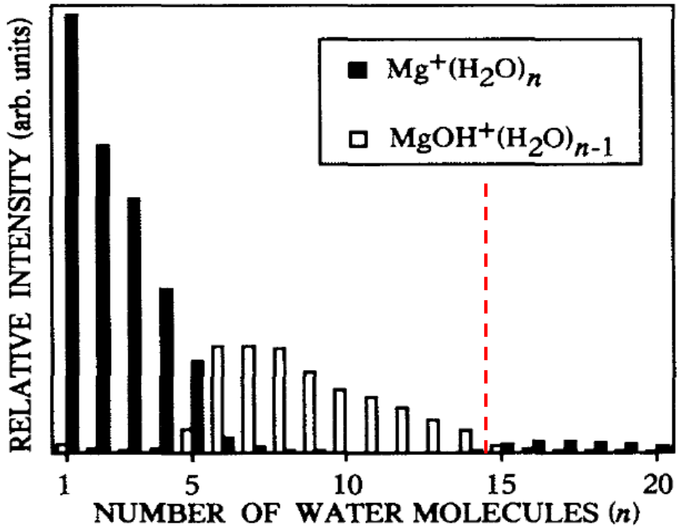


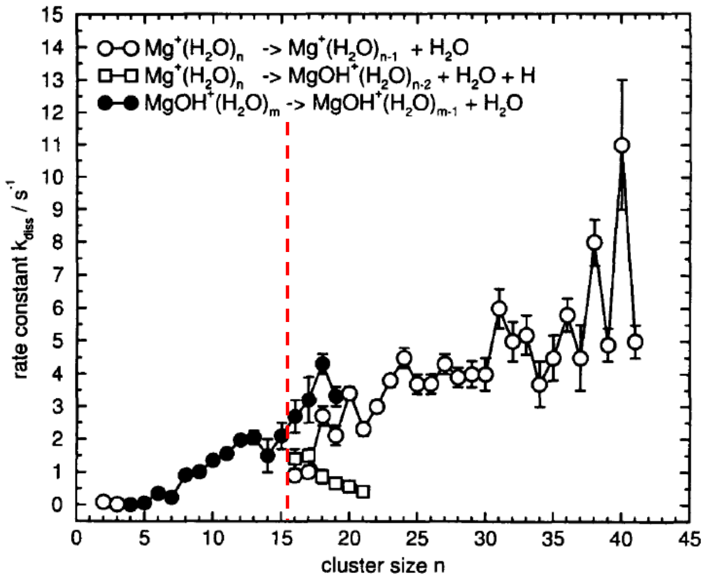
Photochemistry of Hydrogen Dissociation









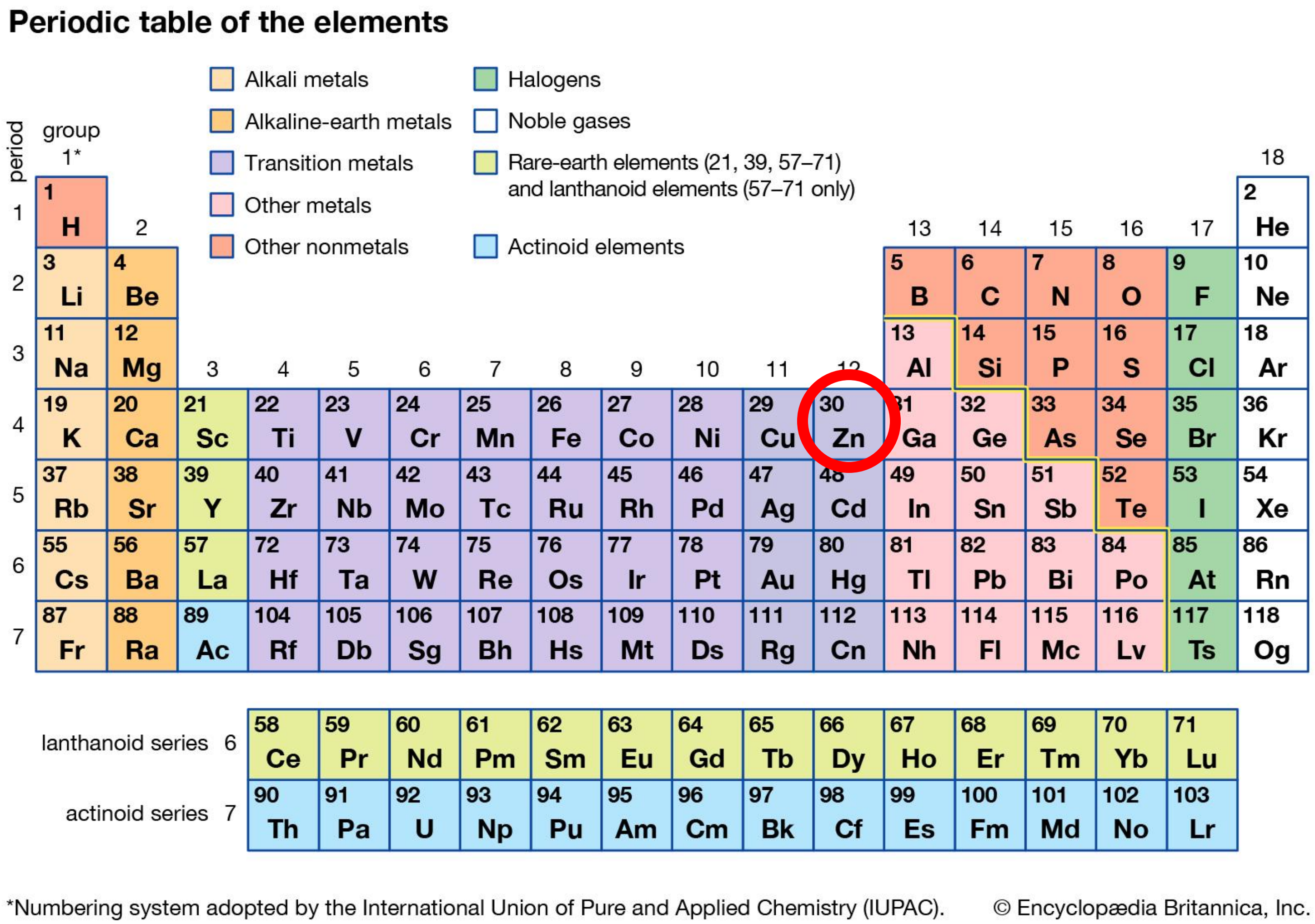


Hydrated Zinc Ions

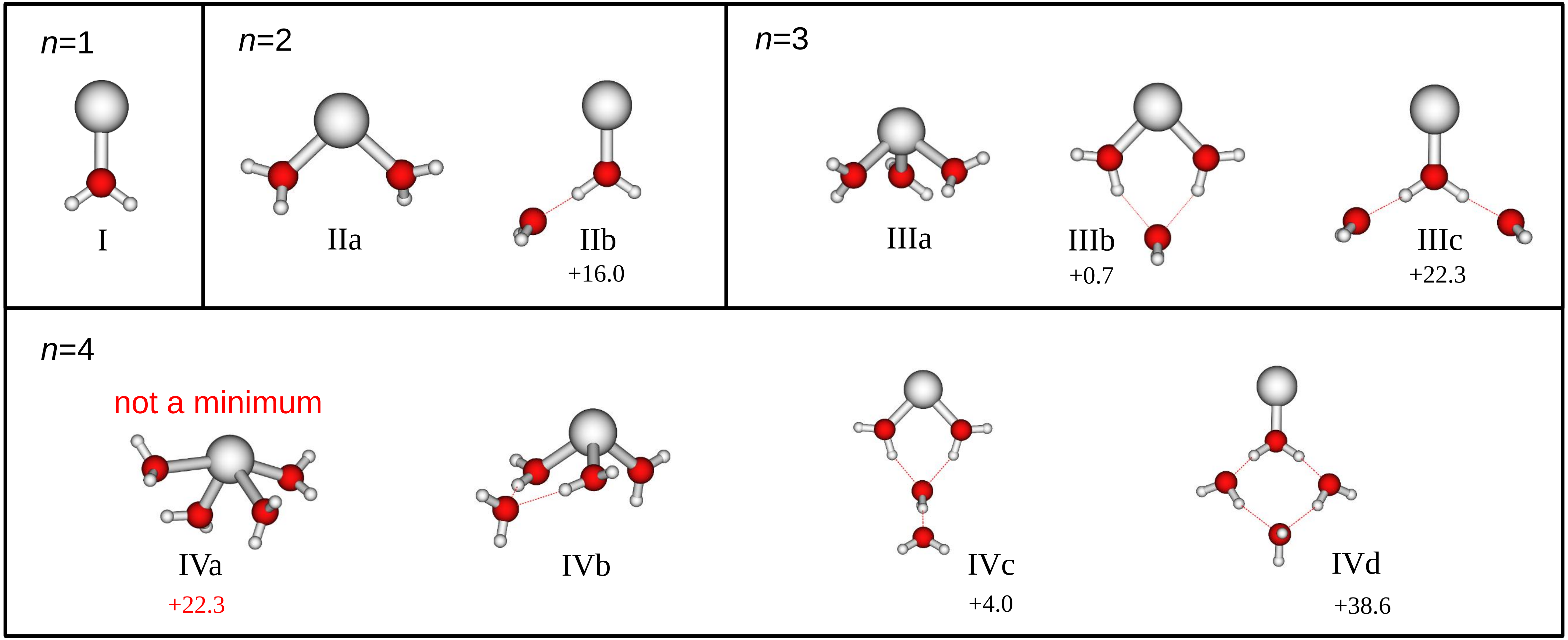
Wikipedia

Electronic Configuration of Zn^+

$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} \underline{4s^1}$

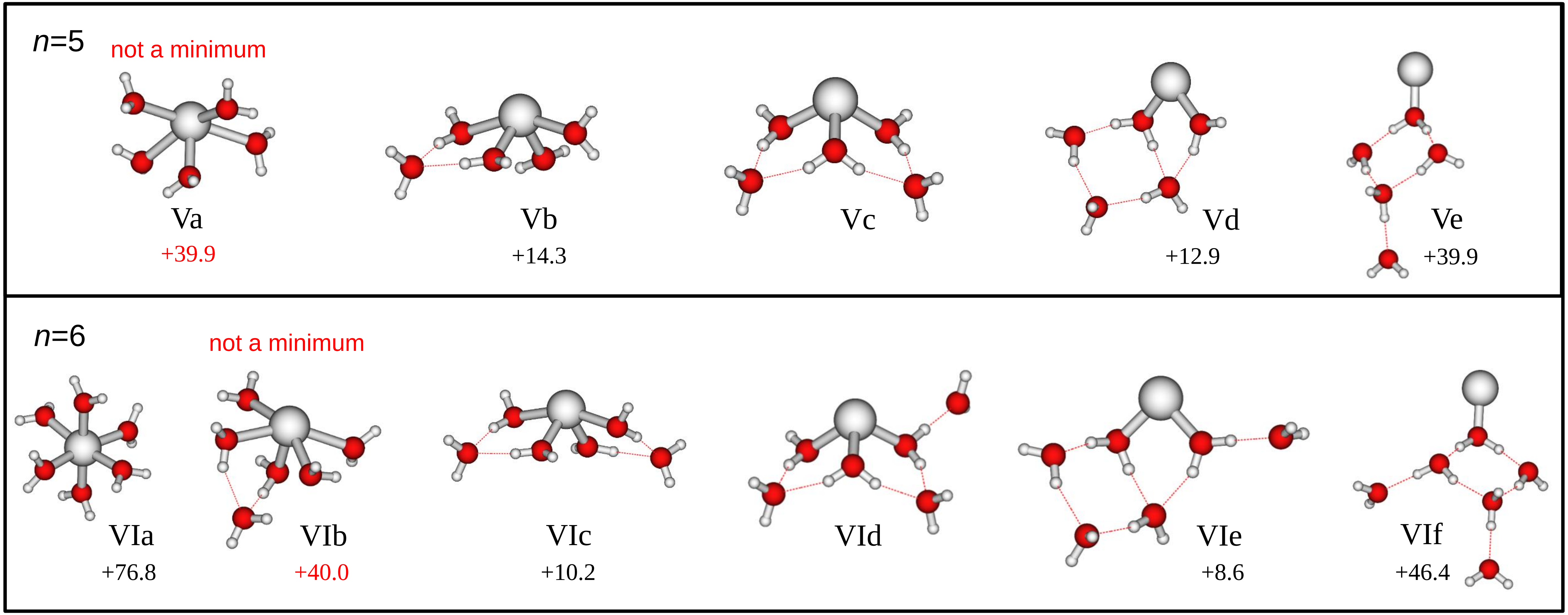


Geometries



$[Zn(H_2O)_n]^+$ // B3LYP/aug-cc-pVDZ // Energies in kJ/mol

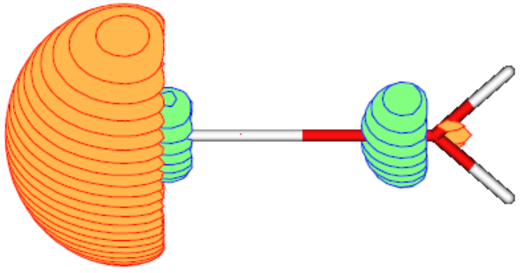
Geometries



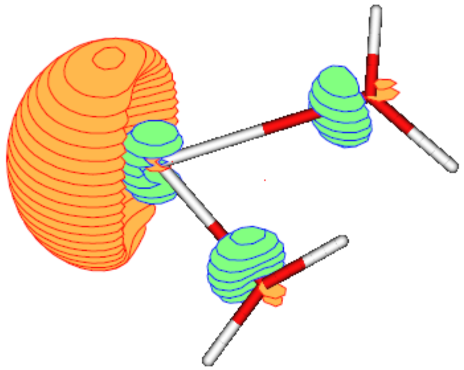
$[Zn(H_2O)_n]^+$ // B3LYP/aug-cc-pVDZ // Energies in kJ/mol

Spin Density

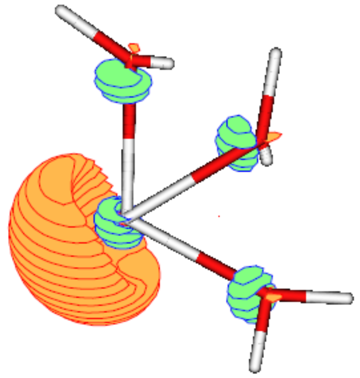
n=1



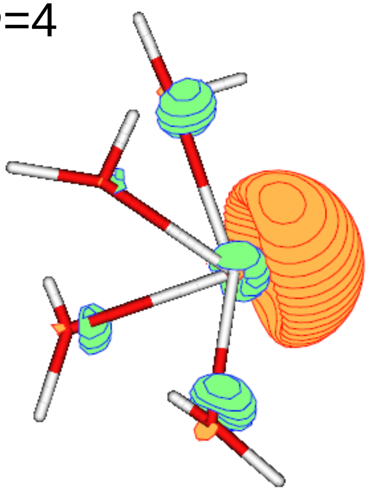
n=2



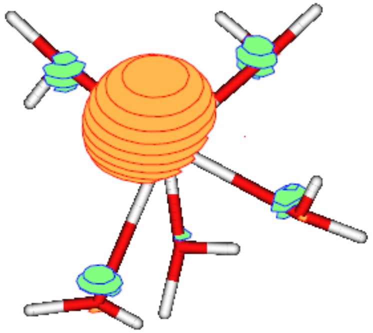
n=3



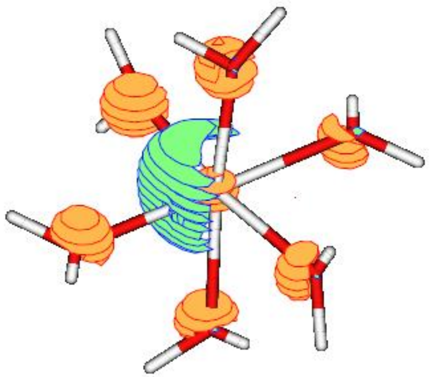
n=4



n=5

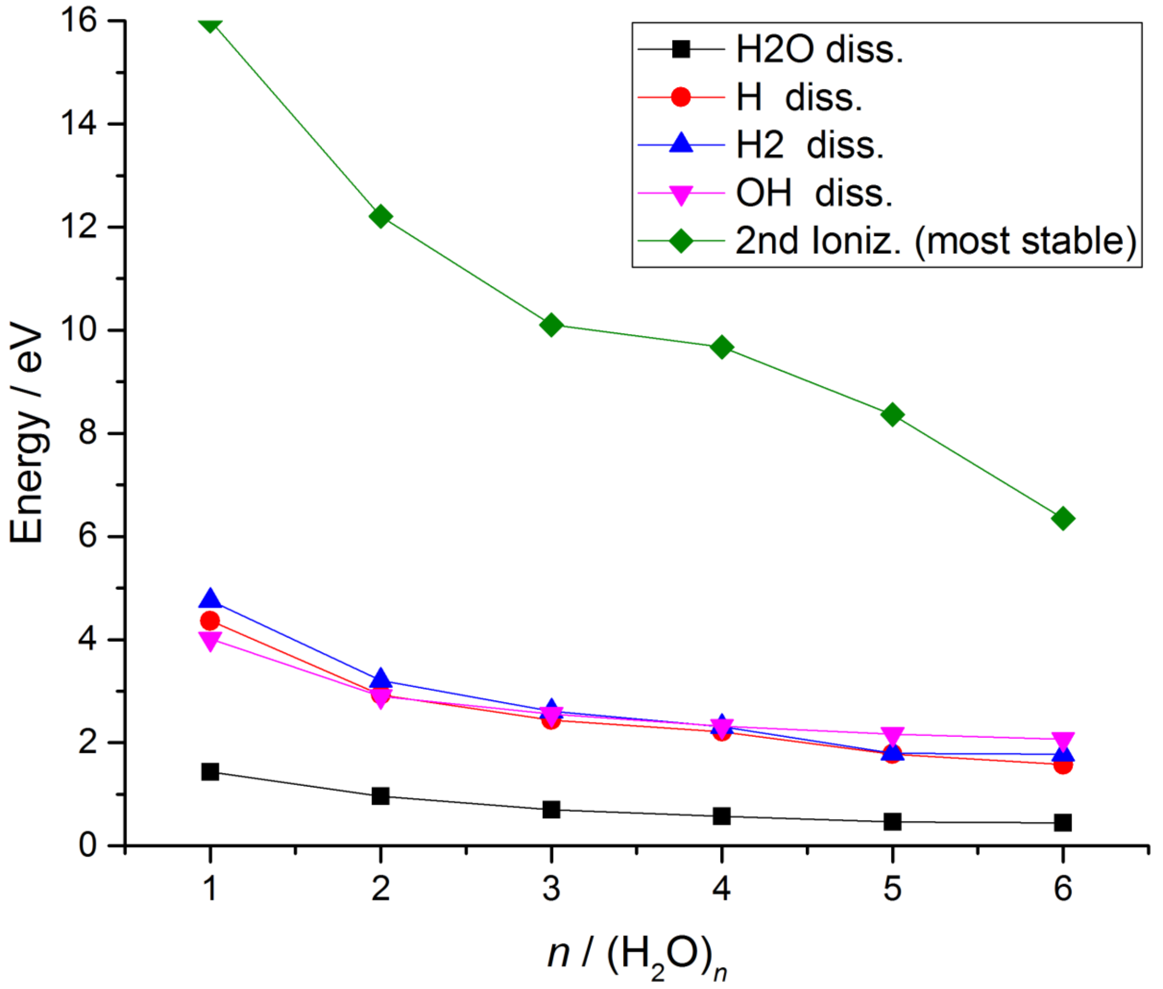


n=6



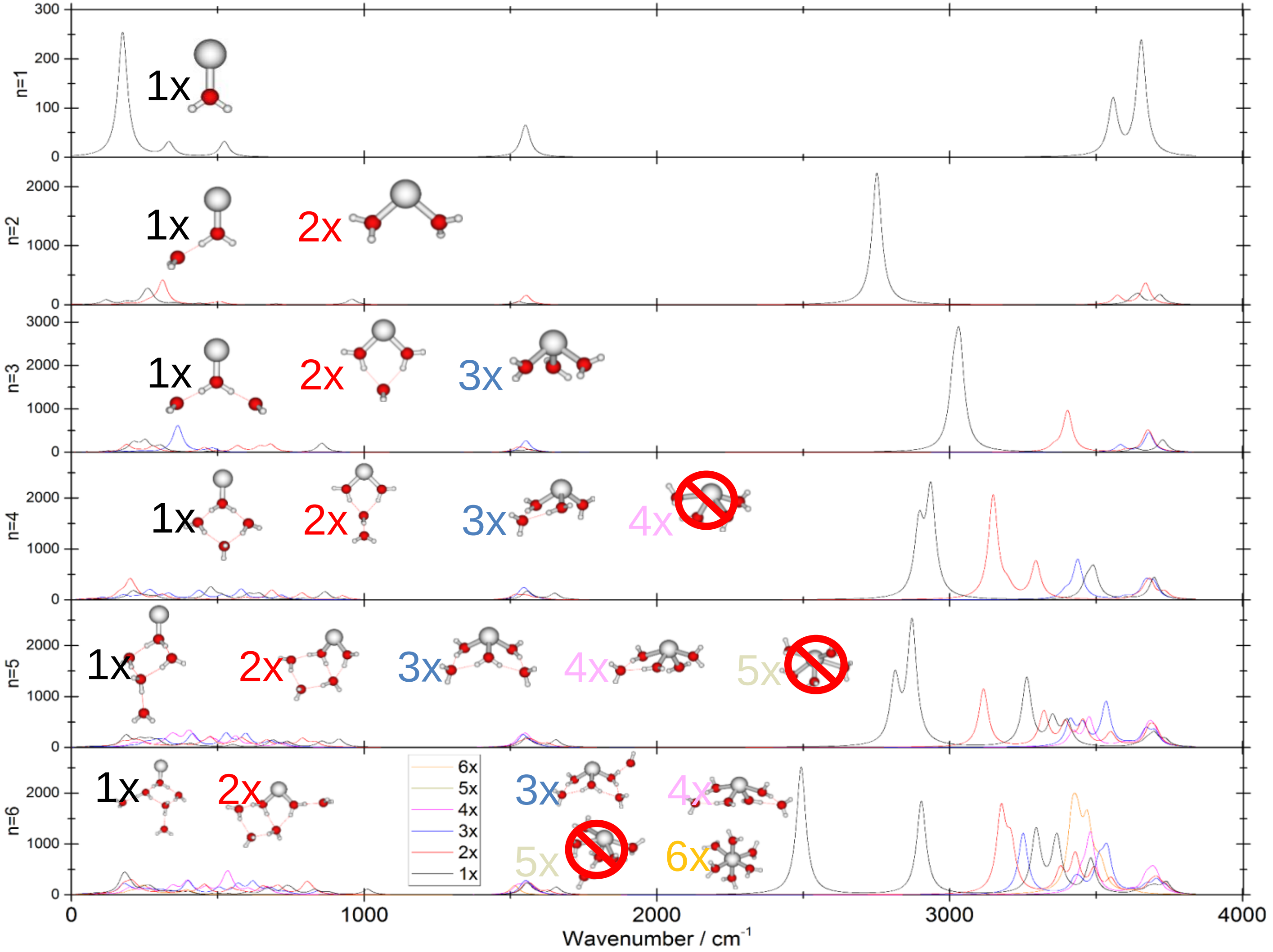
$[Zn(H_2O)_n]^+$ // B3LYP/aug-cc-pVDZ

Dissociation Energies



$[Zn(H_2O)_n]^+$ // B3LYP/aug-cc-pVDZ

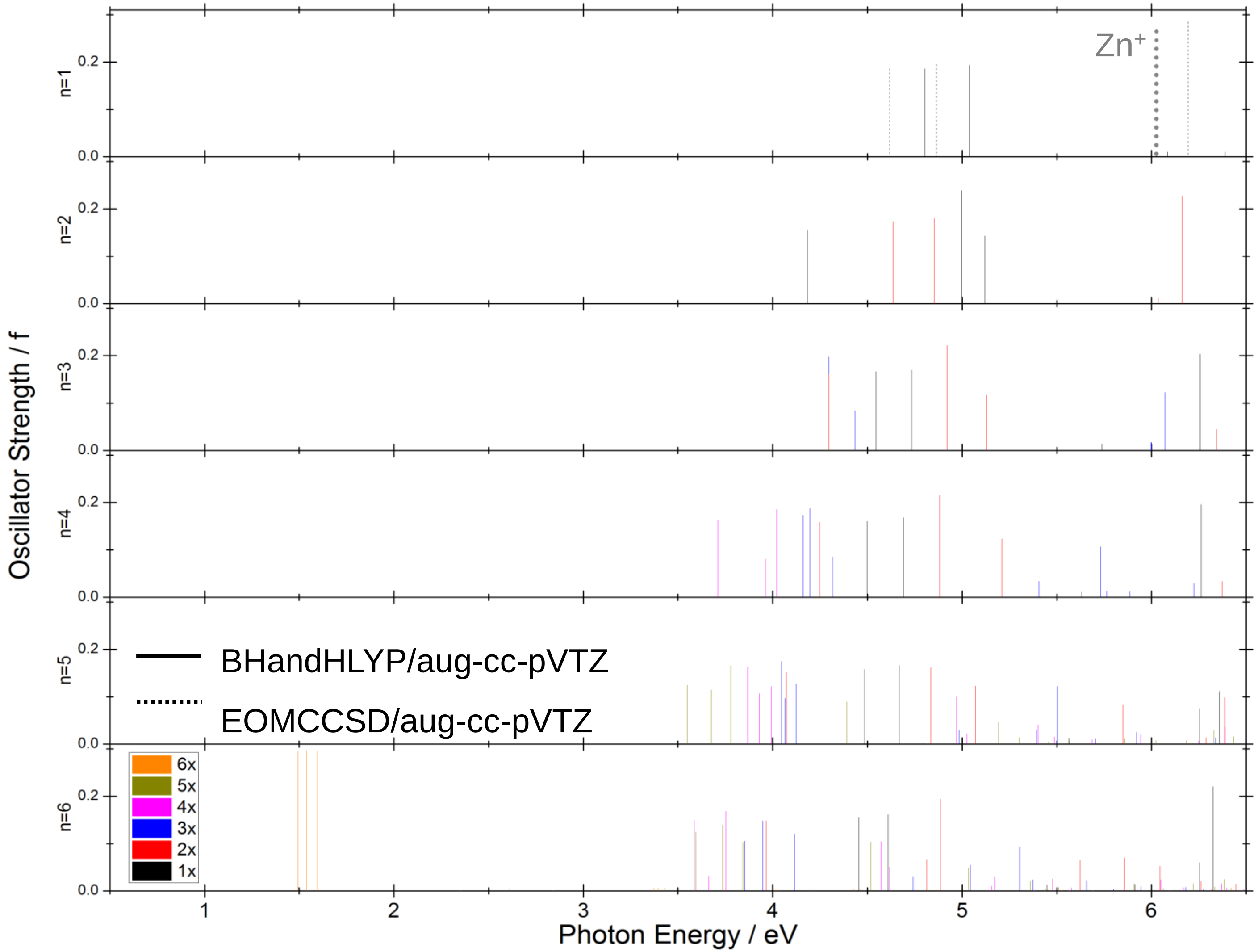
IR Spectra



not a minimum

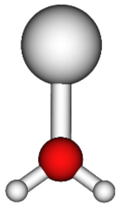
$[Zn(H_2O)_n]^+$ // B3LYP/aug-cc-pVDZ

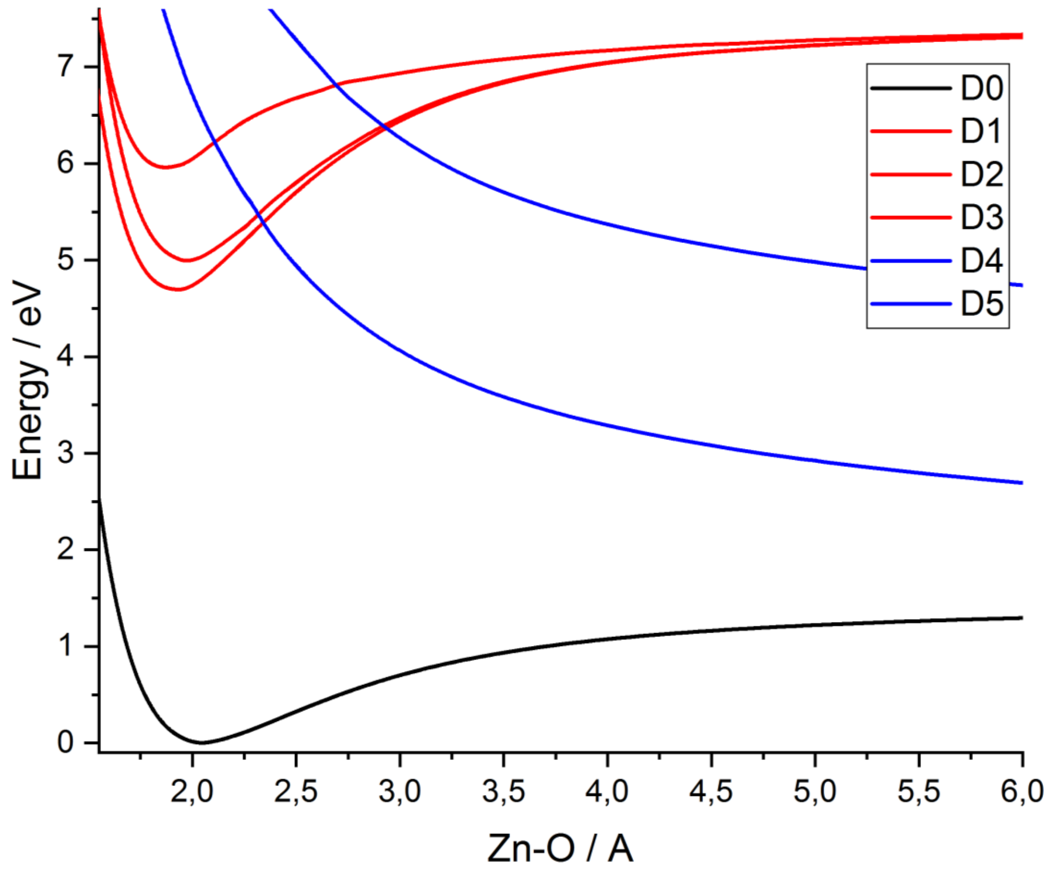
UV Spectra

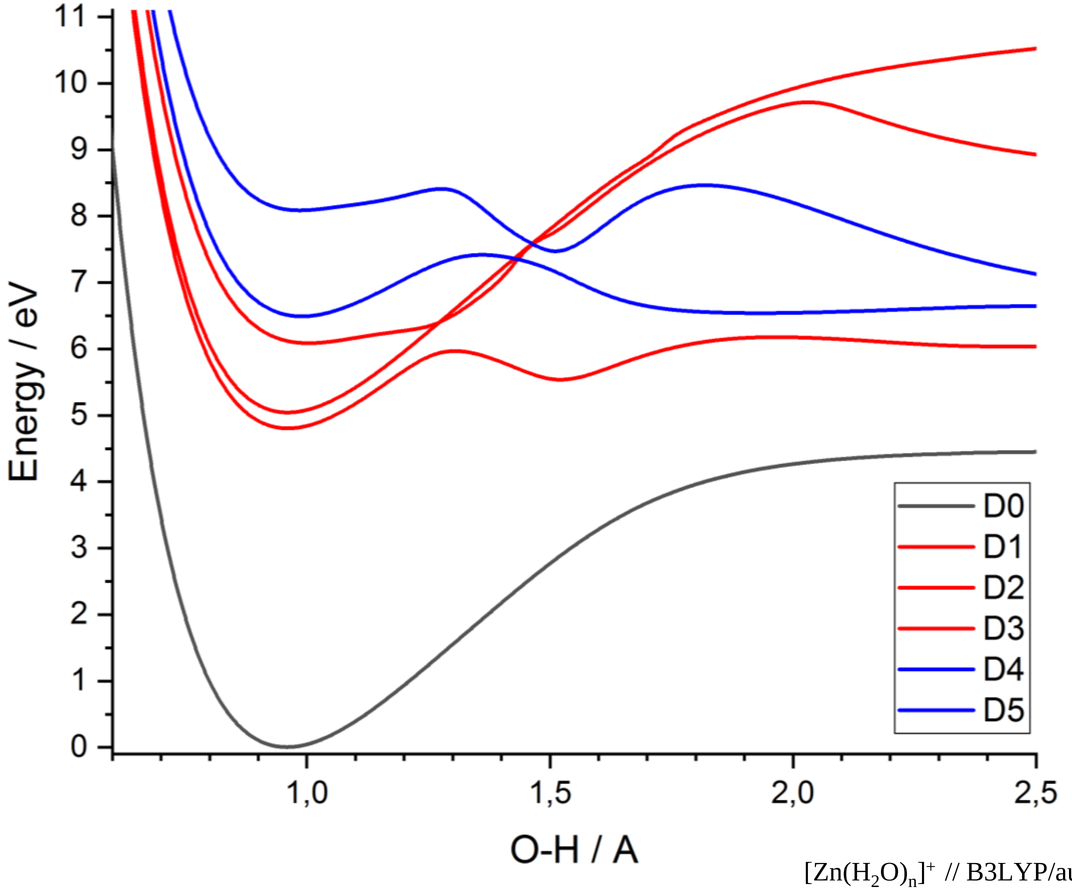


$[Zn(H_2O)_n]^+$ // B3LYP/aug-cc-pVDZ

Potential Energy Plots





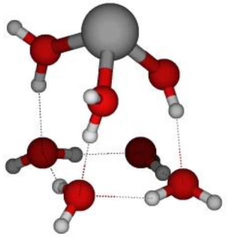


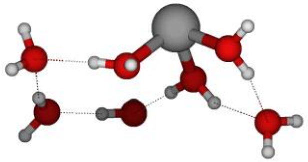
$[Zn(H_2O)_n]^+$ // B3LYP/aug-cc-pVDZ

Geometries of larger Clusters (*n*=7-20)

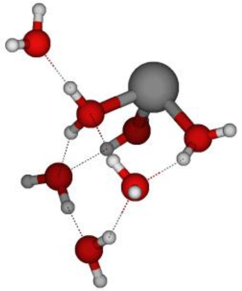
n=7

VIId

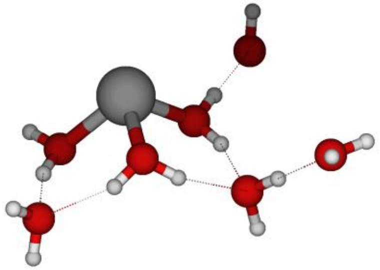




+11.2



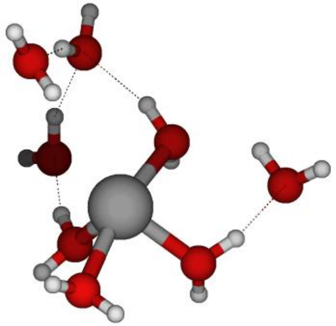
+0.7



+0.9

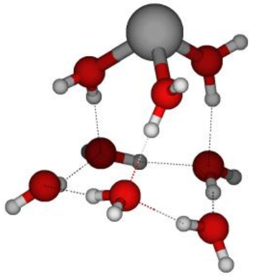
n=8

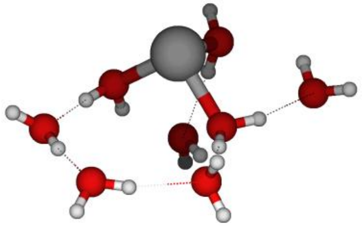
VIIIc



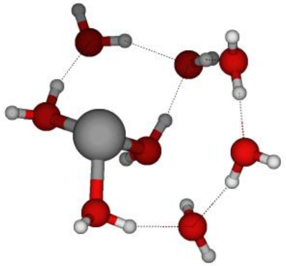
+27.9

VIIId





+20.9



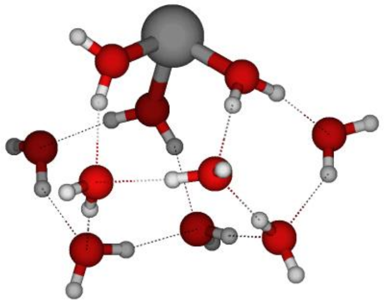
+22.5

$[Zn(H_2O)_n]^+$ // B3LYP/aug-cc-pVDZ // Energies in kJ/mol

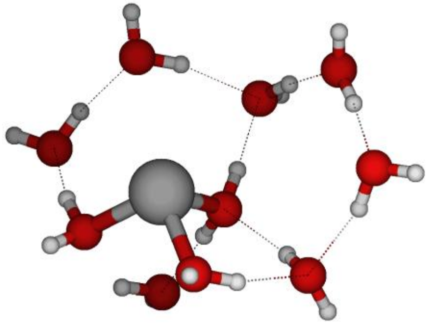
Geometries of larger Clusters (n=7-20)

n=10

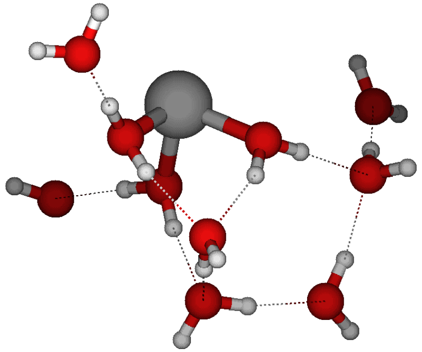
Xd



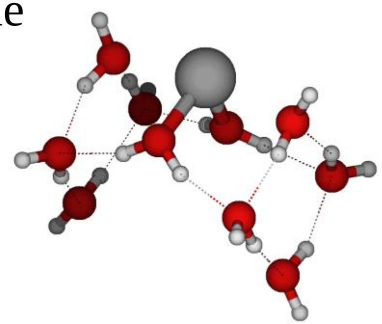
+1.1



+16.6



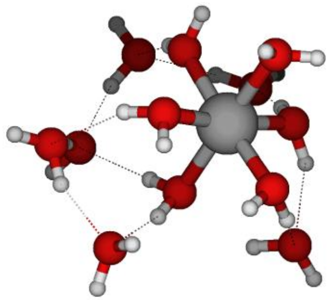
Xe



+3.9

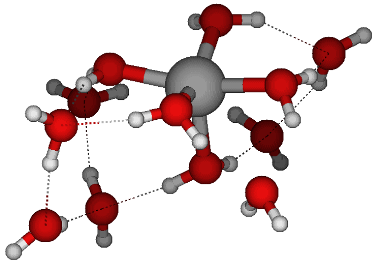
n=12

XIIa



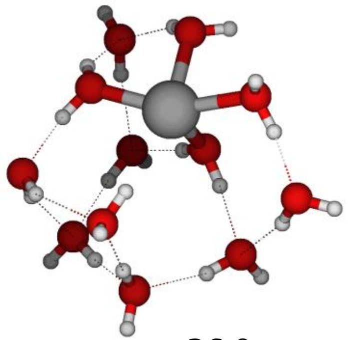
+77.5

XIIb



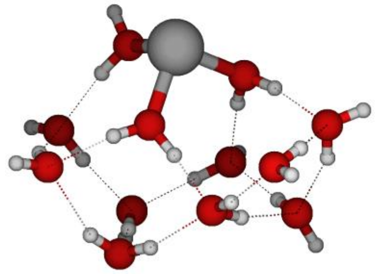
+66.3

XIIc



+26.0

XIId

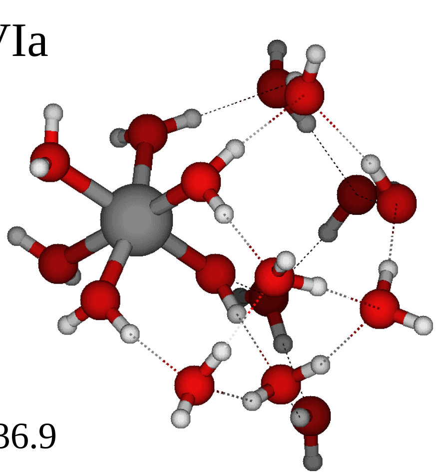


$[Zn(H_2O)_n]^+$ // B3LYP/aug-cc-pVDZ // Energies in kJ/mol

Geometries of larger Clusters (*n*=7-20)

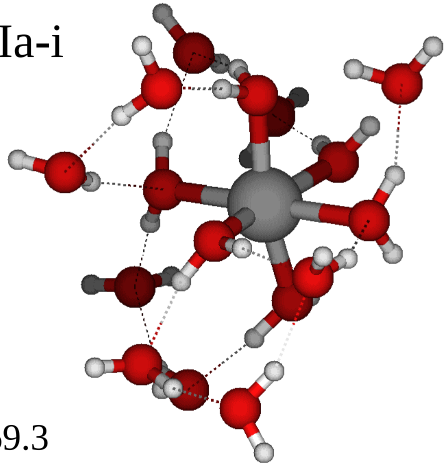
n=16

XVIa



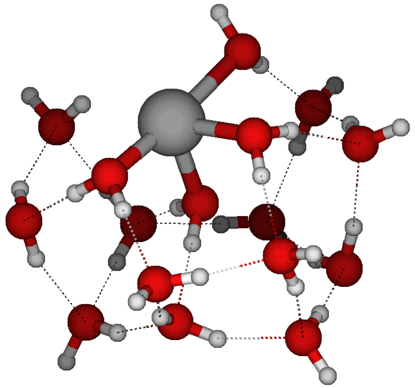
+36.9

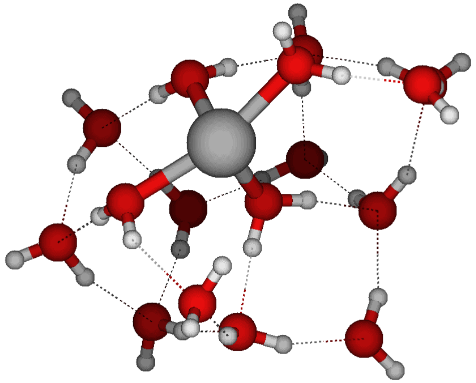
XVIa-i



+69.3

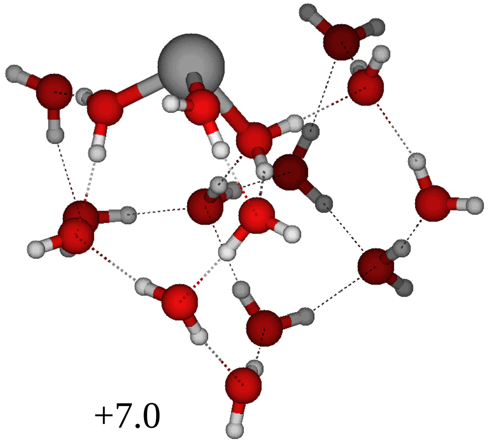
XVIc





+3.2

XVId



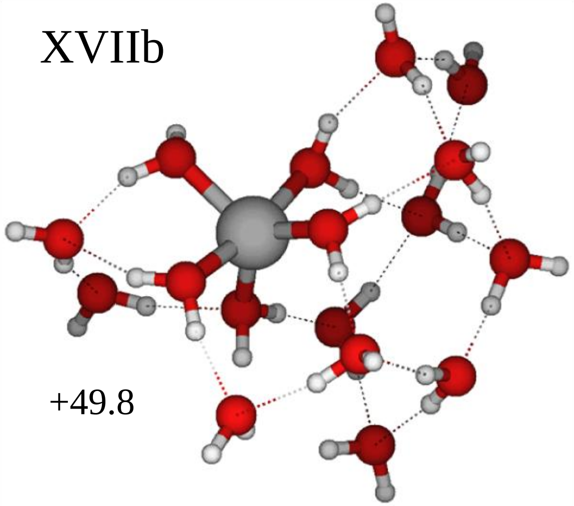
+7.0

$[Zn(H_2O)_n]^+$ // B3LYP/aug-cc-pVDZ // Energies in kJ/mol

Geometries of larger Clusters (*n*=7-20)

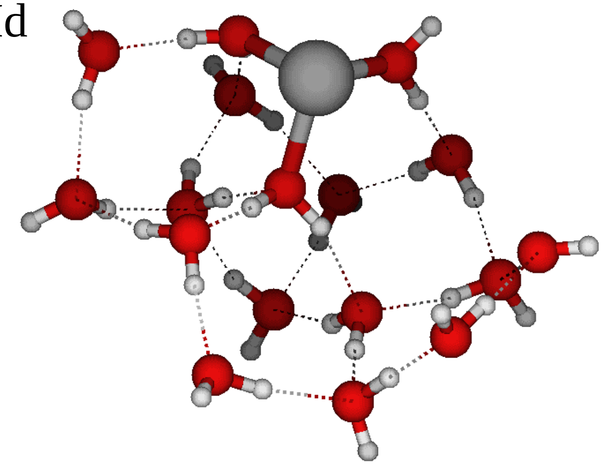
n=17

XVIIb

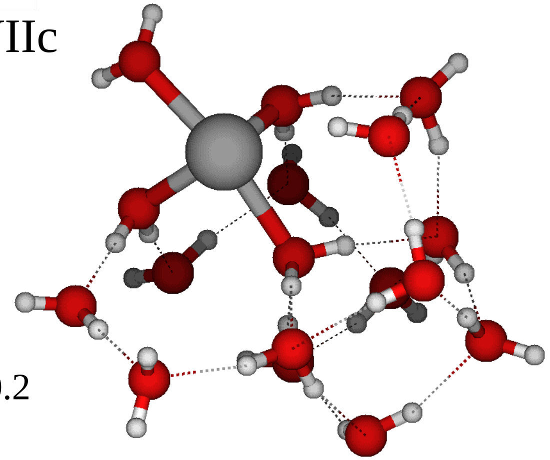


+49.8

XVIId



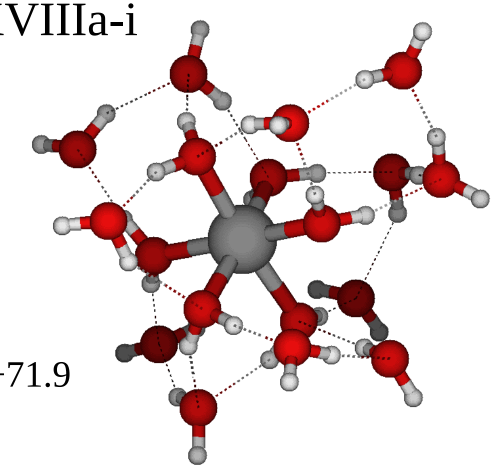
XVIIc



+30.2

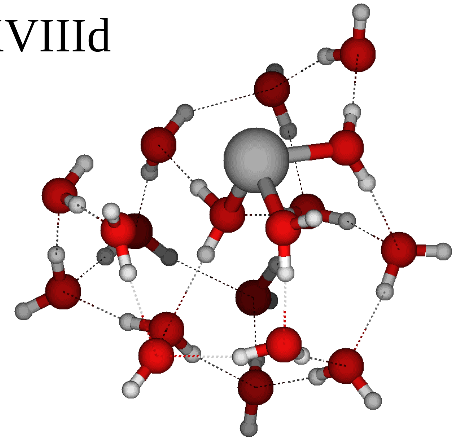
n=18

XVIIIa-i



+71.9

XVIIId

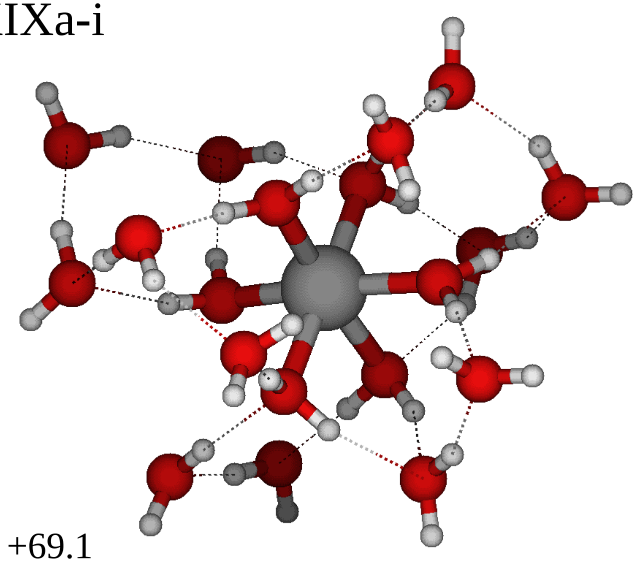


$[Zn(H_2O)_n]^+$ // B3LYP/aug-cc-pVDZ // Energies in kJ/mol

Geometries of larger Clusters (*n*=7-20)

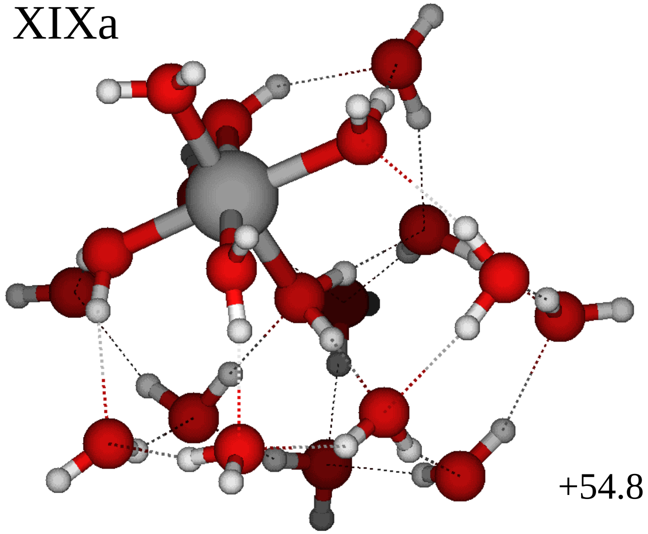
n=19

XIXa-i



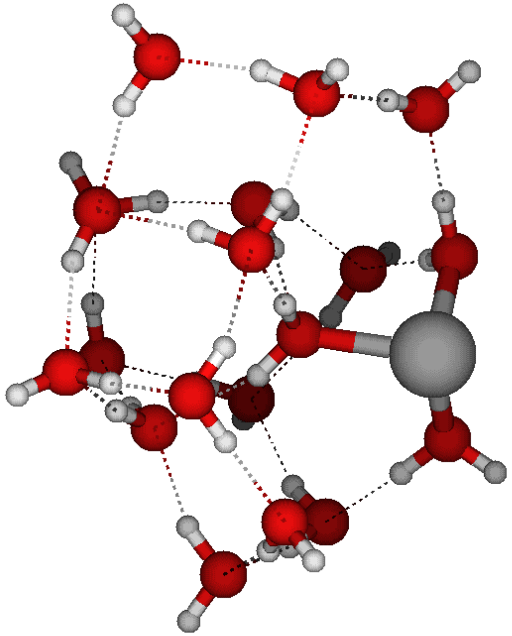
+69.1

XIXa



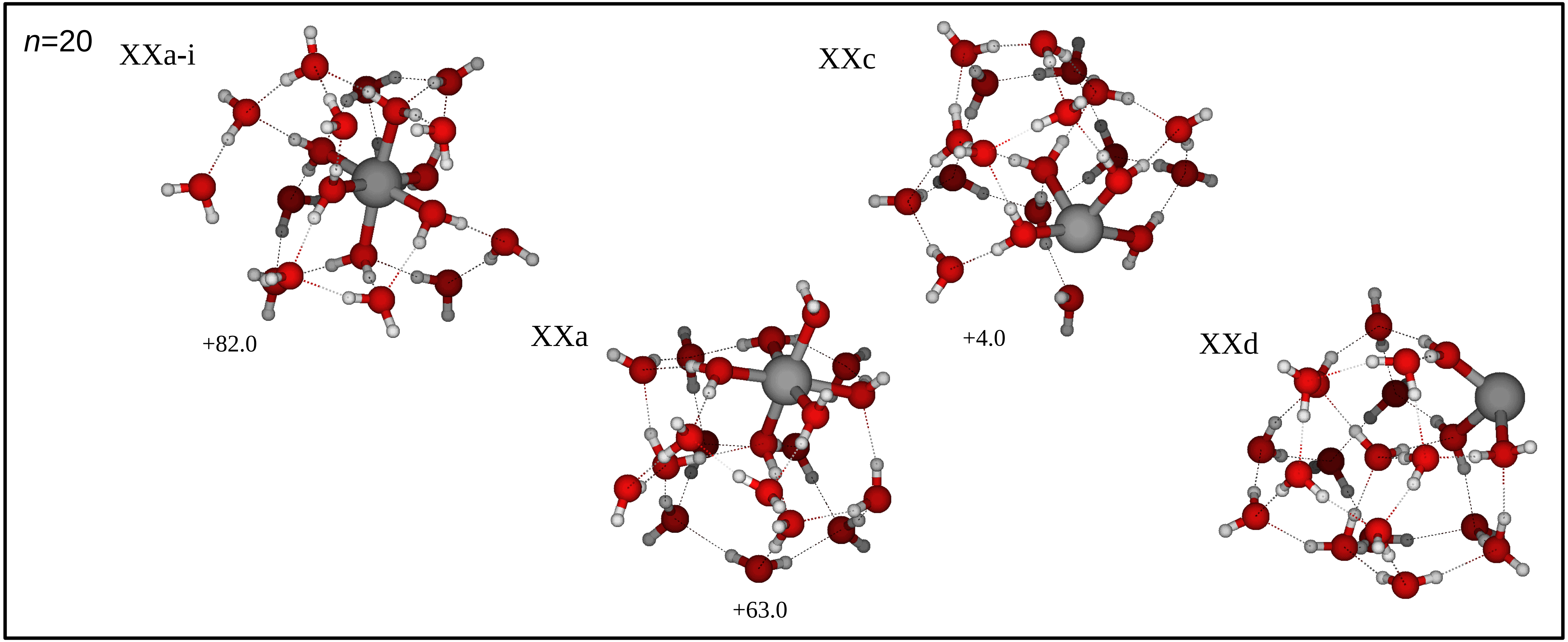
+54.8

XIXd



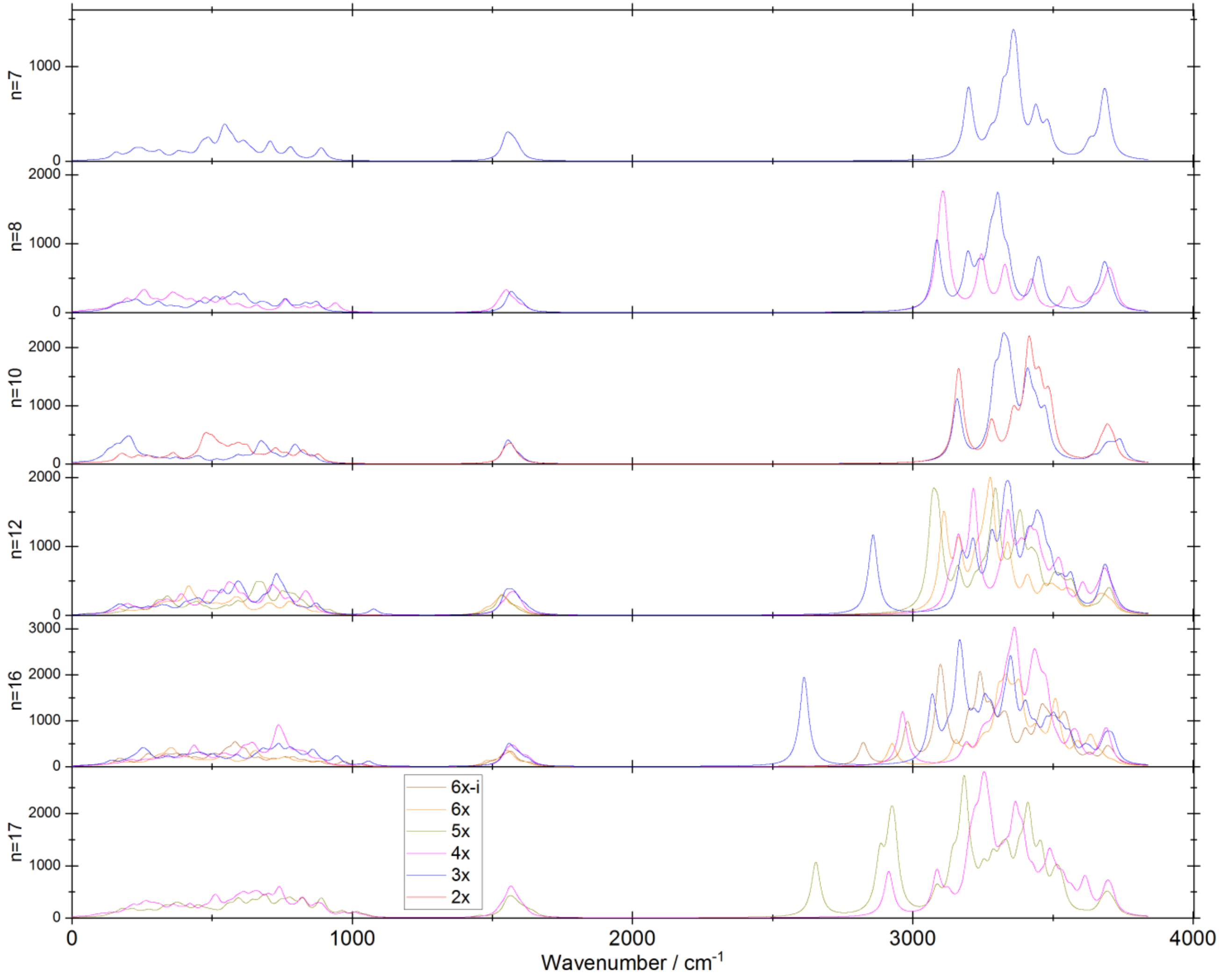
$[Zn(H_2O)_n]^+$ // B3LYP/aug-cc-pVDZ // Energies in kJ/mol

Geometries of larger Clusters (*n*=7-20)



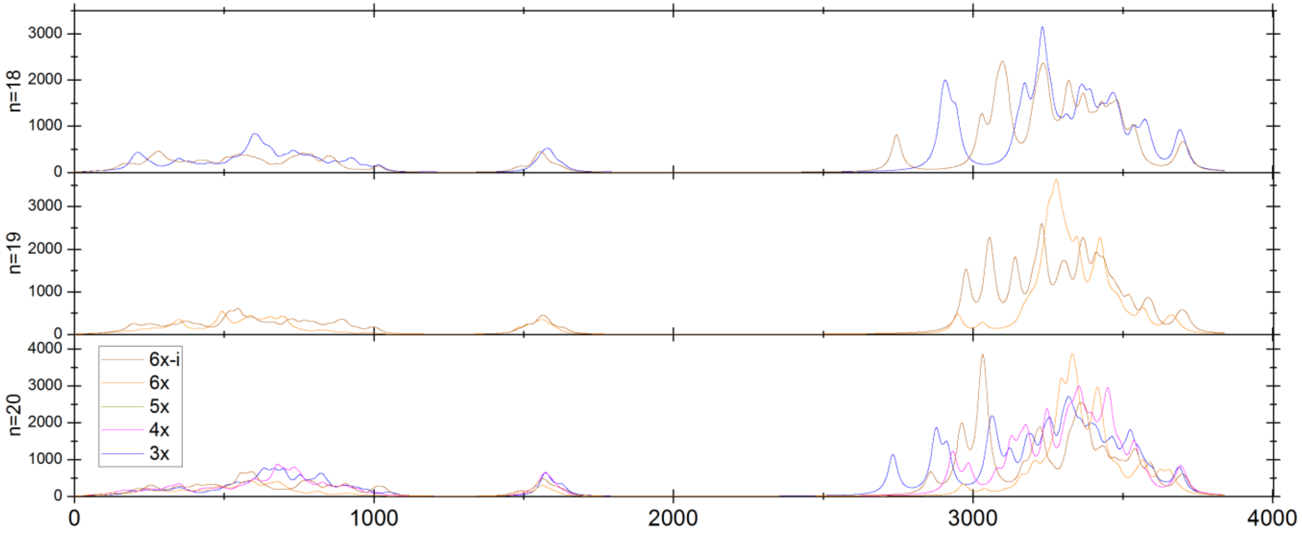
$[Zn(H_2O)_n]^+$ // B3LYP/aug-cc-pVDZ // Energies in kJ/mol

IR Spectra



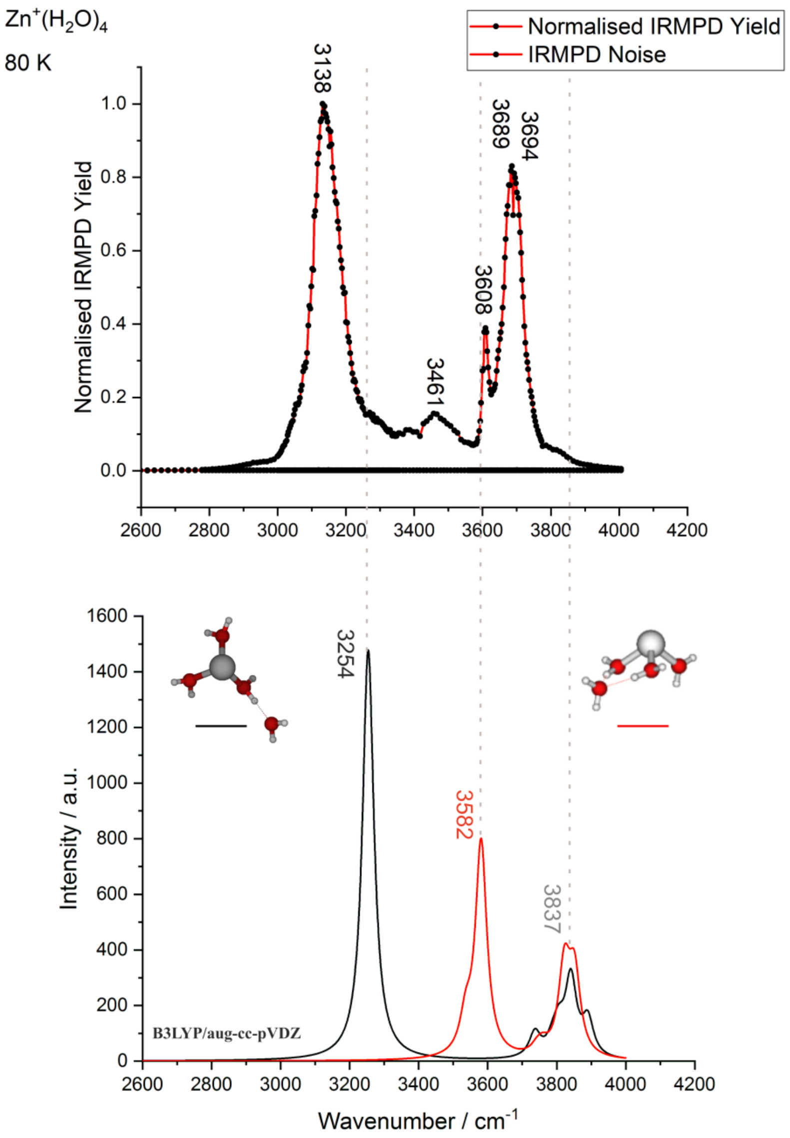
$[Zn(H_2O)_n]^+$ // B3LYP/aug-cc-pVDZ // Energies in kJ/mol

IR Spectra



$[Zn(H_2O)_n]^+$ // B3LYP/aug-cc-pVDZ // Energies in kJ/mol

First Experimental Results



$[Zn(H_2O)_n]^+$ // B3LYP/aug-cc-pVDZ // Energies in kJ/mol

Conclusion

Photodissociation Spectra of $Mg^+(H_2O)_n$ for (n = 1-5, 20, 30, 40, 50, 60, 70)

- two channels: $Mg^+(H_2O)_{m<n}$ - dominant for large clusters
  $MgOH^+(H_2O)_{m<n}$ - dominant for small to medium size clusters (exclusive product in the 5 < n < 15 range)

  water evaporation for small clusters: in higher lying excited states (2 photons)
  in the ground state after fluorescence

  hydrogen diss. for small clusters: in the excited state

  water evaporation for large clusters: in the ground state after fast IC

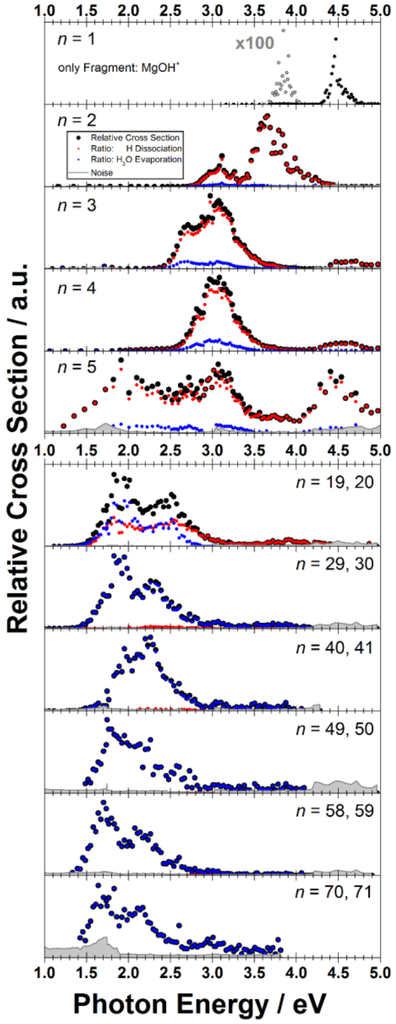
  hydrogen diss. for large clusters: in the ground state

- energy needed for water evaporation for larger clusters:

  0.468(19) eV per H_2O / Literature: 0.447(4) eV (bulk)

- shape of the spectra for larger clusters resembels that of the hydrated electron
  (but probably consists of two different isomers, 5- and 6 times coordinated Mg)

Photodissociation Spectra $Mg^+(H_2O)_n$



Outlook

- Additional calculations on the photochemistry of $[Zn(H_2O)_n]^+$
- Calculations for $[Mg_2(H_2O)_n]^+$

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