Studies on Solvation Structure and Intracluster Reaction of Aqueous Metal Ions by IR Photodissociation Spectroscopy

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Aqueous Metal Ions

- Microscopic model of aqua complexes

- A number of researches have been done for metal cluster ions.
  - Mass spectrometry, collision-induced dissociation, electronic spectra, MO calculations

  (for investigating binding energy, magic number, solvation structure, intracluster reaction)

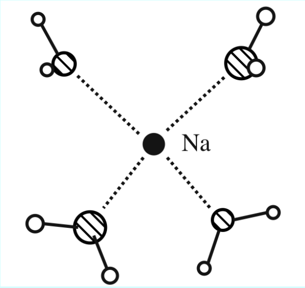
- Relationship between the electronic structure and solvation features

Na^+	Ne $(3s)^0$
Mg^+	Ne $(3s)^1$
Al^+	Ne $(3s)^2$

- Na^+ ion
  - forms the first solvation shell with four water molecules; the cluster has an isotropic tetrahedral structure.

  → This structure is ascribed to the closed-shell electronic structure of Na^+

  Patwari and Lisy, J. Chem. Phys. **118**, 8555 (2003).



$[Mg•(H_2O)_n]^+$ Ions: Previous Study

◆ Electronic spectra

- No band shift for $n > 3$

→ Three water molecules form the first solvation shell.

Misaizu, Sanekata, Fuke, J. Chem. Phys. **100**, 1161 (1994).

◆ MO calculations

- three water molecules form very stable solvation shell.

Watanabe, Iwata, Hashimoto, Misaizu, Fuke, J. Am. Chem. Soc. **117**, 755 (1995).

$[Mg•(H_2O)_n]^+$

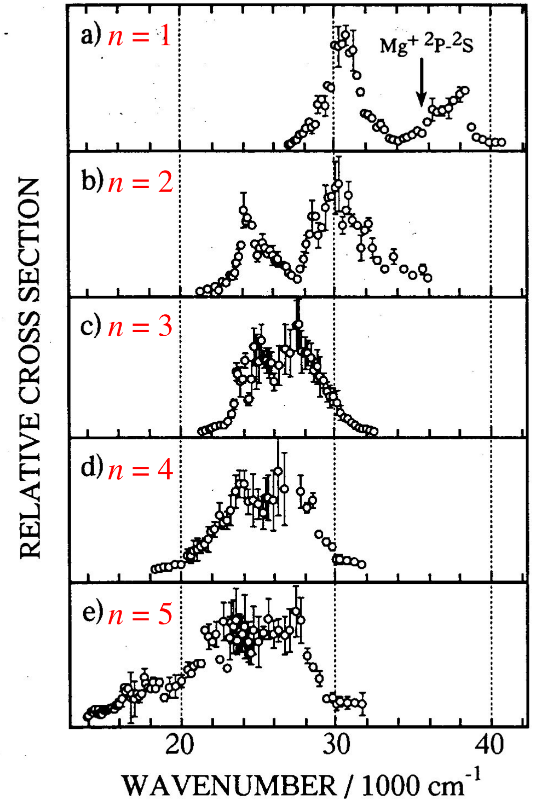


FIG. 10. Photodissociation spectra of $Mg^+(H_2O)_n$ with $n=1$ (a) to 5 (e). These are obtained by taking into account the total yield of the fragment ions. The intensities of the spectra are normalized at their peak positions.

Misaizu, Sanekata, Fuke, J. Chem. Phys. **100**, 1161 (1994).

$[Al\cdot(H_2O)_n]^+$ Ions: Previous Study

- Photodissociation experiments
  - $[Al\cdot(H_2O)_{n \geq 4}]^+ + h\nu$ (248 nm) → $[Al\cdot(H_2O)_3]^+$
  - Is $[Al\cdot(H_2O)_3]^+$ quite stable? Do three water molecules form the first solvation shell?

    Misaizu, Tsukamoto, Sanekata, Fuke, Z. Phys. D **26**, S177 (1993).
- MO calculations
  - Insertion of Al^+ to OH group and formation of $[H–Al–OH]^+$ ion for $n \geq 2$.

    Watanabe and Iwata, J. Phys. Chem. **100**, 3377 (1996).

There are no reports on the detail of the hydration structure of Mg and Al ions.

In This Study,

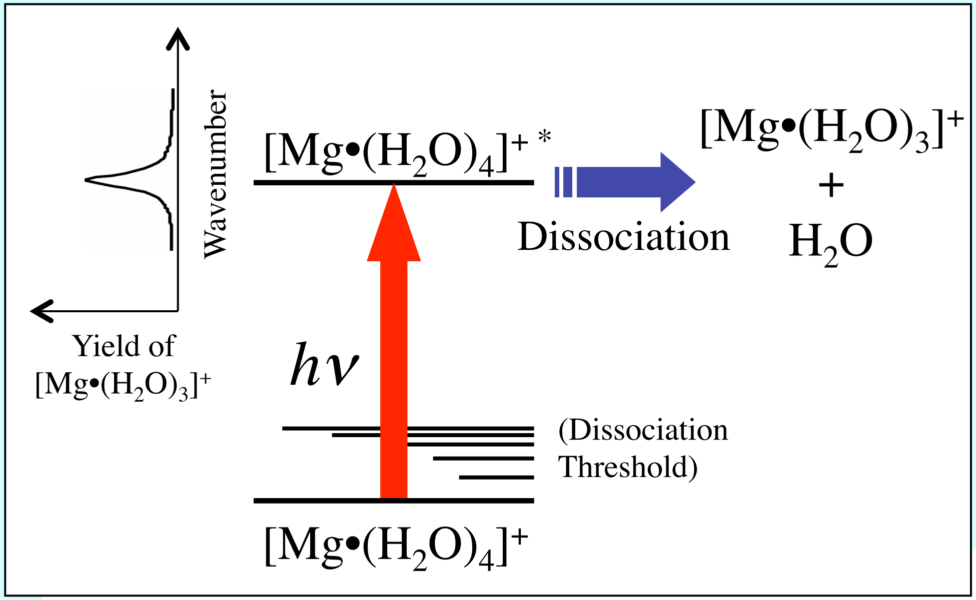
- Aqueous clusters of Mg^+ and Al^+
  - $[Mg\cdot(H_2O)_n]^+$、$[Al\cdot(H_2O)_n]^+$
  - $[Mg\cdot(H_2O)_n\cdot Ar]^+$、$[Al\cdot(H_2O)_n\cdot Ar]^+$

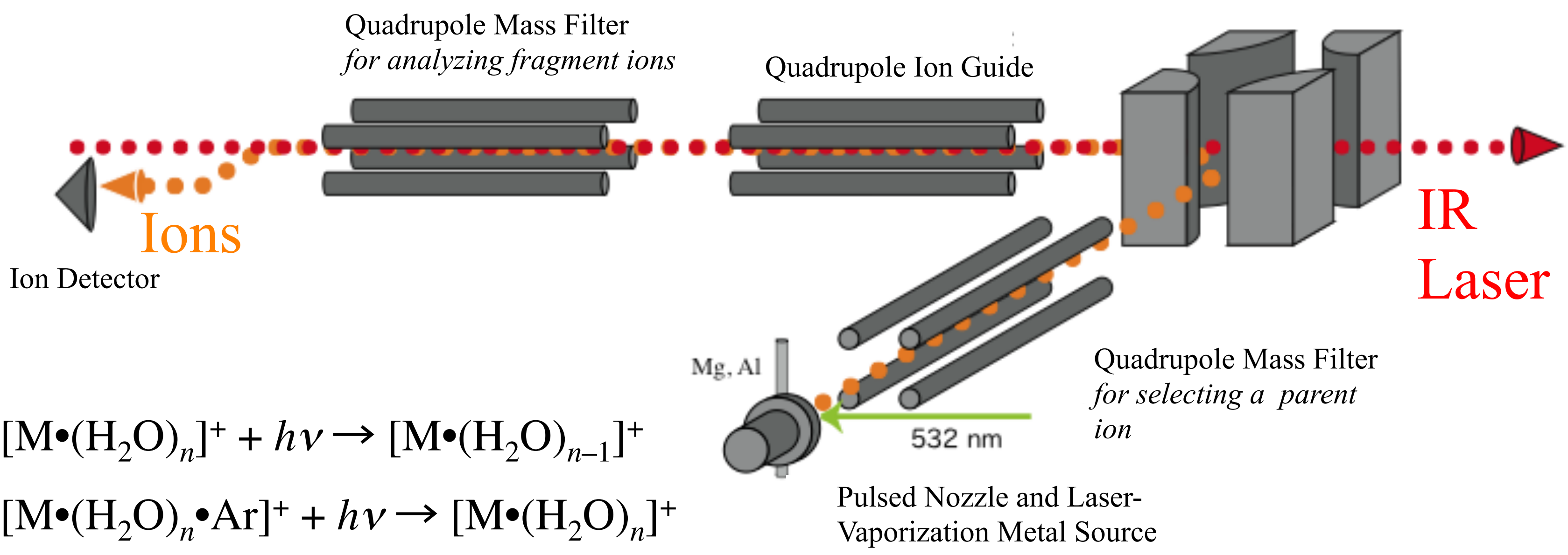
- IR photodissociation spectroscopy
  - OH stretching region

    → quite sensitive to the cluster structure

- DFT calculations
  - GAUSSIAN 98, B3LYP/6-31+G*
  - Geometry optimization
  - vibrational analysis. Comparison with the observed spectra will provide probable isomer forms.

IR Photodissociation Spectroscopy

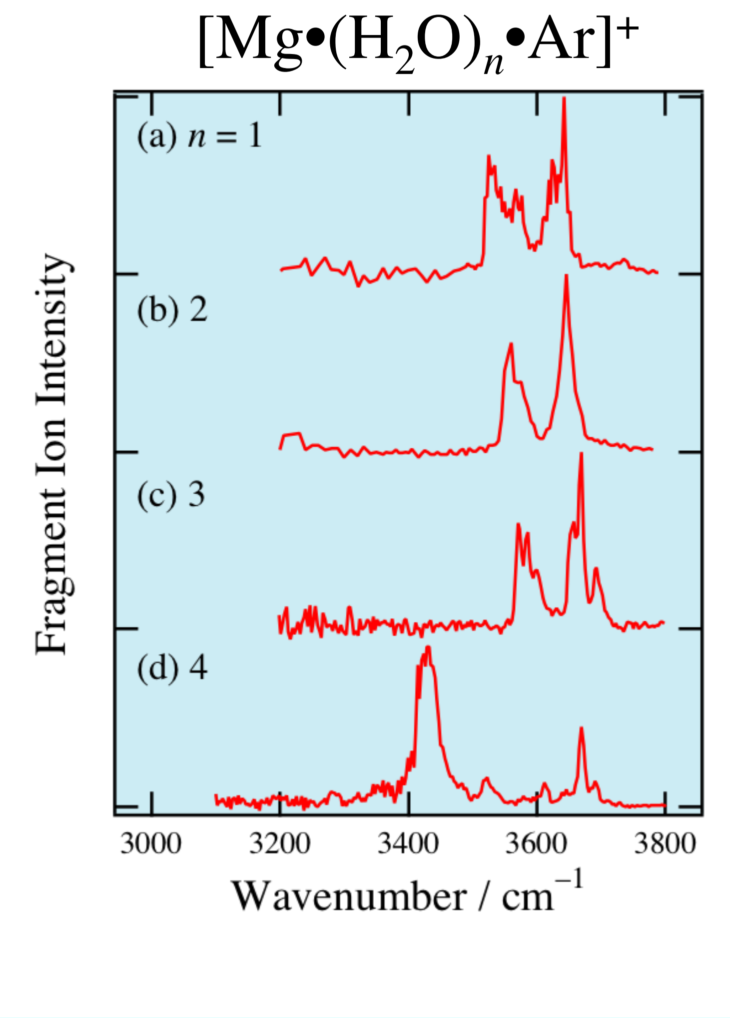




$$[M•(H_2O)_n]^+ + h\nu \rightarrow [M•(H_2O)_{n-1}]^+$$

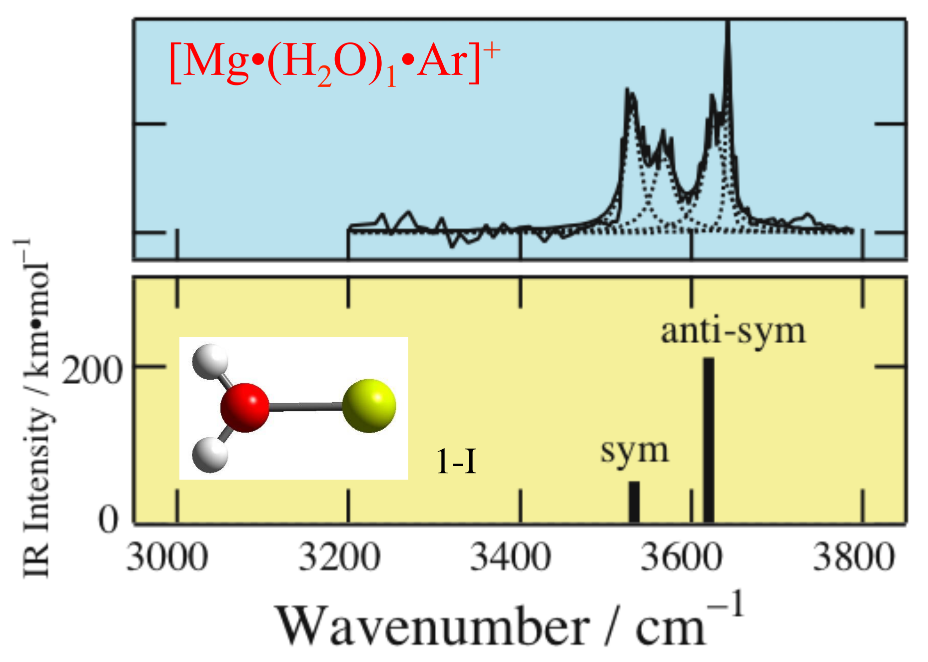
$$[M•(H_2O)_n•Ar]^+ + h\nu \rightarrow [M•(H_2O)_n]^+$$

IR spectra of $[Mg{\cdot}(H_2O)_{1\text{-}4}{\cdot}Ar]^+$



- Two bands are observed in the region $> 3500\ cm^{-1}$ for $n = 1\text{–}3$.
- The $n = 4$ ion has a strong band in the region $< 3500\ cm^{-1}$.

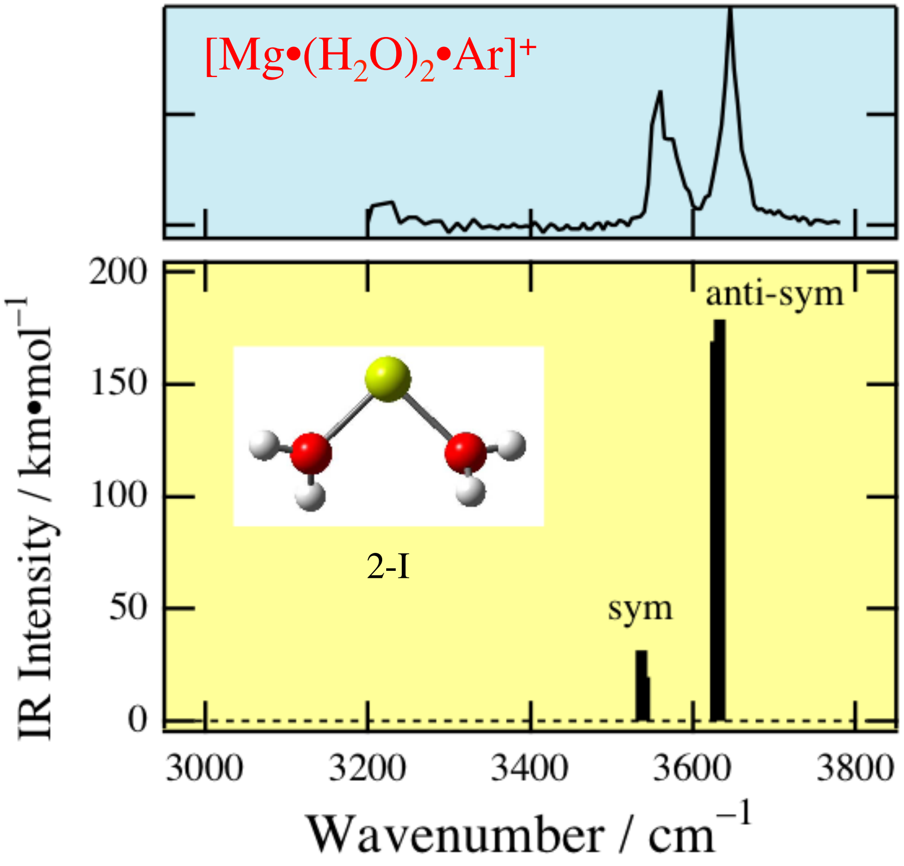
$[Mg{\cdot}(H_2O)_1]^+$



◆ Two bands are observed.

- The observed spectrum can be reproduced by the spectrum calculated for Isomer 1-I.
- $Mg^+{\bullet\bullet\bullet}OH_2$ bonding is formed in Isomer 1-I.

$[Mg{\cdot}(H_2O)_2]^+$



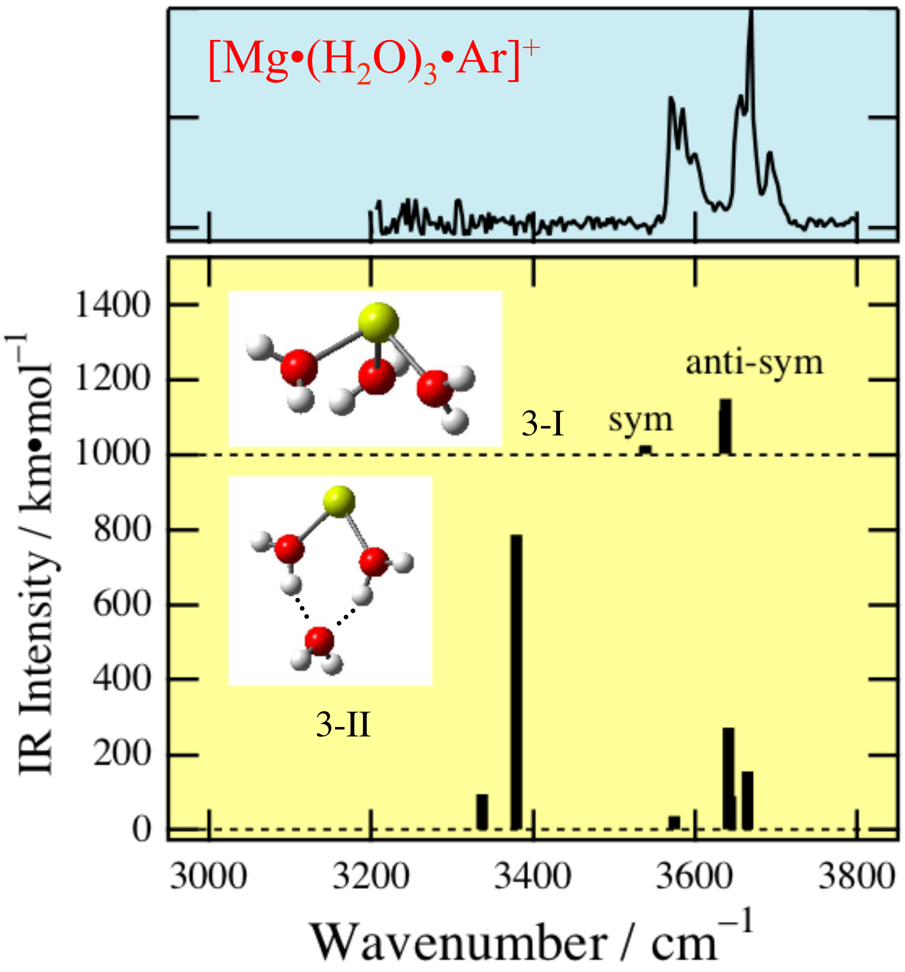
- ◆ Two bands are observed in the region above 3500 cm^{-1}.
- ◆ No band in the region below 3500 cm^{-1}.
  - No hydrogen bond between H_2O–H_2O
  - Isomer 2-I explains the observed spectrum.
  - Two $Mg^+{\bullet\bullet\bullet}OH_2$ bonds
- ◆ Water molecules avoid the $(3s)^1$ electron of Mg^+ and are solvated on one side of Mg^+.

$[Mg{\bullet}(H_2O)_2]^+$

SOMO contour map

Daigoku and Hashimoto, J. Chem. Phys. **121**, 3569 (2004).

$[Mg\cdot(H_2O)_3]^+$



- ◆ No band in the region below 3500 cm^{-1}
  - No hydrogen bond
  - The spectrum of Isomer 3-I well reproduces the observed spectrum.
- ◆ Three water molecules are bonded on one side of Mg^+, and the $(3s)^1$ electron are located on the other side.

$[Mg\cdot(H_2O)_4]^+$

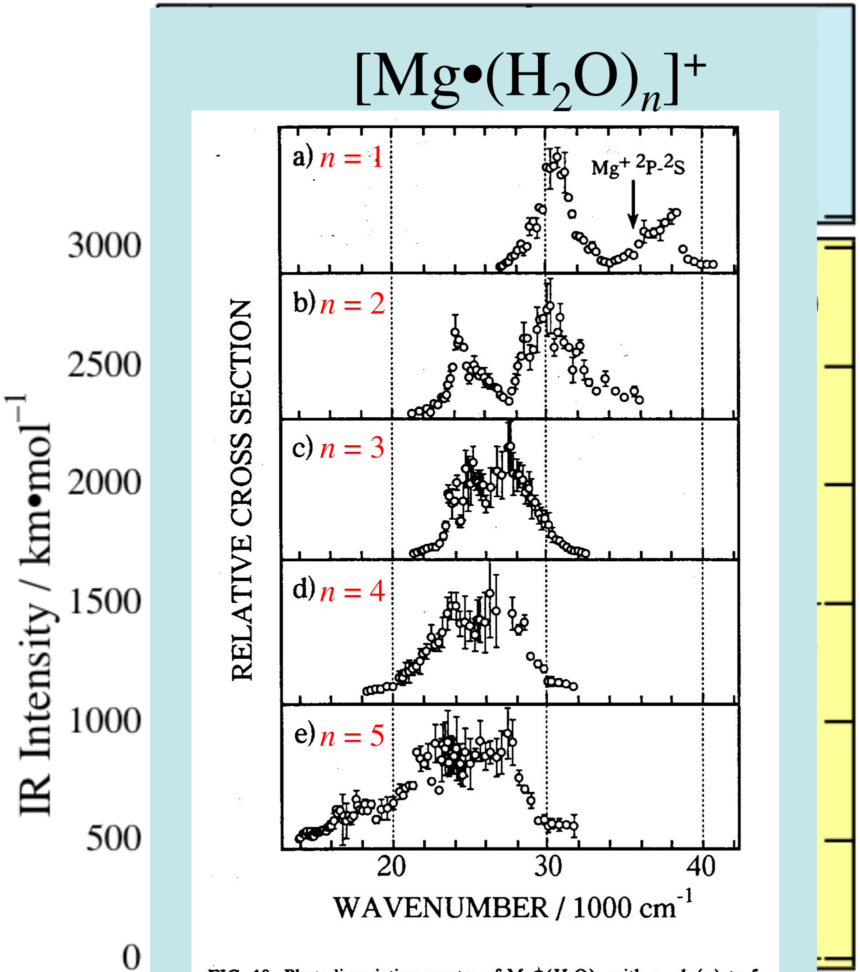
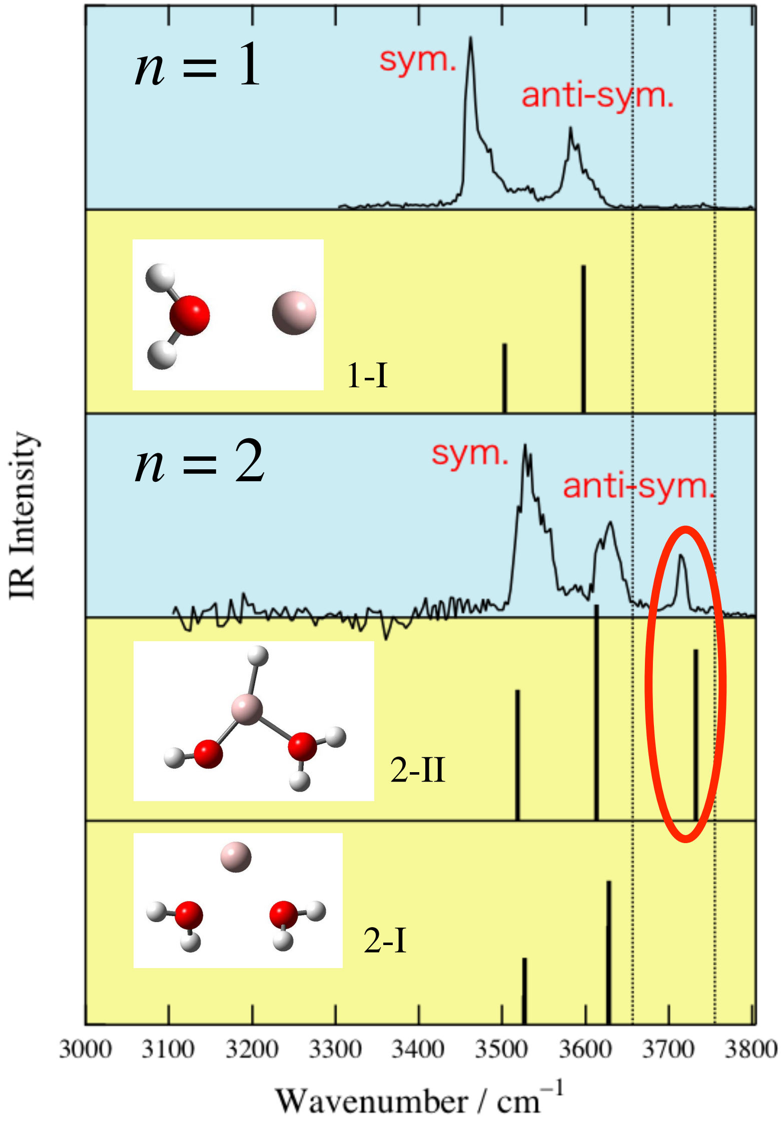


FIG. 10. Photodissociation spectra of $Mg^+(H_2O)_n$ with $n=1$ (a) to 5 (e). These are obtained by taking into account the total yield of the fragment ions. The intensities of the spectra are normalized at their peak positions.

Misaizu, Sanekata, Fuke, J. Chem. Phys. **100**, 1161 (1994).

- A strong band below 3500 cm^{-1}
  - Hydrogen-bonded OH
  - formation of H_2O–H_2O hydrogen bond
- The spectrum observed is reproduced by the spectrum calculated for Isomer 4-I.
  - Three water molecules form the first solvation shell.
  - Cyclic structure with Mg^+ and three H_2O molecules

IR Spectrum of $[Al\cdot(H_2O)_{1,2}\cdot Ar]^+$



◆ Two bands are observed for *n* = 1

- $Al^+\cdots OH_2$ bonding

◆ An additional band is observed around 3700 cm^{-1} for *n* = 2.

- This band is reproduced by Isomer 2-II

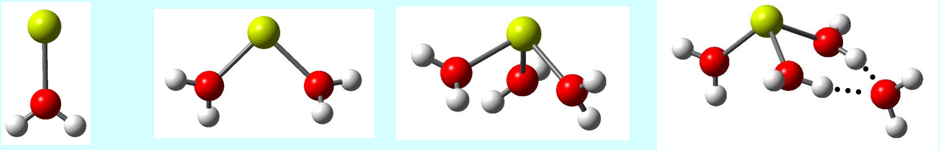
◆ Insertion of Al^+ into the OH bond occurs, and the $[H–Al–OH]^+$ ion core is produced for *n* = 2.

Electronic Structure and Intracluster Reaction

◆Mg^+ ($3s^1$)

- sp hybridization occurs; water molecules are bonded to Mg^+ with avoiding the $(3s)^1$ distribution
- In larger clusters the hydrogen elimination reaction occurs, forming $[MgOH]^+$ ion.

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



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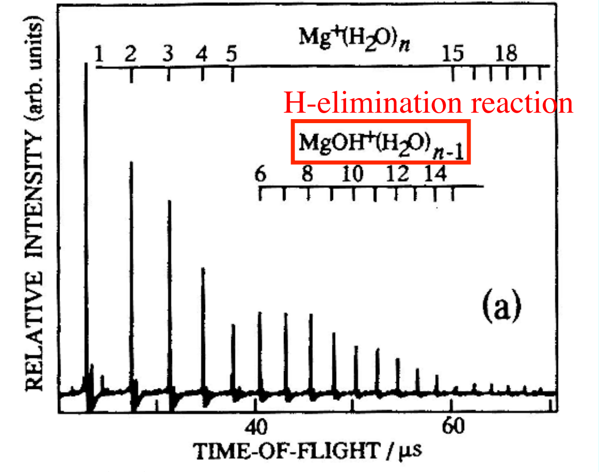
Mass spectrum of Mg^+–H_2O system



H-elimination reaction

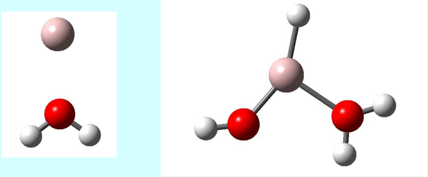
Misaizu, Sanekata, Fuke, J. Chem. Phys. **100**, 1161 (1994).

◆Al^+ ($3s^2$)

- $(3s)^2$ electronic structure is not suitable for the sp hybridization *.
- Al^+ cannot take two 3s electrons, and the insertion reaction occurs.

$$[Al\bullet(H_2O)_n]^+ \rightarrow [H–Al–OH\bullet(H_2O)_{n-1}]^+$$

- Additional water molecules are bound to the $[H–Al–OH]^+$ ion core.



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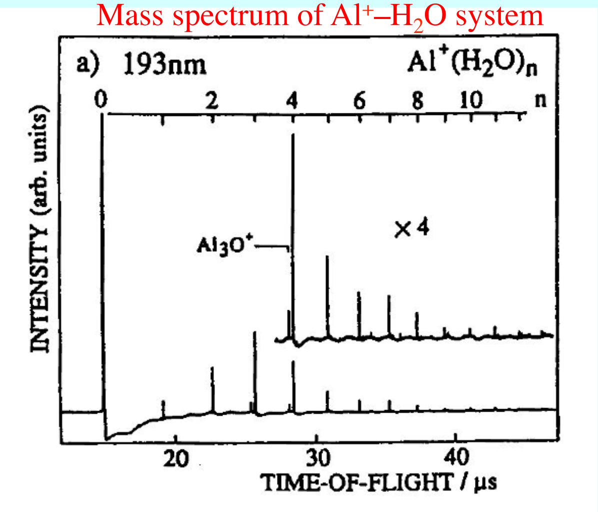
* $E(3p^1) – E(3s^1) = 4.64$ eV for Mg^+

$E(3s^1 3p^1) – E(3s^2) = 7.42$ eV for Al^+

Mass spectrum of Al^+–H_2O system



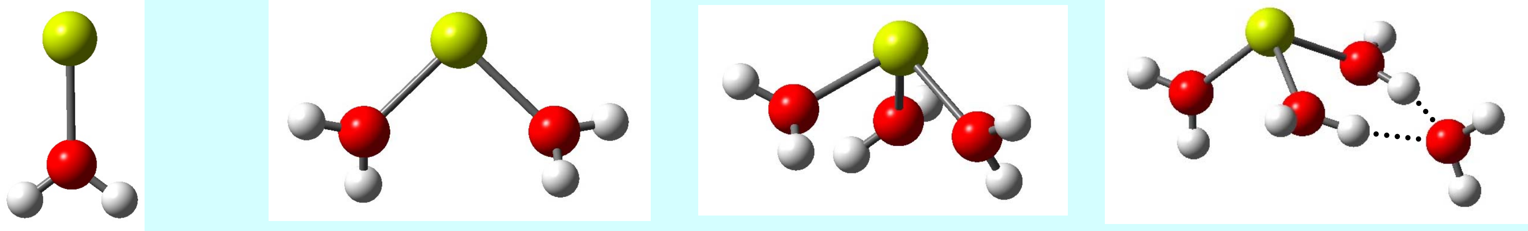
Misaizu, Tsukamoto, Sanekata, Fuke, Z. Phys. D, **26**, s177 (1993).

Conclusion (2)

◆ $[\mathrm{Mg}\bullet(\mathrm{H_2O})_n]^+$

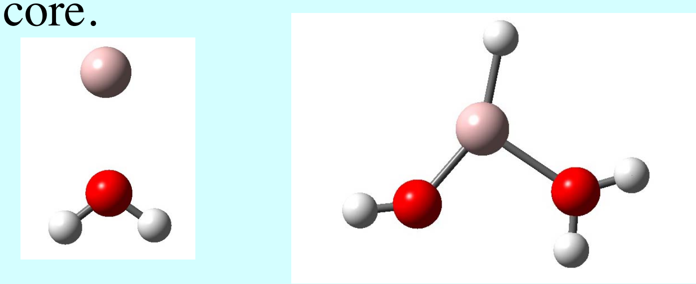
Three water molecules form the first solvation shell.

The fourth molecule is bound to the shell and forms a ring structure.



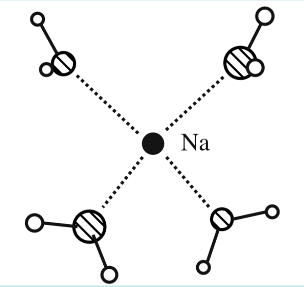
◆ $[\mathrm{Al}\bullet(\mathrm{H_2O})_n]^+$

Solvation of two water molecules induces the insertion reaction, forming $[\mathrm{H{-}Al{-}OH}]^+$ ion core.



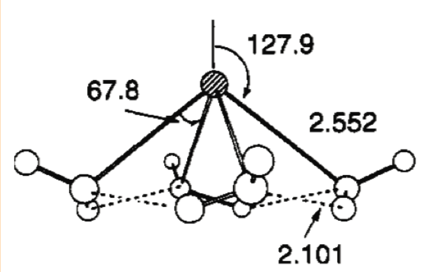
◆ Cluster structure and intracluster reaction are highly dependent on the electronic structure of metal ions.

Relationship between the Charge and Structure



Na$^+$ (3s^0)

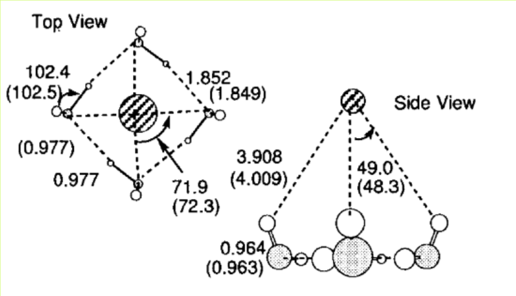
Isotropic Solvation



Hashimoto and Morokuma, J. Am. Chem. Soc. **116**, 11436 (1994).

Na (3s^1)

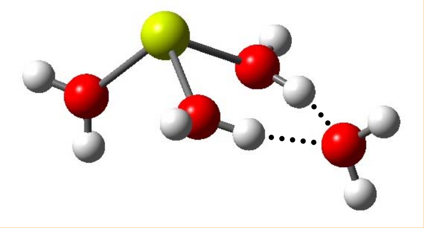
sp hybridization induces biased hydration



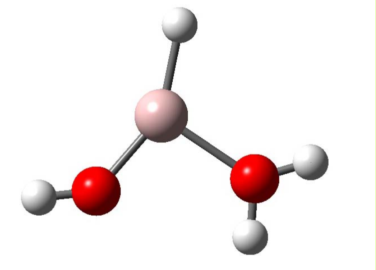
Hashimoto et al., J. Phys. Chem. A **104**, 3299 (2000).

Na$^-$ (3s^2)

No reaction → Na$^-$•••H electrostatic interaction prevents reaction?



Mg$^+$ (3s^1)



Al$^+$ (3s^2)

Reaction occurs.

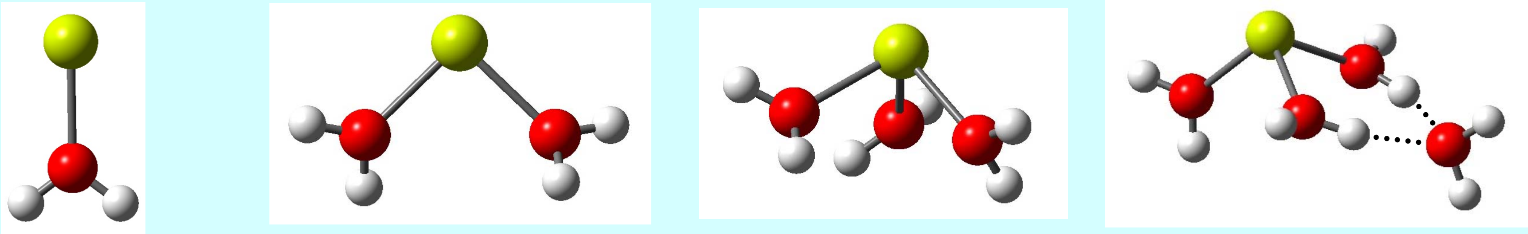
Both of the electronic structure and the charge control the cluster structure

Conclusion (2)

- $[\mathrm{Mg{\bullet}(H_2O)}_n]^+$

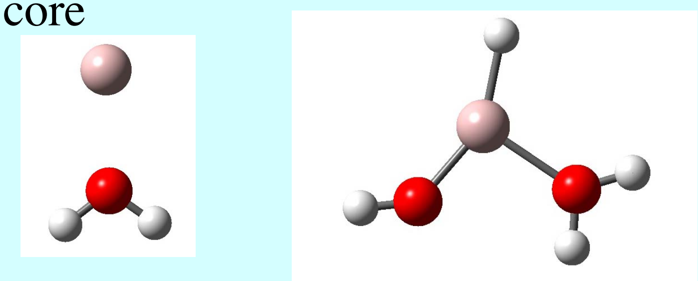
  Three water molecules form the first solvation shell.

  The fourth molecule is bound to the shell and forms a ring structure.



- $[\mathrm{Al{\bullet}(H_2O)}_n]^+$

  Solvation of two water molecules induces the insertion reaction, forming $[\mathrm{H{-}Al{-}OH}]^+$ ion core



- Cluster structure and intracluster reaction are highly dependent on the electronic structure and the charge of metal ions.