ICTP-IAEA Workshop – Trieste, September 12-16

Capture and Concentration of Radiocesium Highly Dispersed in the Environment: A Proposal

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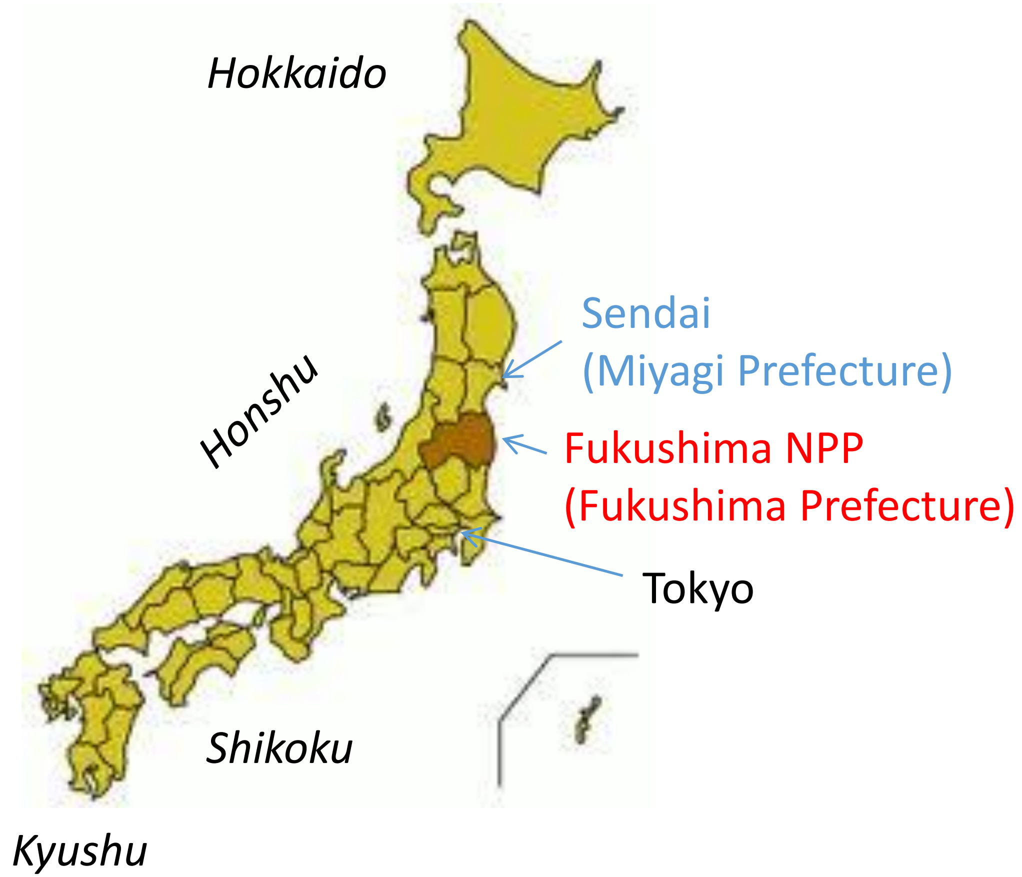
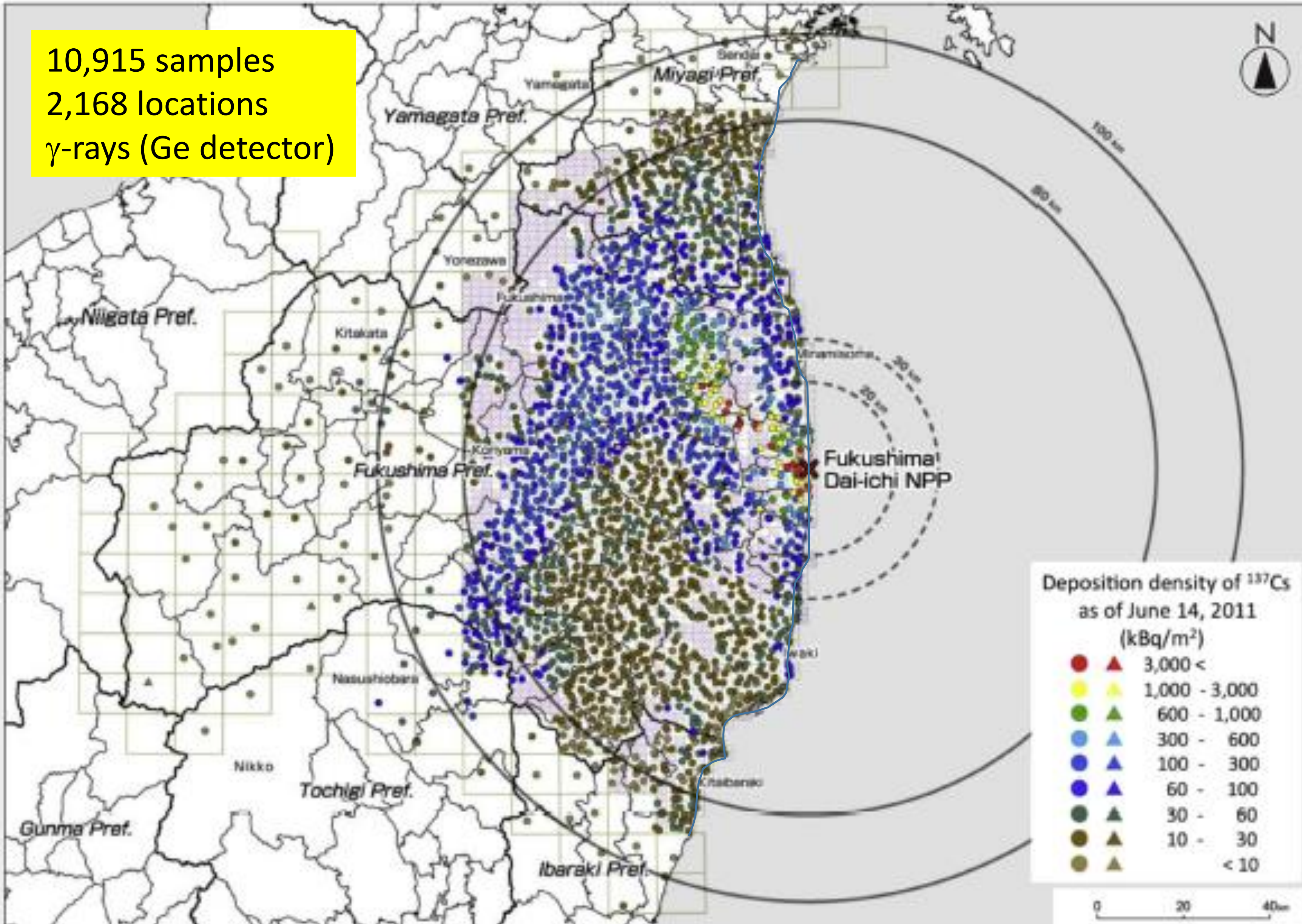
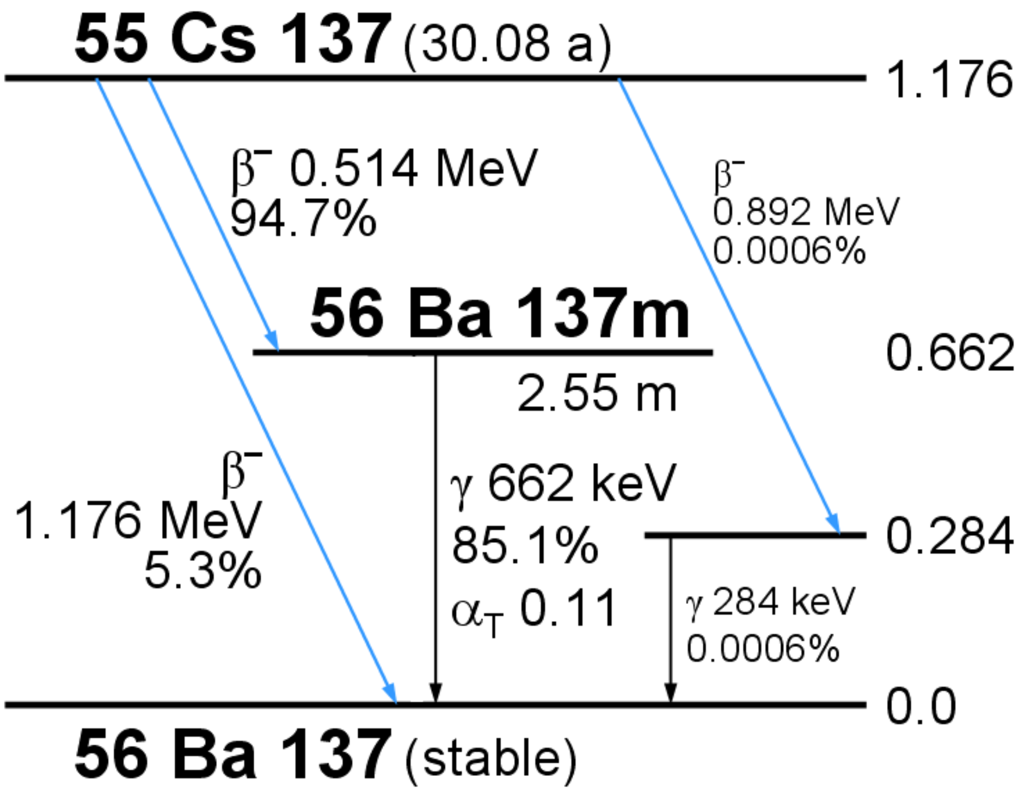
OUTLINE:
Environmental contamination from the Fukushima Accident
Proposed soil decontamination process
Macrocycles for the complexation of Cesium
Structural and computational studies


Hokkaido
Honshu
Sendai
(Miyagi Prefecture)
Fukushima NPP
(Fukushima Prefecture)
Tokyo
Shikoku
Kyushu

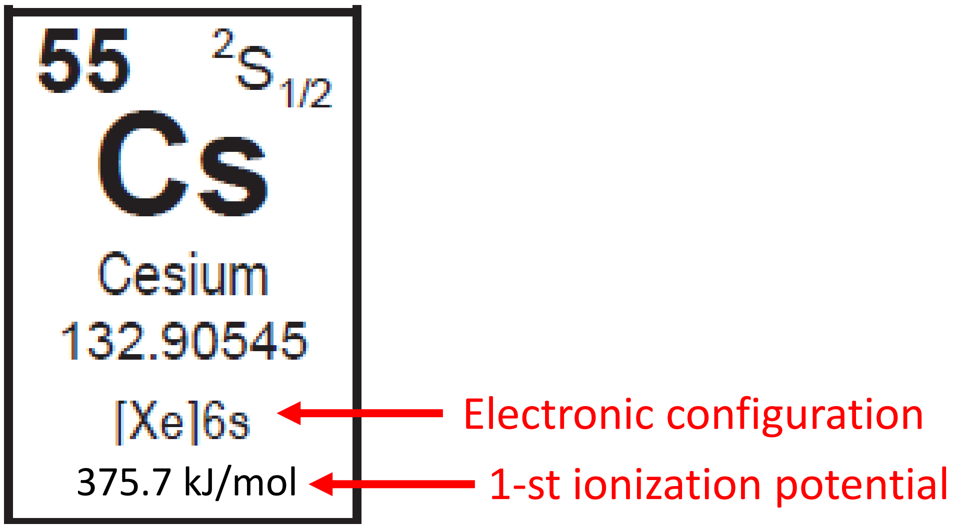


Saito *et al.*, *J. Env. Radioact.* 139 (2015) 308-319

Cs-137 Decay Processes



(Source: Nucleonica.Net)

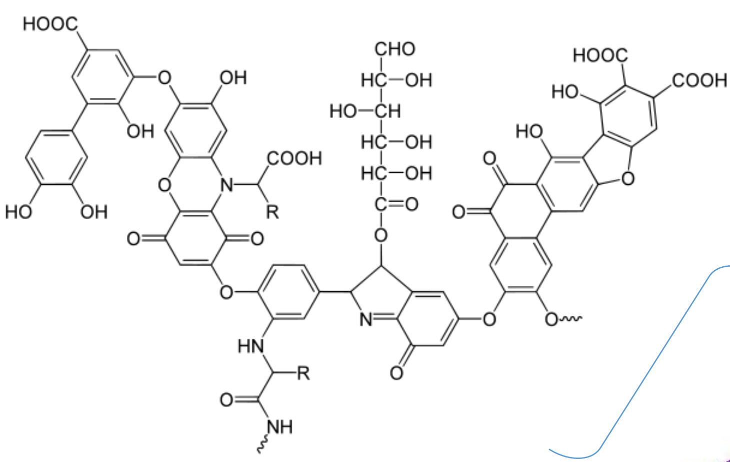


Cs-137 as Cs^+ ion in the environment

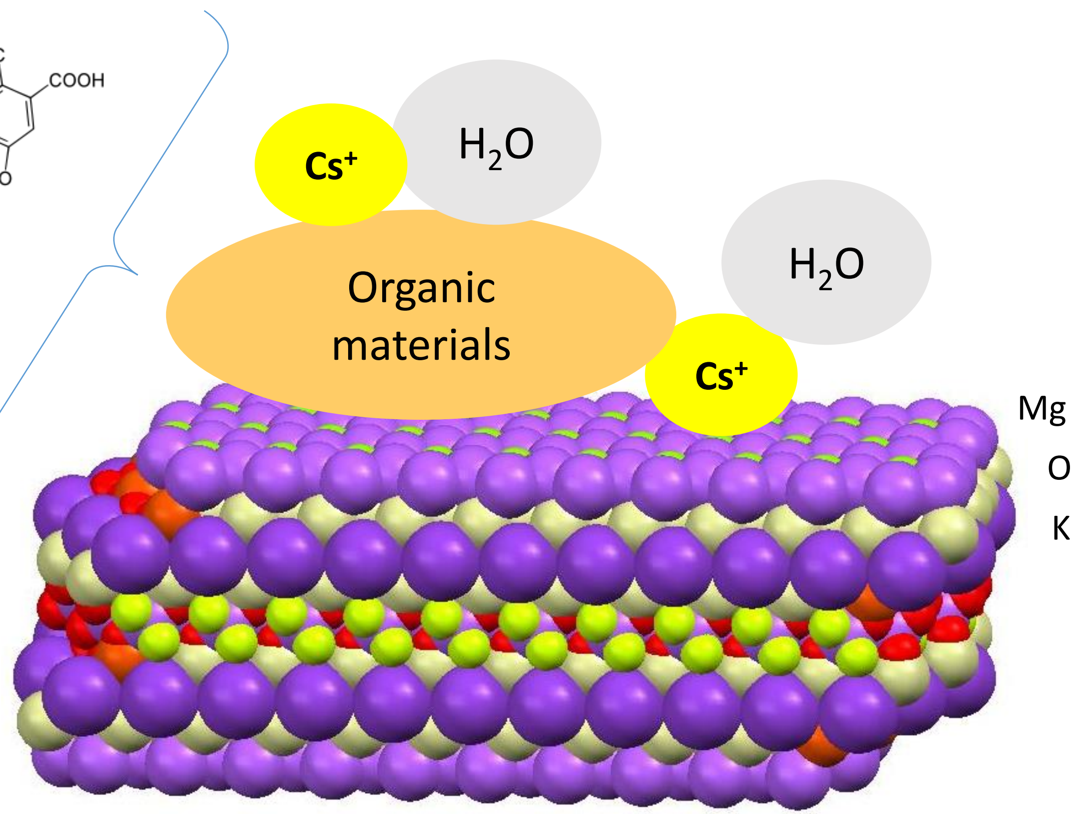
Soil Contamination – Microscopic View

☞ Strong adhesion to clay minerals >> top 5 cm of soil

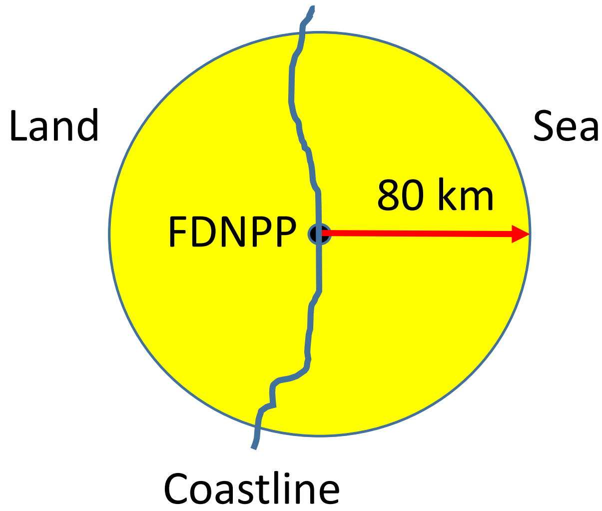
Ref.: Fujii et al., *Soil Sci. & Plant Nutr.* (2014)



Humic acid



Volume of ^{137}Cs-contaminated Soil



$$(½)S = (½)\pi R^2 = 10^4 \text{ km}^2$$

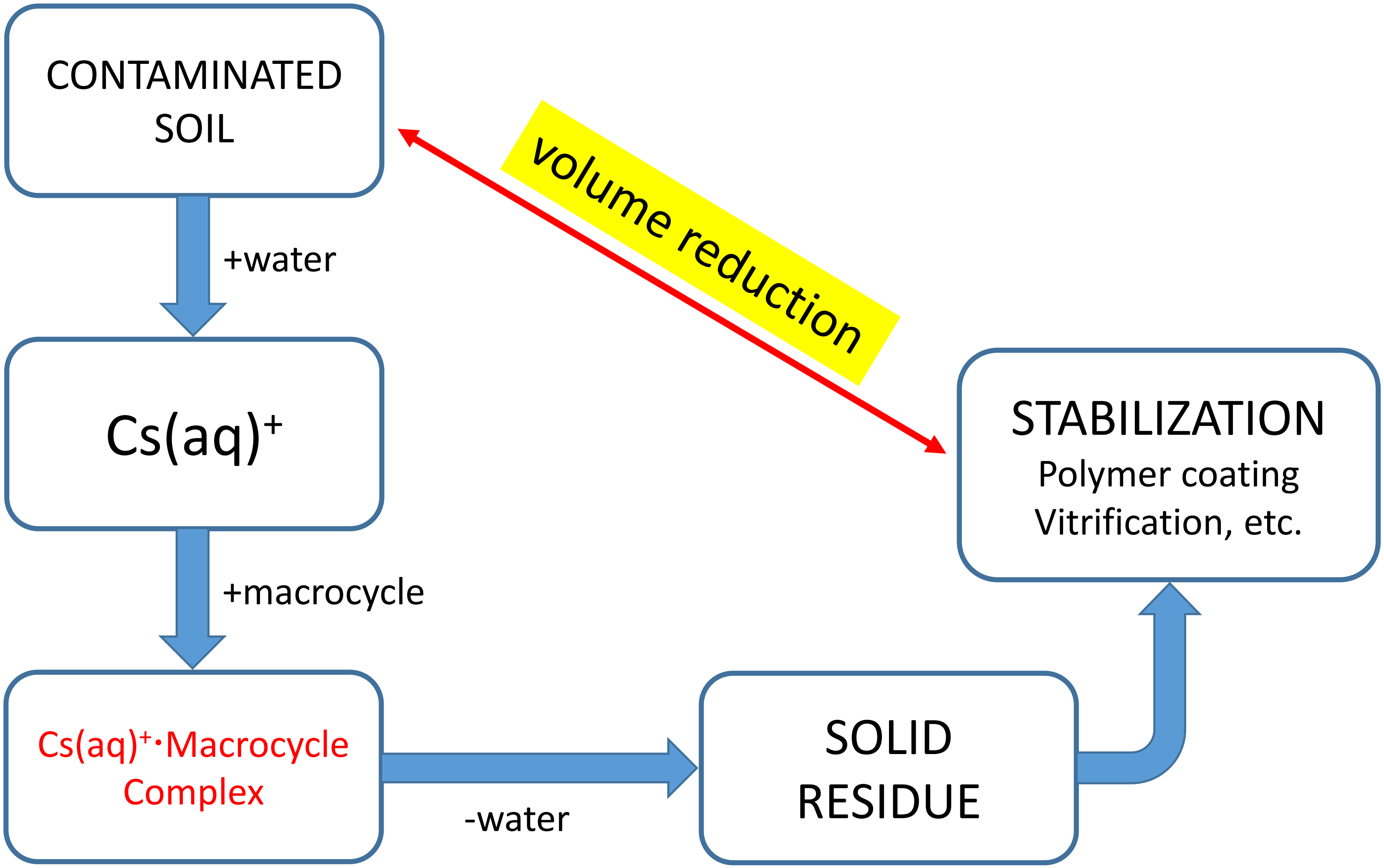
(Fukushima Pref.: 13,782 sq.km)
(Japan: 377,972 sq.km)

Volume of contaminated soil:

$$V = 10^4 \times 10^3 \text{ m}^2 \times 5 \times 10^{-2} \text{ m} = 5 \times 10^5 \text{ m}^3 \cong 10^6 \text{ m}^3$$

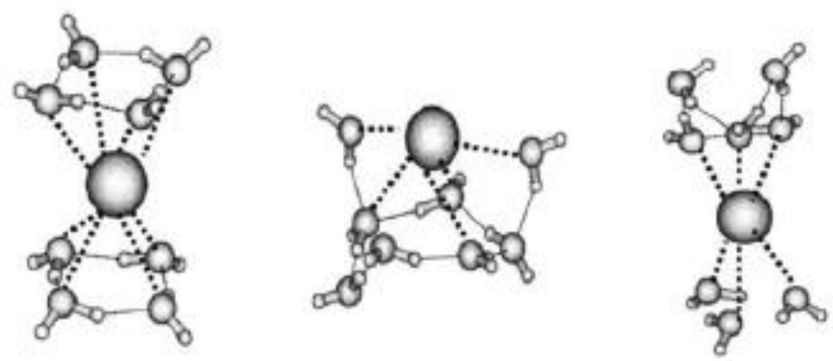
Official estimate: $28 \times 10^6 \text{ m}^3$

Soil Decontamination Process



Cs^+ Hydration

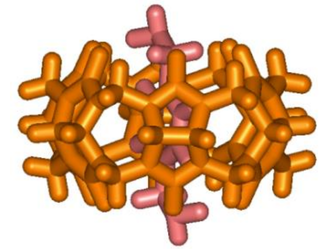
- Mähler & Persson, *Inorg. Chem.* 51 (2012) 425-438
- Large-angle X-ray Scattering (LAXS)
- Double Difference Infrared Spectroscopy (DDIR)
- Cs^+ is unable to form well-defined hydrated structures in the solid-state (no crystal structures available)
- Cs^+ (& K^+, Rb^+) is a structure breaker for bulk water
- Ionic radii: ~1.73 Å for 8-coordinate geometry: $Cs^+(H_2O)_8$
- Cs–O = 3.07 Å
- Ali *et al.*, *JCP* 2007:



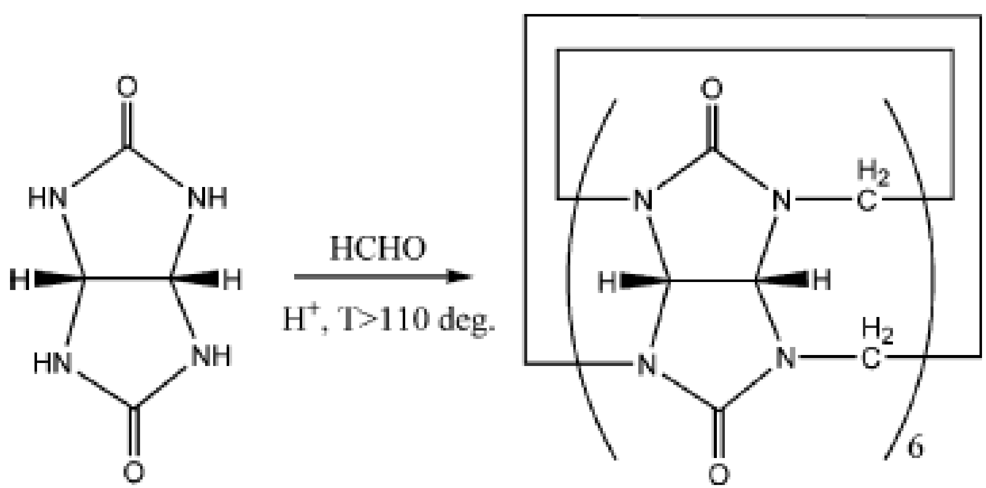
Macrocycle: Essential Requirements

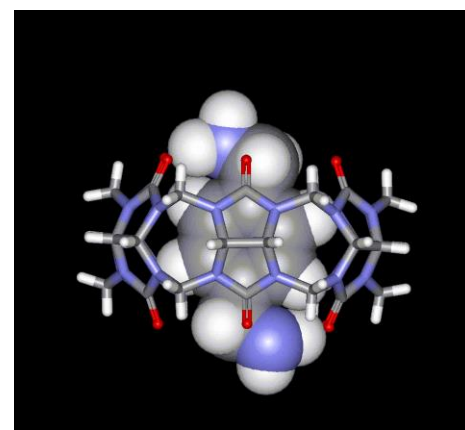
- Cs^+ ion can be coordinated
- Chemical stability (oxidation, H^+)
- Photochemical stability (UV-vis.)
- Easy to synthesize (fewer steps)
- Economical

Cucurbit[n]uril



- Behrend’s polymer (1905)
- Mock (1981): crystal structure of CB[6]
- *Cucurbituril*, a pumpkin-shaped macrocyle
- Supramolecular chemistry (Kim, Day, Isaacs, Tao)

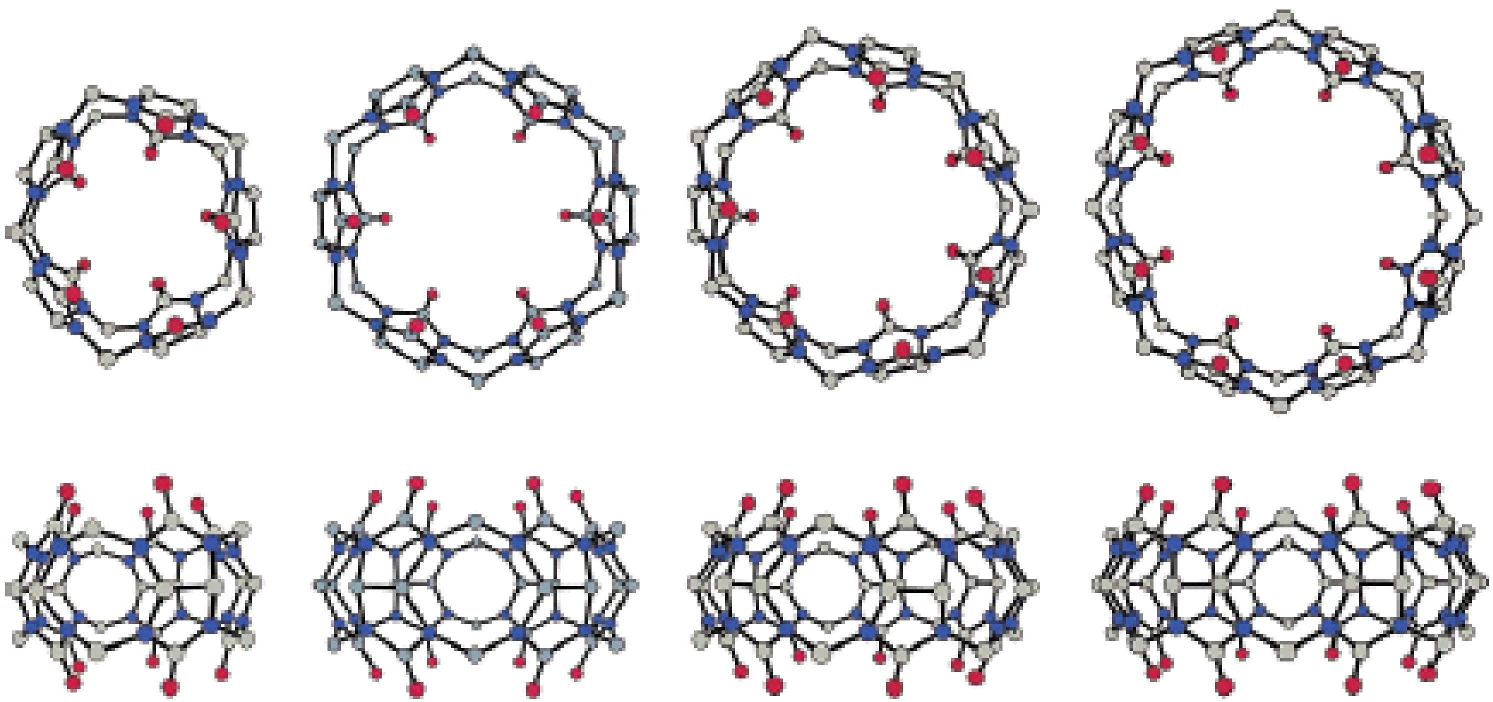




Ph(NH2)2@CB[6]

Cucurbit[*n*]urils, *n*=5-8

CB[5] CB[6] CB[7] CB[8]

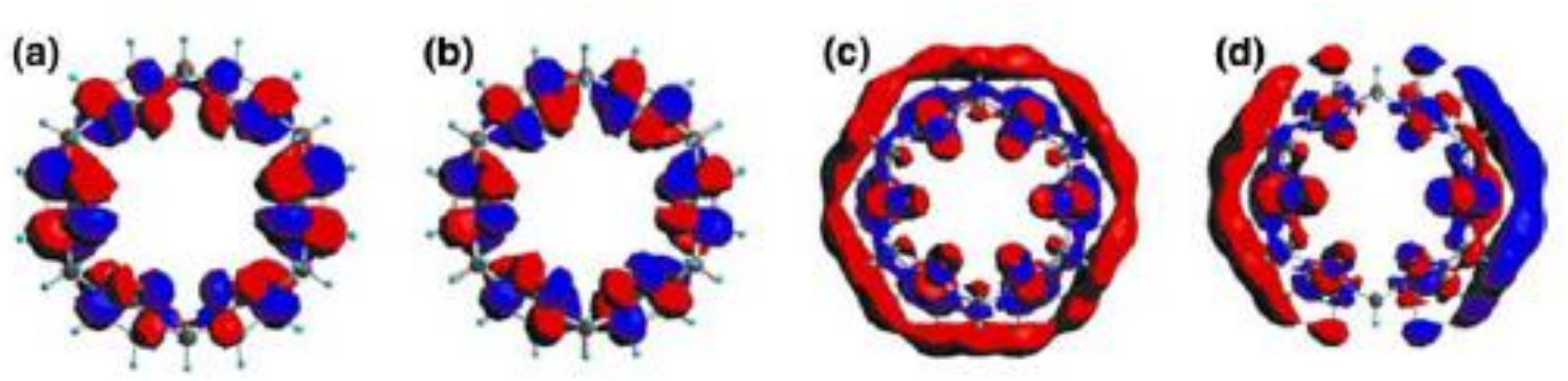


	CB[5]	CB[6]	CB[7]	CB[8]
Volume (Å^3):	82	164	279	479

From: Lee *et al.*, *Acc. Chem. Res.* 36 (2003) 621

DFT study of free CB[6]

F.P., *Chem. Phys. Lett.* 390 (2004) 214



HOMO-1 HOMO LUMO LUMO+1

Method	CB			TCB		
	H–L	IP	EA	H–L	IP	EA
B3LYP	7.02	7.05	−1.91	4.11	5.89	−0.12
B3PW91	7.16	7.15	−1.95	4.15	5.95	−0.11
B3P86	7.17	7.72	−1.39	4.12	6.47	0.43

Basis set: MIDI!

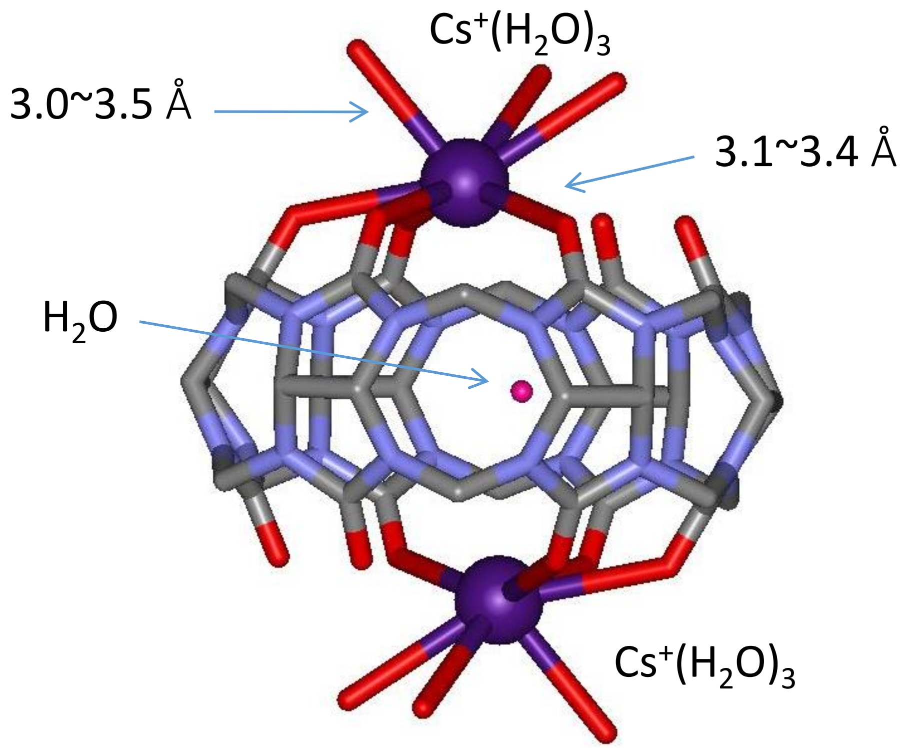
Cs^+/CB[6] interaction

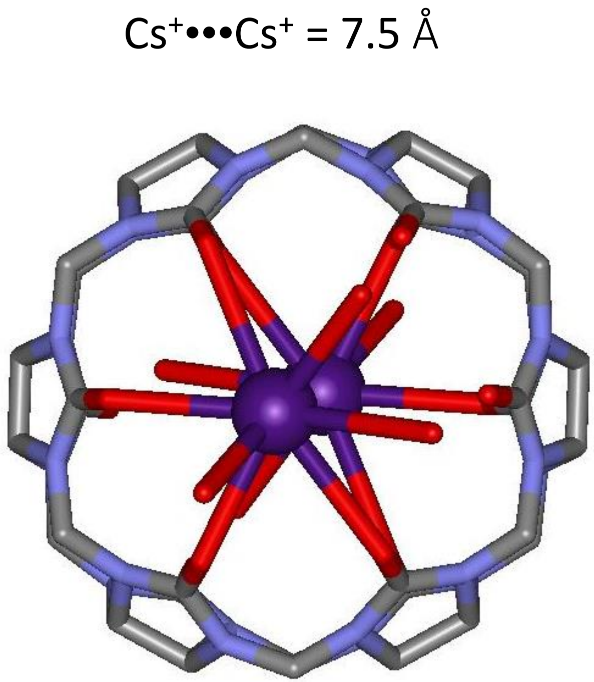
(as explored with DFT methods)

- Interaction with hydrated Cs^+ ion
- Hydration effects (coordination, H-bonding)
- Effect of water and Cl^- encapsulation
- Competition with alkali & alkaline-earth metals
- Structural modification of the macrocycle (introduction of a chromomophore/fluorophore) for the optical detection of cesium ions

$Cs^+(H_2O)_3$:CB[6] complex (x-tal structure)

Crystal structure determined by Whang et al. *Angew. Chem. Int. Ed.* 37 (1998) 78

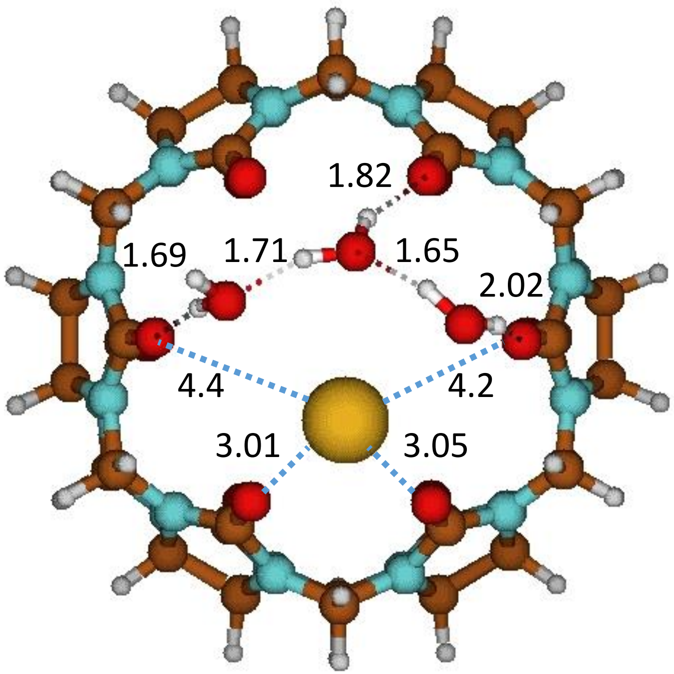




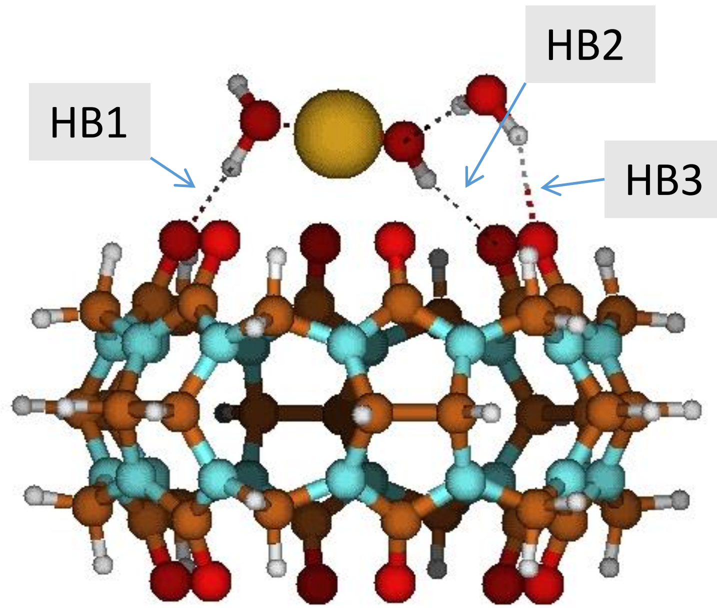
Crystal packing effects; One water molecule inside the cage;
Counterion outside the cage (not shown) (CSD refcode: NEXQUC)

CB[6]:$Cs^+(H_2O)_3$

F.P., *Dalton Trans.* 42 (2013) 6083



$q(Cs^+)=+0.81$ au
q(H2O)~0.0 au

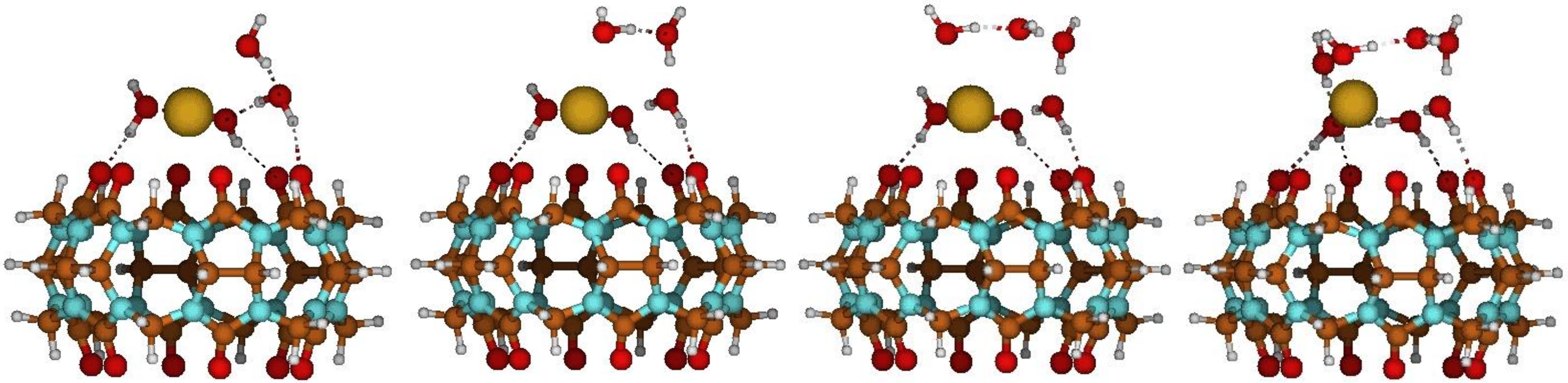


Be(Cs^+W3:CB[6])=78.0 kcal/mol

3 H-bonds

CB[6]:$Cs^+(H_2O)_n$, n=4-7

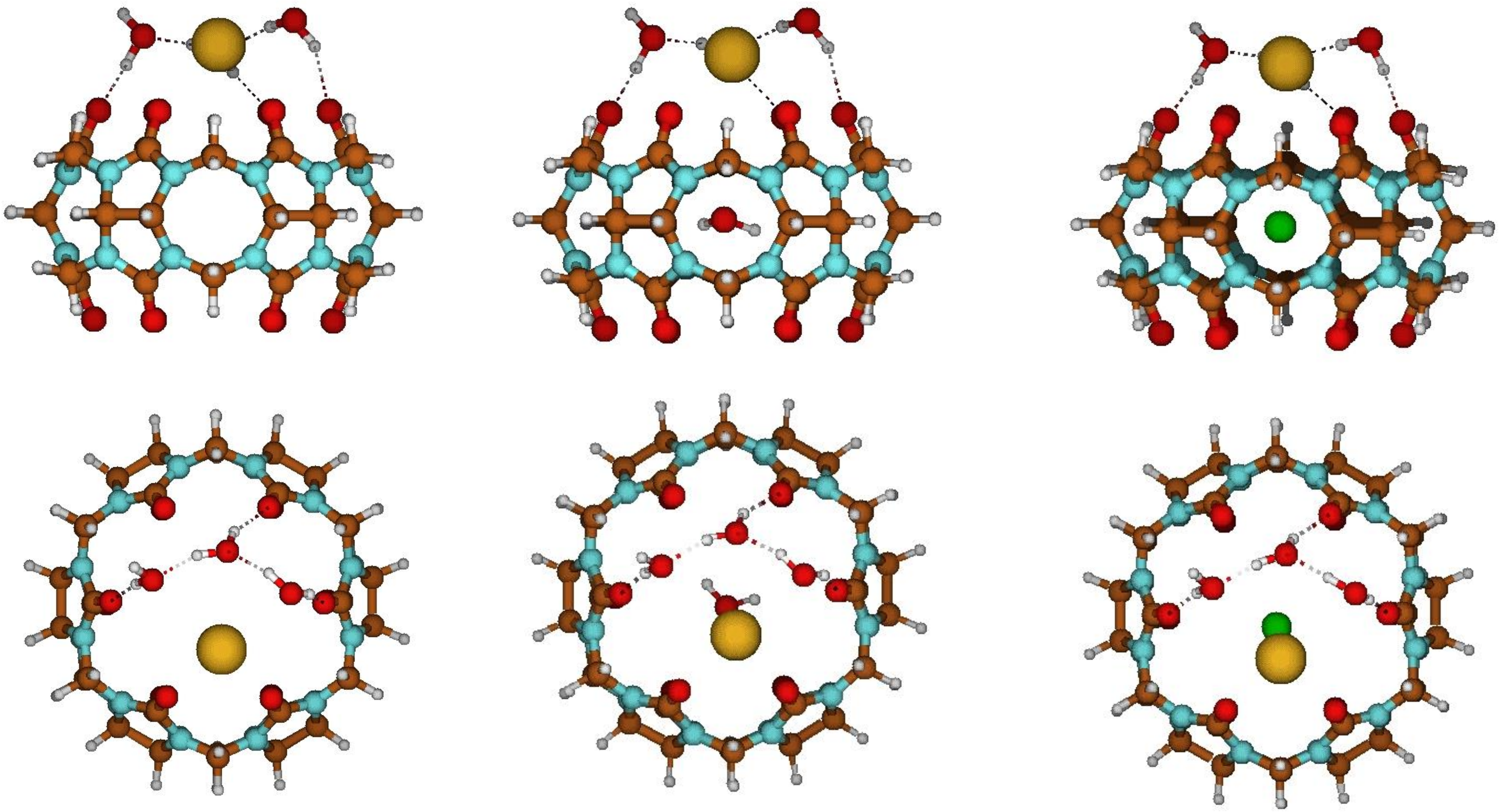
F.P., *Dalton Trans.* 42 (2013) 6083



	n=4	n=5	n=6	n=7
Be: (Kcal/mol)	79.0 (3HB)	78.7 (3HB)	78.2 (3HB)	84.4 (4HB)
$q(Cs^+)$: (au)	0.79	0.78	0.77	0.76

Encapsulation of H_2O and Cl^- anion

F.P., *Dalton Trans.* 42 (2013) 6083

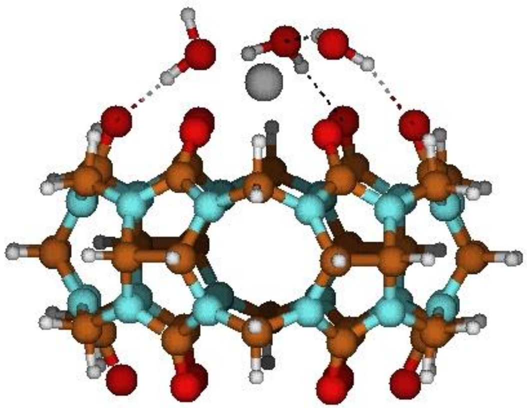


Be:	78.0	83.6	149.7
(Kcal/mol)		Dipole-ion int. @ 4.920 Å	Ion-pair @ 5.009 Å

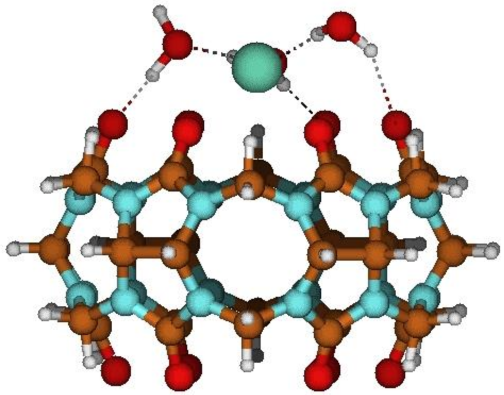
Competitive binding of M^+ (M=Na, K, Rb)

F.P., *Dalton Trans.* 42 (2013) 6083

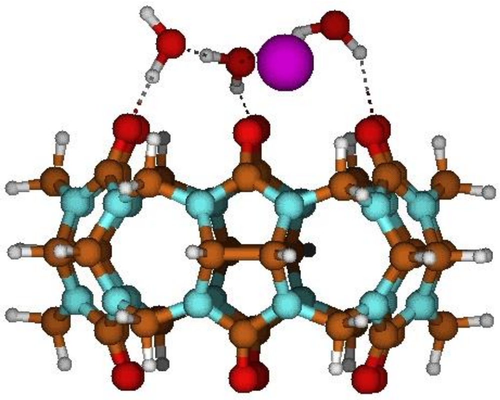
$Na^+(H_2O)_3$



$K^+(H_2O)_3$



$Rb^+(H_2O)_3$



	$Na^+(H_2O)_3$	$K^+(H_2O)_3$	$Rb^+(H_2O)_3$
Be: (Kcal/mol)	96.8	86.4	82.9
$q(M^+)$: (au)	0.59	0.74	0.78

Strength of the H_2O-M^+ bond

F.P., *Dalton Trans.* 42 (2013) 6083

Li^+: 43.7 Kcal/mol

Na^+: 31.8 Kcal/mol

K^+: 22.4 Kcal/mol

Rb^+: 19.9 Kcal/mol

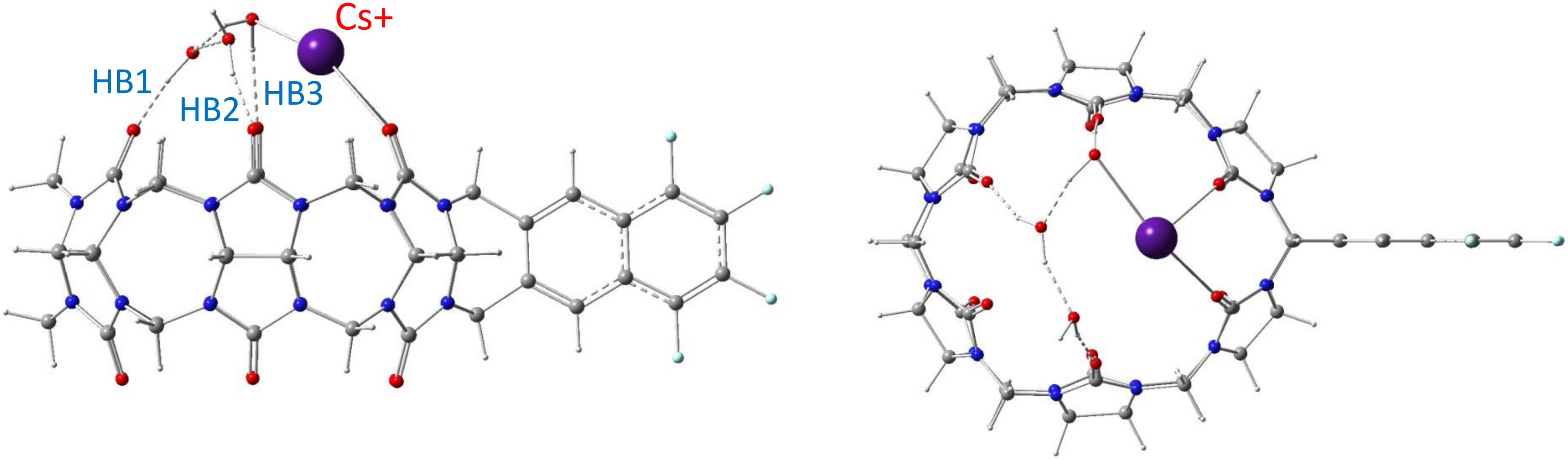
Cs^+: 17.1 Kcal/mol

$Cs^+(H_2O)_3$:CB[6]-naphthalene-F_4

Cs–O=C: 3.041 Å, 3.082 Å

$Cs–OH_2$: 3.021 Å

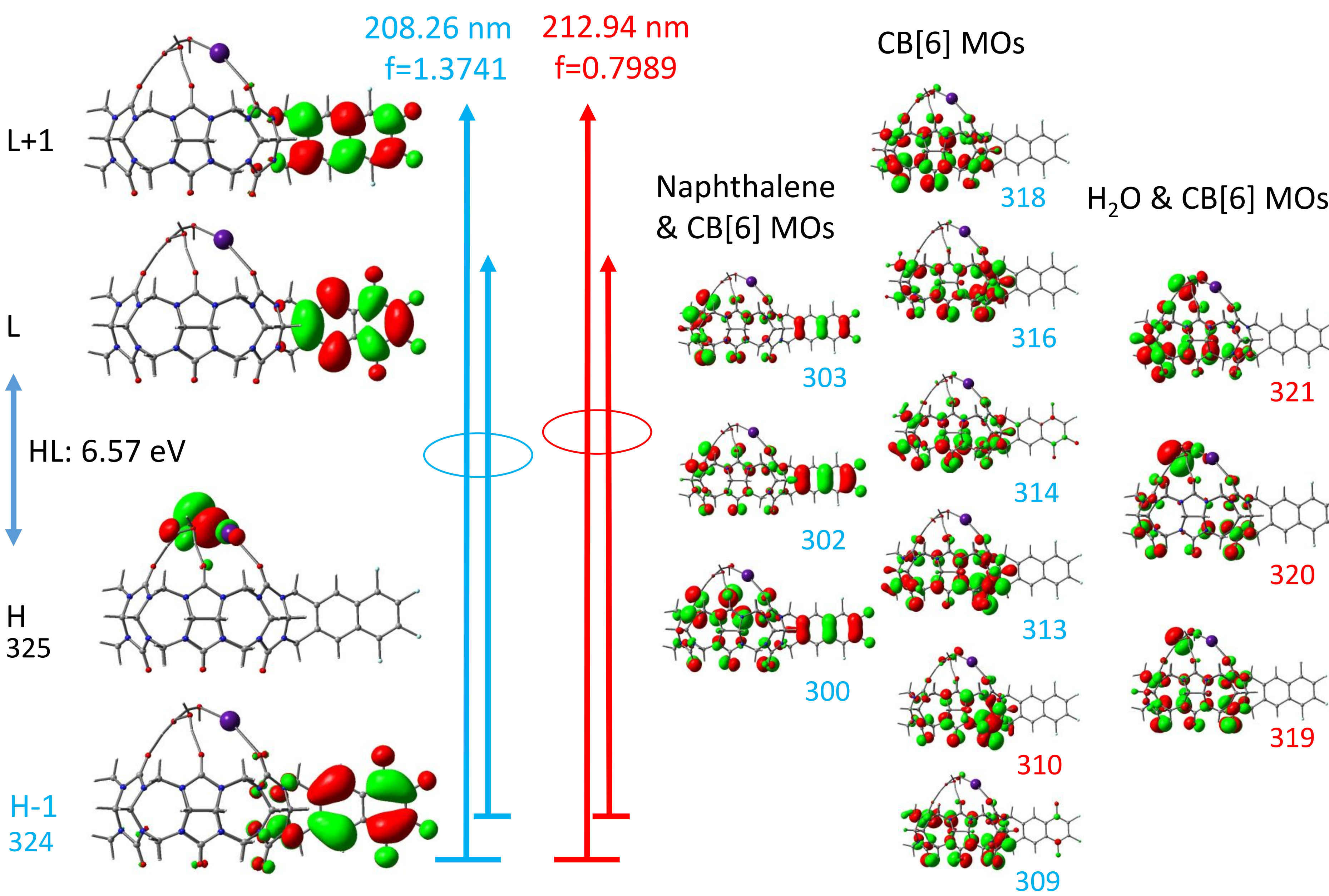
C=O···HOH: 1.714 Å, 1.813 Å, 2.021 Å



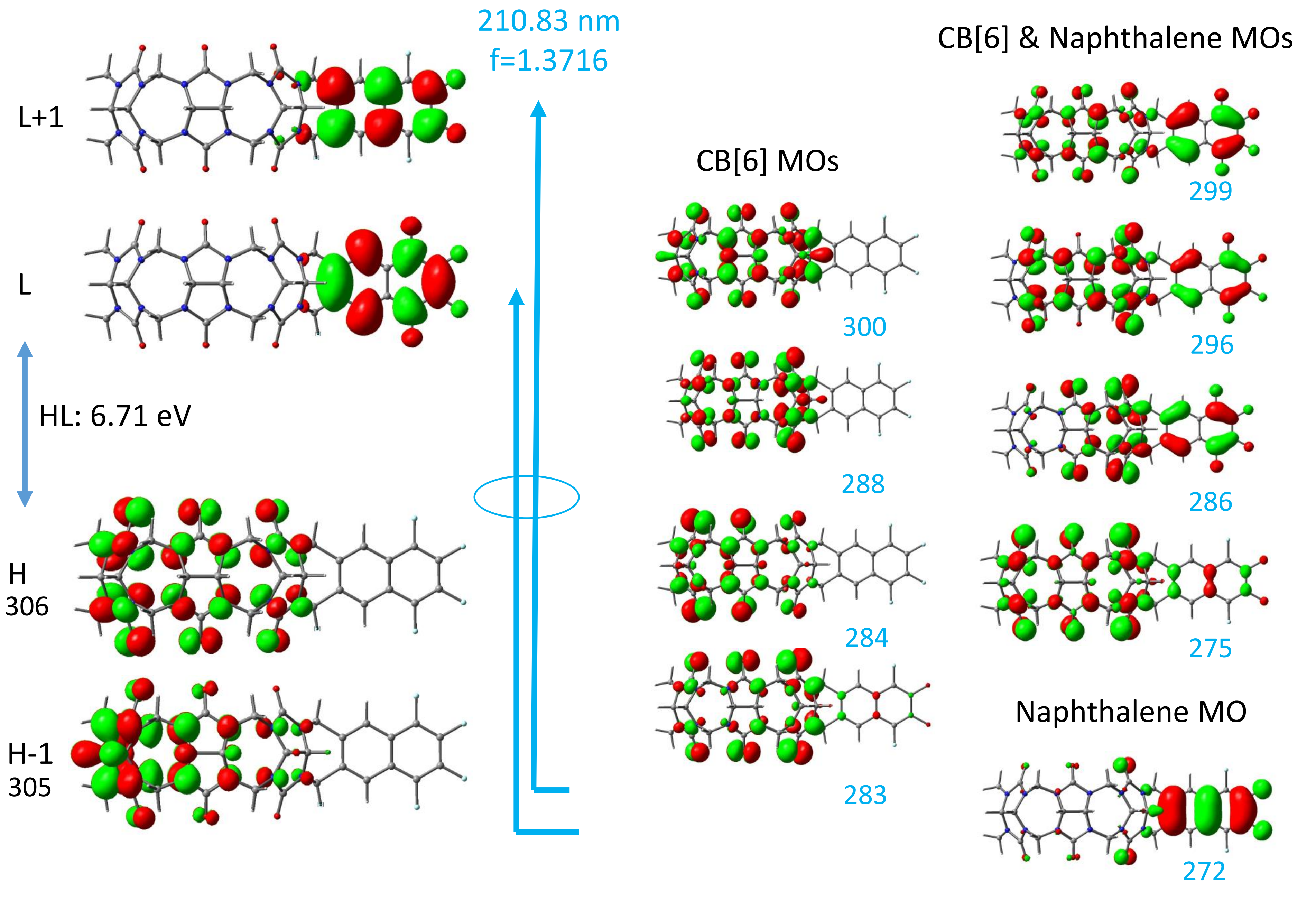
Geometry-optimized @ B3LYP/D95(SDD)

F.P., *Theo. Chem. Acct.* (2016) 135:61

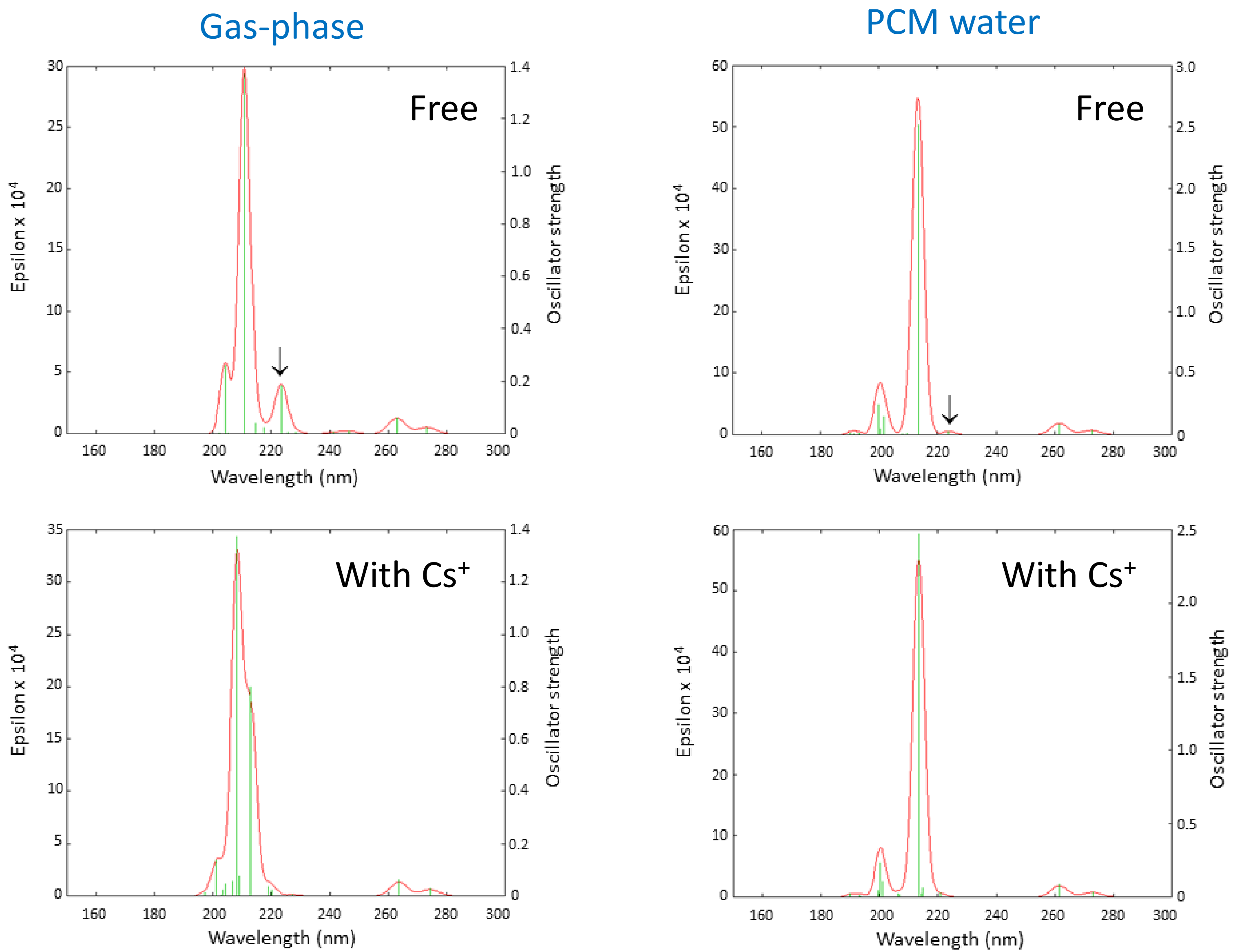
TD-DFT (TD-CAM-B3LYP) Results for $Cs^+(H_2O)_3$:CB[6]-naphthalene-F_4:



TD-DFT (TD-CAM-B3LYP) Results for CB[6]-naphthalene-F_4:



Theoretical Absorption Spectra



F.P., *Theo. Chem. Acct.* (2016) 135:61

Summary

- CBs are economical, chemically & structurally stable macrocycles
- Complexation of Cs^+ requires its *partial desolvation* of $Cs^+(H_2O)_{7,8}$
- Strength of the $M{-}OH_2$ bond is important for complexation
- Double binding to CB[6] possible (as observed in the solid-state)
- Encapsulation of H_2O or Cl^- increases Cs^+ binding by CBs
- CB-acenes as chemosensors for optical detection of Cs-137
- Sr-90 *vs* Cs-137 recognition (work in progress)
- How does high-energy radiation damage the macrocycle?
- *Thanks to JSPS for financial support (Grants-in-Aid, Kakenhi-C)*