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ORIGIN OF THE BRIGHT PHOTOLUMINESCENCE OF FEW-ATOM SILVER CLUSTERS CONFINED IN LTA ZEOLITES

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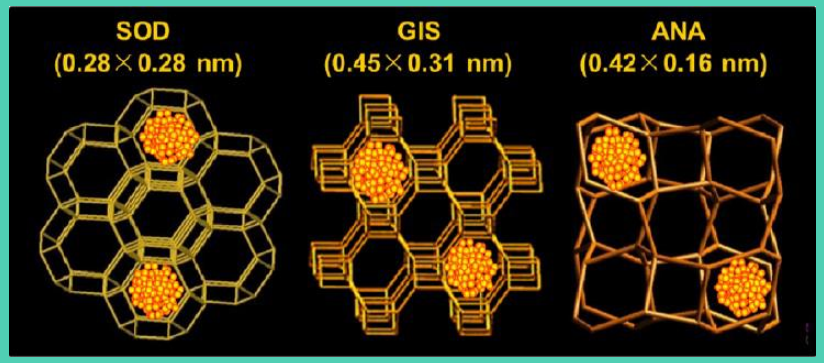
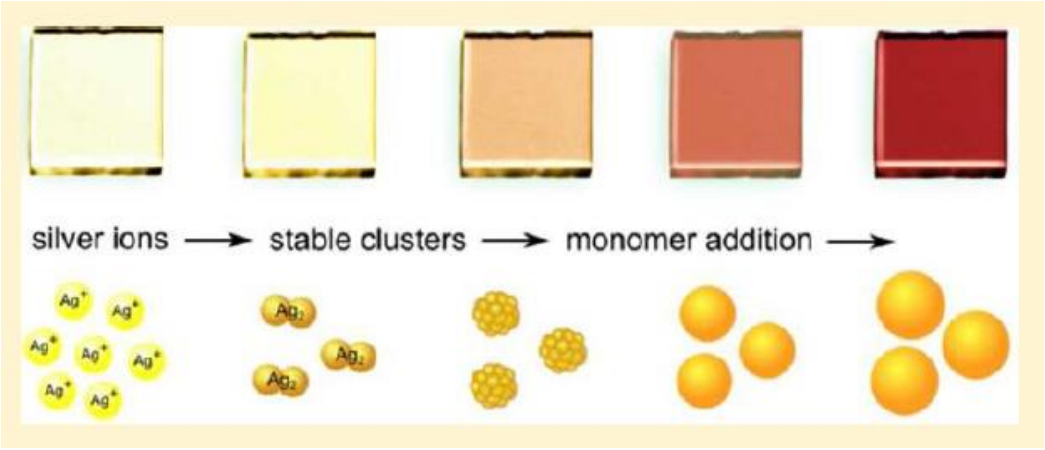


Debasmita Ghosh
03/09/2018

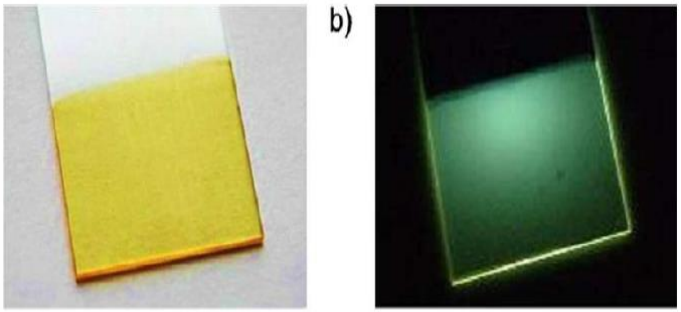
Volume 361
686-690
August 17, 2018

IMPORTANCE

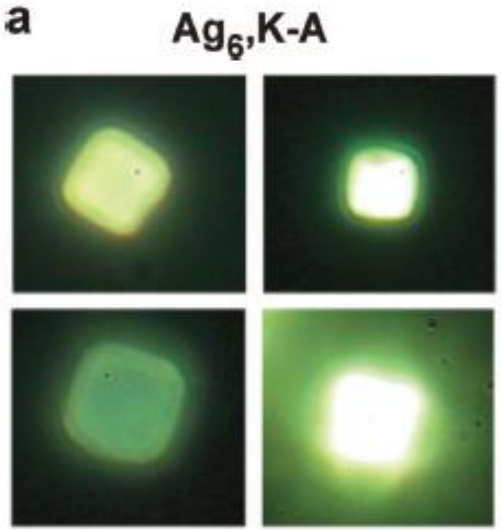
Silver clusters stabilized in glassy matrices



Rademann et al., J. Am. Chem. Soc., **2012**, 134, 18824



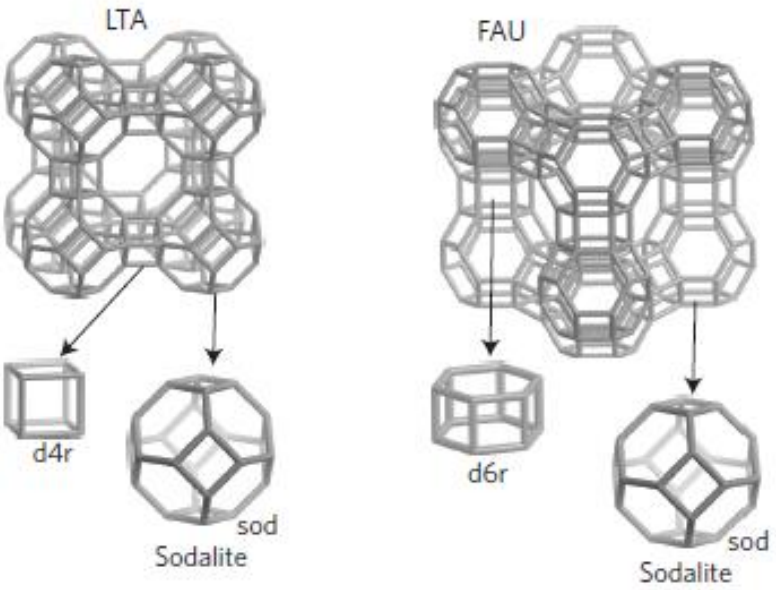
Characterization of fluorescence in heat-treated silver-exchanged zeolites



Vosch et al., J. Am. Chem. Soc., **2009**, 131, 3049

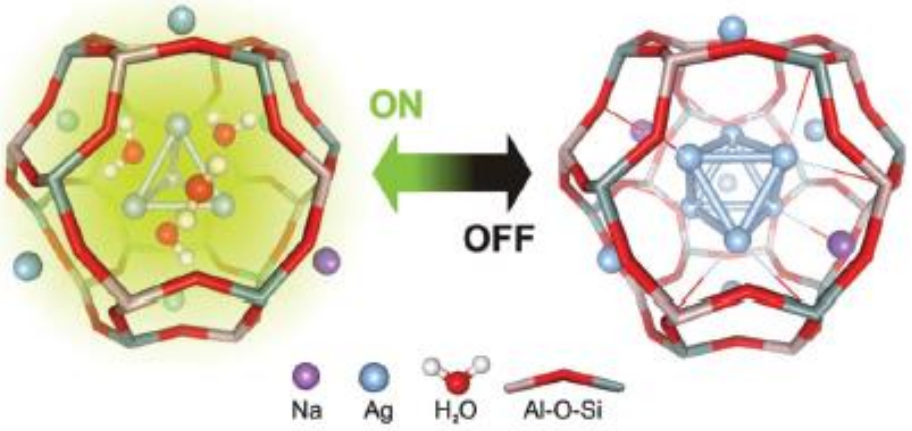
IMPORTANCE

Tuning the energetics and tailoring the optical properties of silver clusters confined in zeolites



Samori et al., NATURE MATERIALS, ***2016,*** *15, 1017*

Reversible opto-structural switching of luminescent silver clusters confined in LTA zeolites



Lievens et al., Nanoscale, ***2018,*** *10, 11467*

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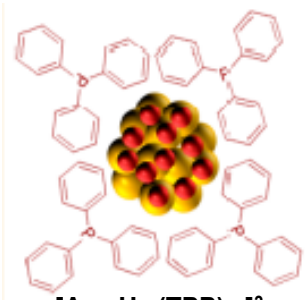
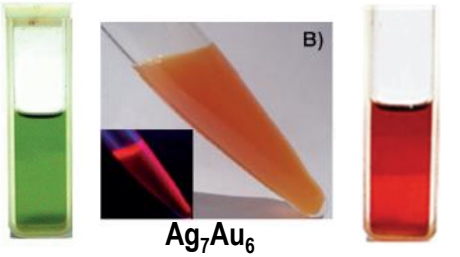
WHY SILVER CLUSTERS EMIT LIGHT?

RELEVANCE

NOBLE METAL CLUSTERS



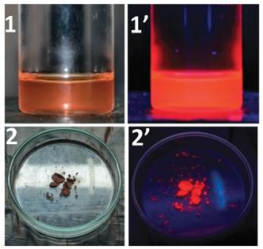
$[Ag_{18}H_{16}(TPP)_{10}]^{3-}$



Ag_7Au_6

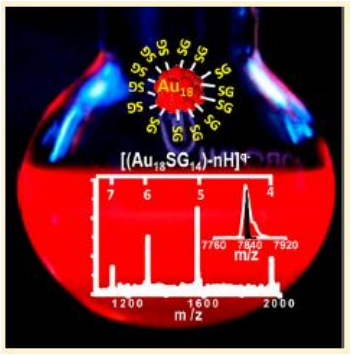
$[Ag_{51}BDT_{19}]^{3-}$

$[Ag_{59}DCBT_{32}]^{3-}$

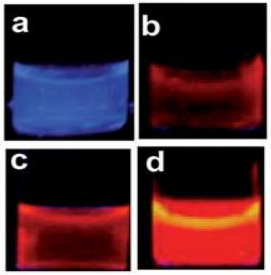


Visible UV

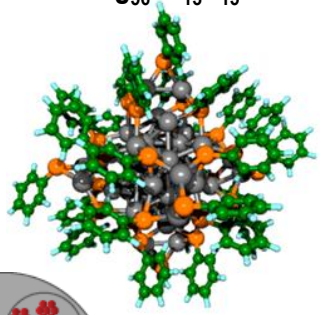
$Ag_{56}Se_{13}S_{15}$



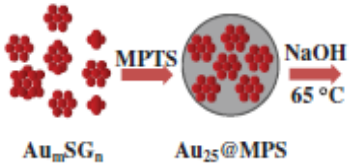
$Au_{18}SG_{14}$



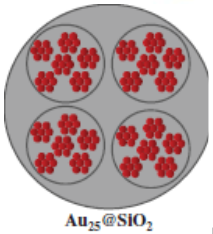
AuAg@BSA



$[Ag_{44}(SeR)_{30}]^{3-}$



Au_mSG_n Au_{25}@MPS



$Au_{25}@SiO_2$

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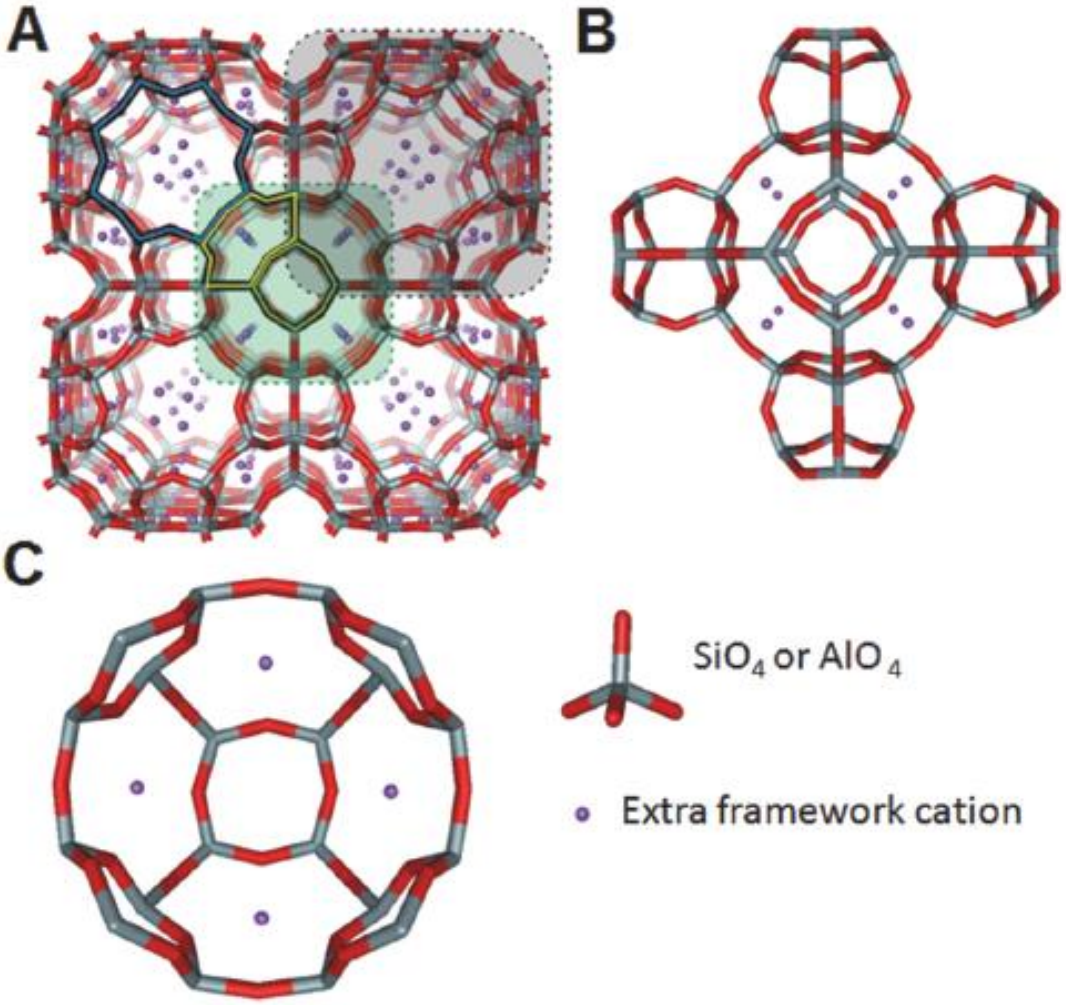

Schematic representation of (A) LTA unit cell displaying the sodalite (green dashed area) and super cage (gray dashed area); the eight ring (8R), single six ring (S6Rs), and double four rings (D4Rs) are highlighted in blue, yellow and green respectively, (B) Isolated sodalite cage with D4R connectors, and (C) Transversal section of a sodalite cage.

SAMPLE PREPARATION

Zeolite material (K-LTA) (1 gm) + $AgNO_3$ aqueous solution (500 mL)

↓

Agitated for 2 hours (dark)

↓

Filtered and washed (several times with milliQ water) the powder sample

↙ ↘

Calcined overnight at 450°C (5°C/min)
Heat treated sample

Dried at 80°C for 1 hour

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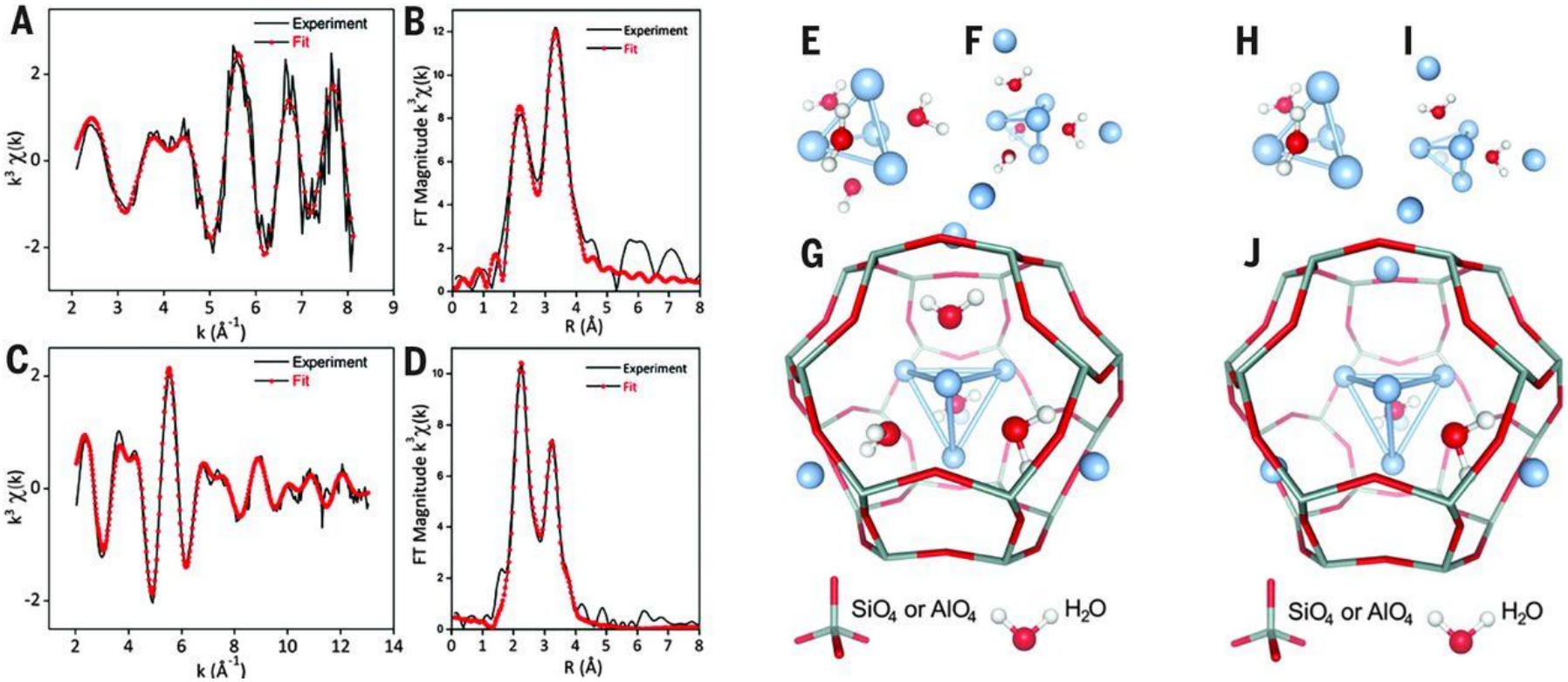

Ag K-edge XEOL and transmission-detected EXAFS and FTs of heat-treated Ag_3K_9-LTA and derived structures. (A) XEOL-detected and (C) transmission-detected k^3-weighted Ag K-edge EXAFS with the (B) phase-corrected XEOL-detected FT and (D) transmission-detected FT best fits. (E to J) Structures of (E) $Ag_4(H_2O)_4$ and (H) $Ag_4(H_2O)_2$, including [(F) and (I)] Ag_R cations and [(G) and (J)] embedded in the sodalite cage (~0.66 nm free diameter).

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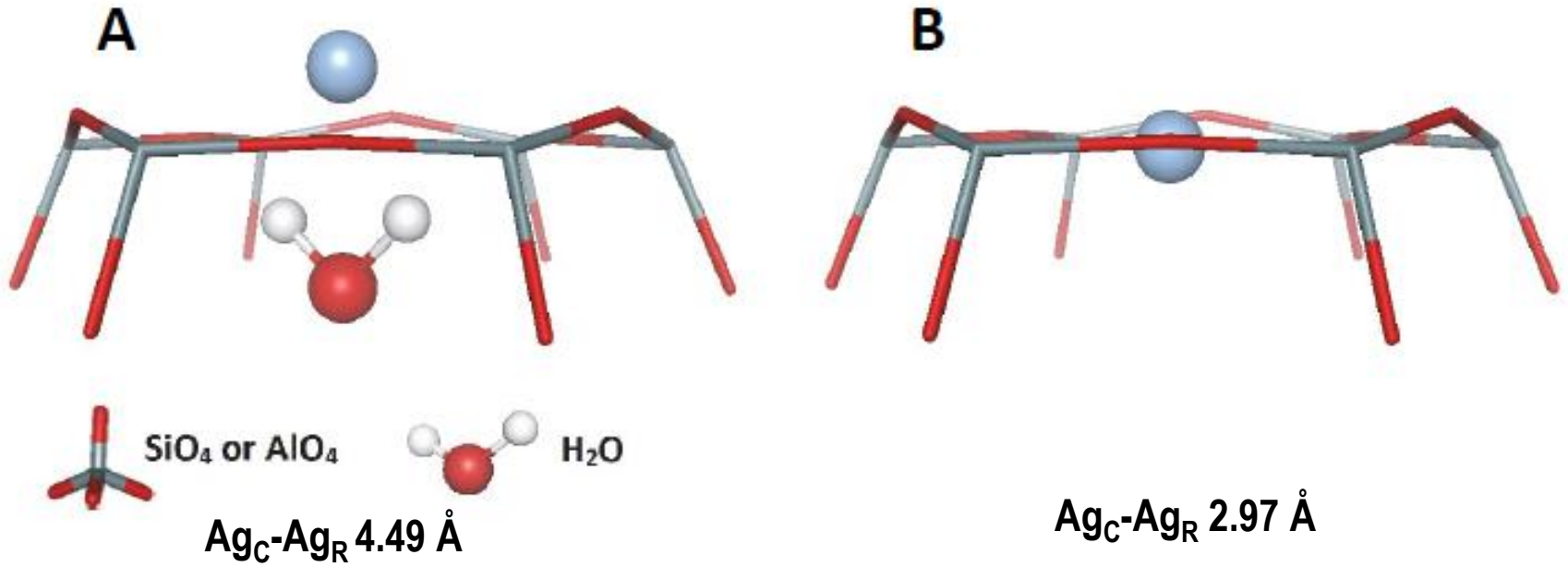

Position of the Ag_R (blue) at the center of the S6R of the LTA zeolite; (A) outside the sodalite cage when water molecule is present (crystallographic position IIα) and (B) inside the sodalite cage when no water molecule is present (crystallographic position IIβ).

Ag_C-Ag_C 2.82 Å (XEOL)

Ag_C-Ag_C 2.7 Å (transmission)

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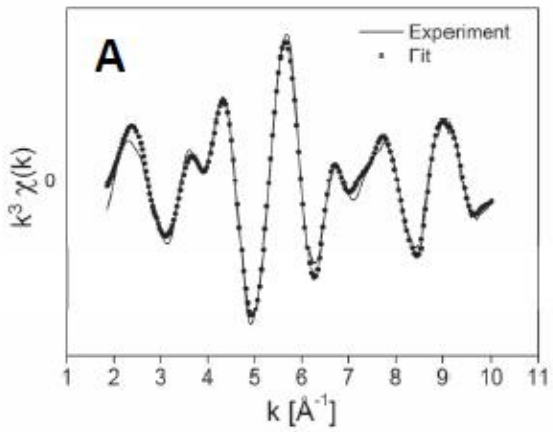
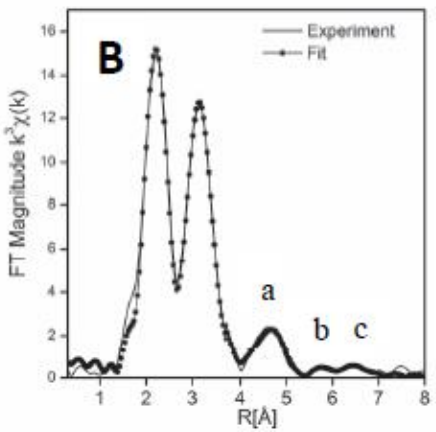
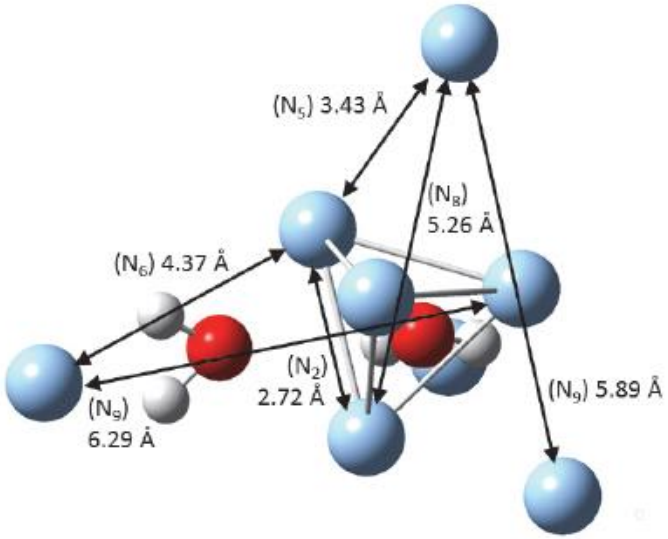




Transmission-detected Ag K-edge k_3-weighted EXAFS (A) with the corresponding phase corrected FT (B) best fits of heat-treated Ag_3K_9-LTA zeolite material measured at liquid nitrogen temperature including high-R Ag-Ag contributions up to 6 Å.

Ag_C-Ag_R 5.24 Å
Ag_R-Ag_R 6.13 Å



Structure of $Ag_4(H_2O)_2$ cluster and surrounding Ag_R cations built in the XRD crystallographic model of a Ag_{12}-LTA sodalite cage (omitted) including the distances and corresponding shells

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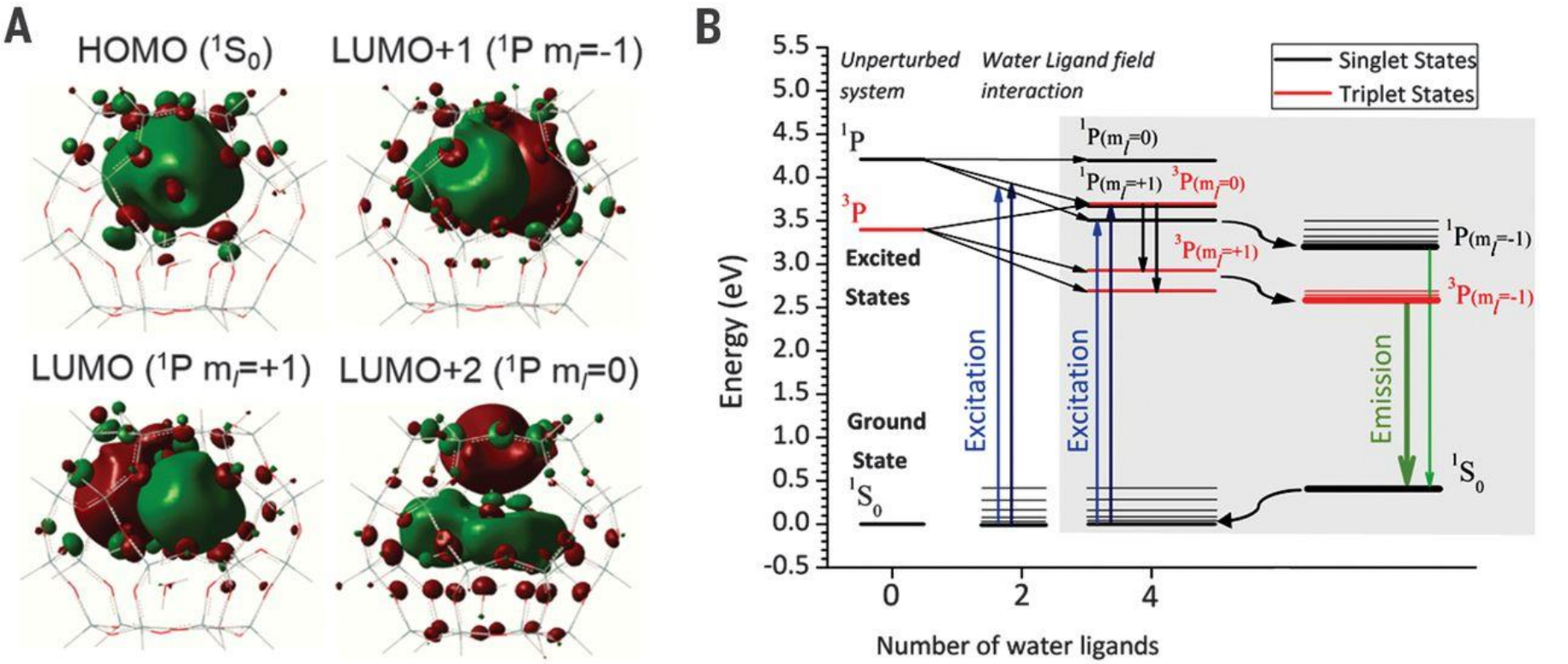

Frontier orbitals of $[Ag_4(H_2O)_4(Si_{24}H_{24}O_{36})]^{2+}$ and energy level diagram of $Ag_4(H_2O)_2^{2+}$ and $Ag_4(H_2O)_4^{2+}$ clusters in Ag_3K_9-LTA. (A) Frontier orbitals consist of one single symmetric s-type HOMO ($^1S_0$) and three singlet one-node p-type ^1P (m_l = –1, +1, or 0) LUMOs (p_x, p_y, p_z) delocalized over all the Ag and O atoms of the cluster. Atom colors are Si, gray; O, red; Ag, blue; hydrogen, white. (B) Energy level diagram showing the ground-state $^1S_0$ and the excited states ^3P and ^1P of water-free unperturbed Ag_4^{2+} clusters and the ground-state $^1S_0$ and the six singlet ^1P and triplet ^3P excited states of $Ag_4(H_2O)_2^{2+}$ and $Ag_4(H_2O)_4^{2+}$ perturbed by means of water ligand field interaction. Blue arrows represent the allowed transitions, and the green arrows represent the luminescent transitions between the relaxed states.

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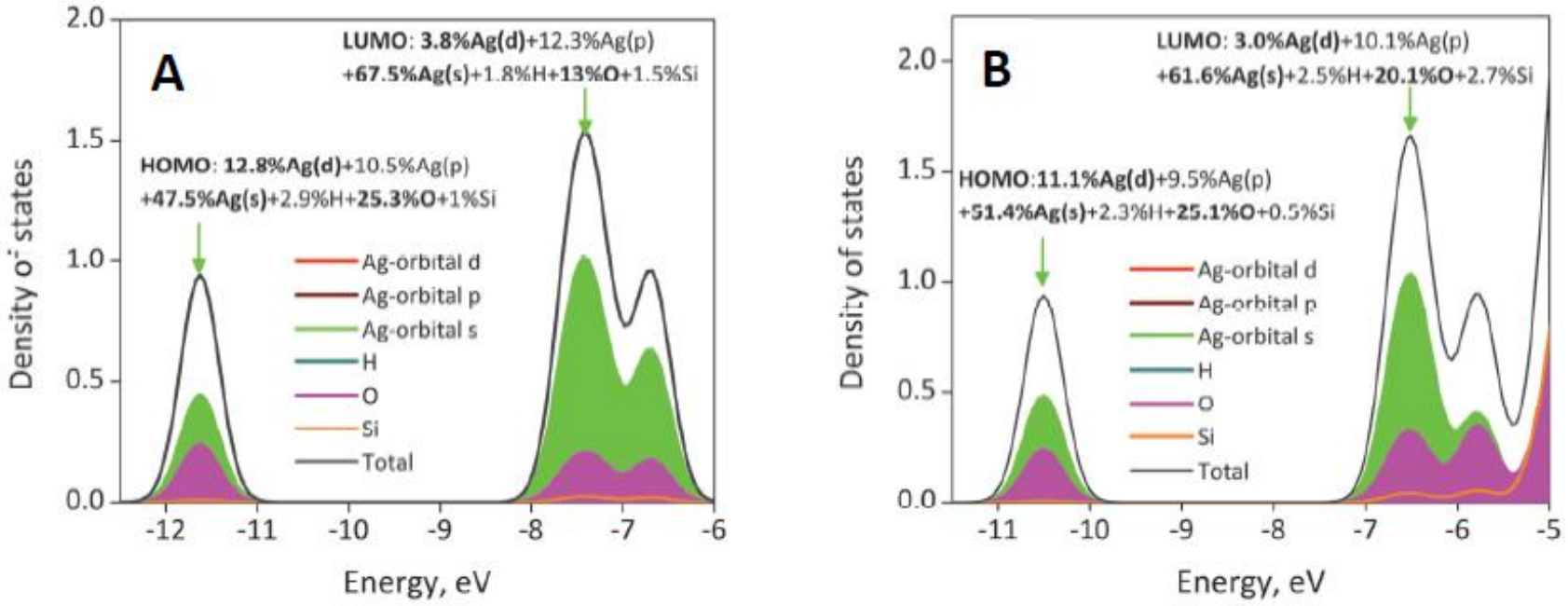
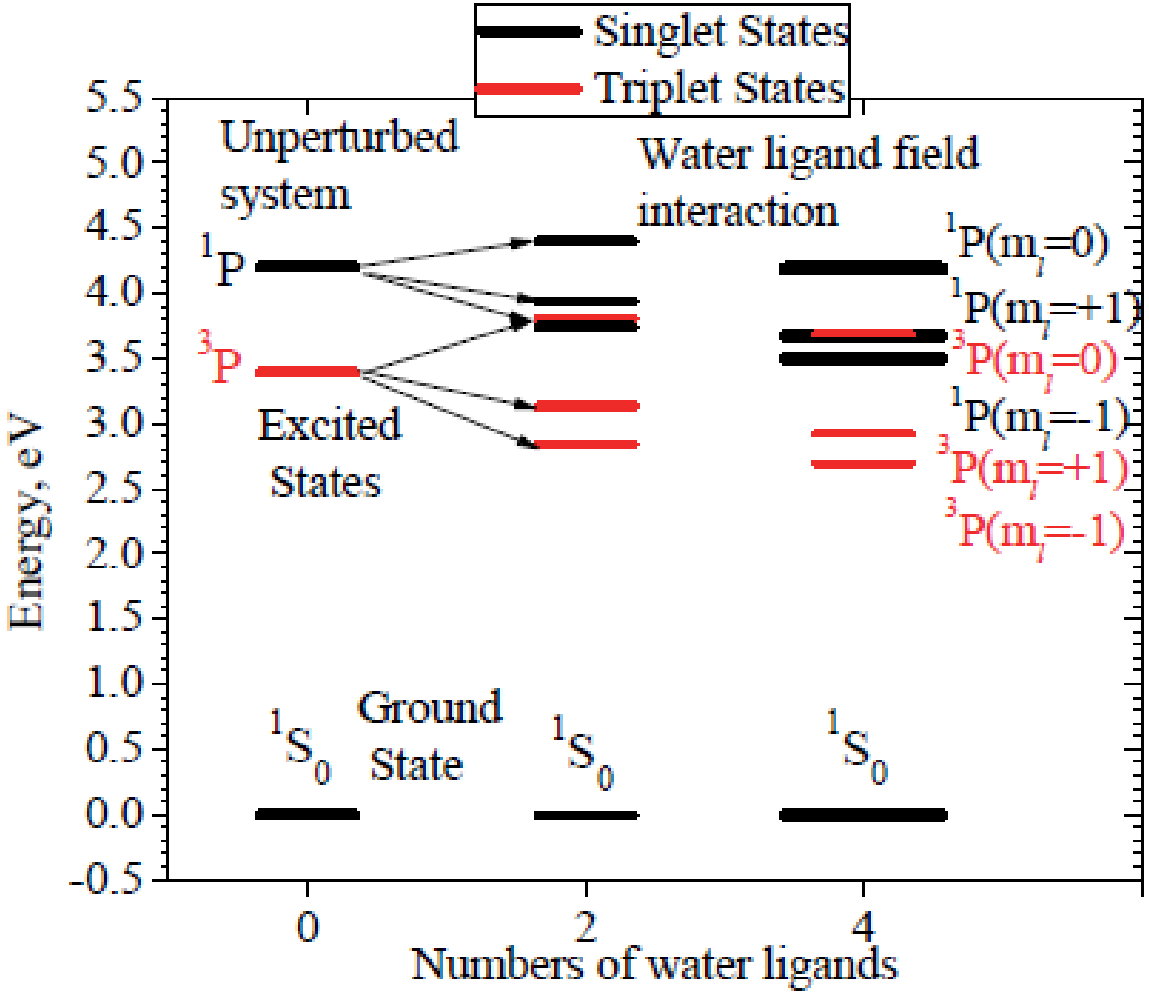


Densities of states of $[Ag_4(H_2O)_2(Si_{24}H_{24}O_{36})]^{2+}$ (A) and $[Ag_4(H_2O)_4(Si_{24}H_{24}O_{36})]^{2+}$ (B) (B3LYP/LANL2DZ). The solid line represents the total DOS, the s(Ag) and the oxygen components are shown by the green and the magenta area, respectively.



Energy level diagram of the $[Ag_4(H_2O)_2(Si_{24}H_{24}O_{36})]^{2+}$ and $[Ag_4(H_2O)_4(Si_{24}H_{24}O_{36})]^{2+}$ clusters calculated using the B3LYP/LANL2DZ functional/basis set.

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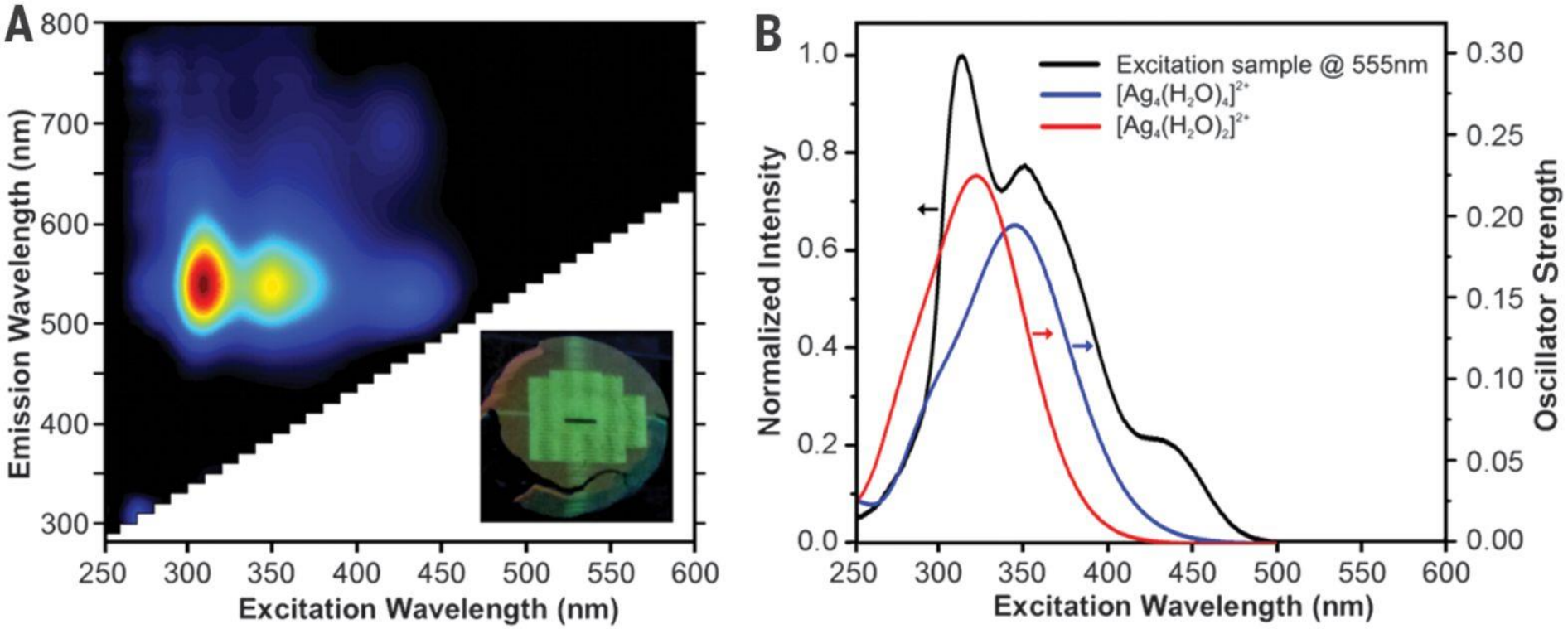

Steady-state excitation-emission of Ag_3K_9-LTA. (A) 2D excitation–emission plot. (Inset) The picture of an x-ray–irradiated sample under 366 nm illumination. (B) Excitation spectrum $\lambda_{detection}$ = 555 nm of as-prepared Ag_3K_9-LTA. Calculated $^1S_0$ HOMO to ^1P (S = 0; L = 1; m_l = –1, +1) LUMOs absorption spectra of x = 2 and x = 4 $[Ag_4(H_2O)_x]^{2+}$ isomers showing a good agreement with experiments.

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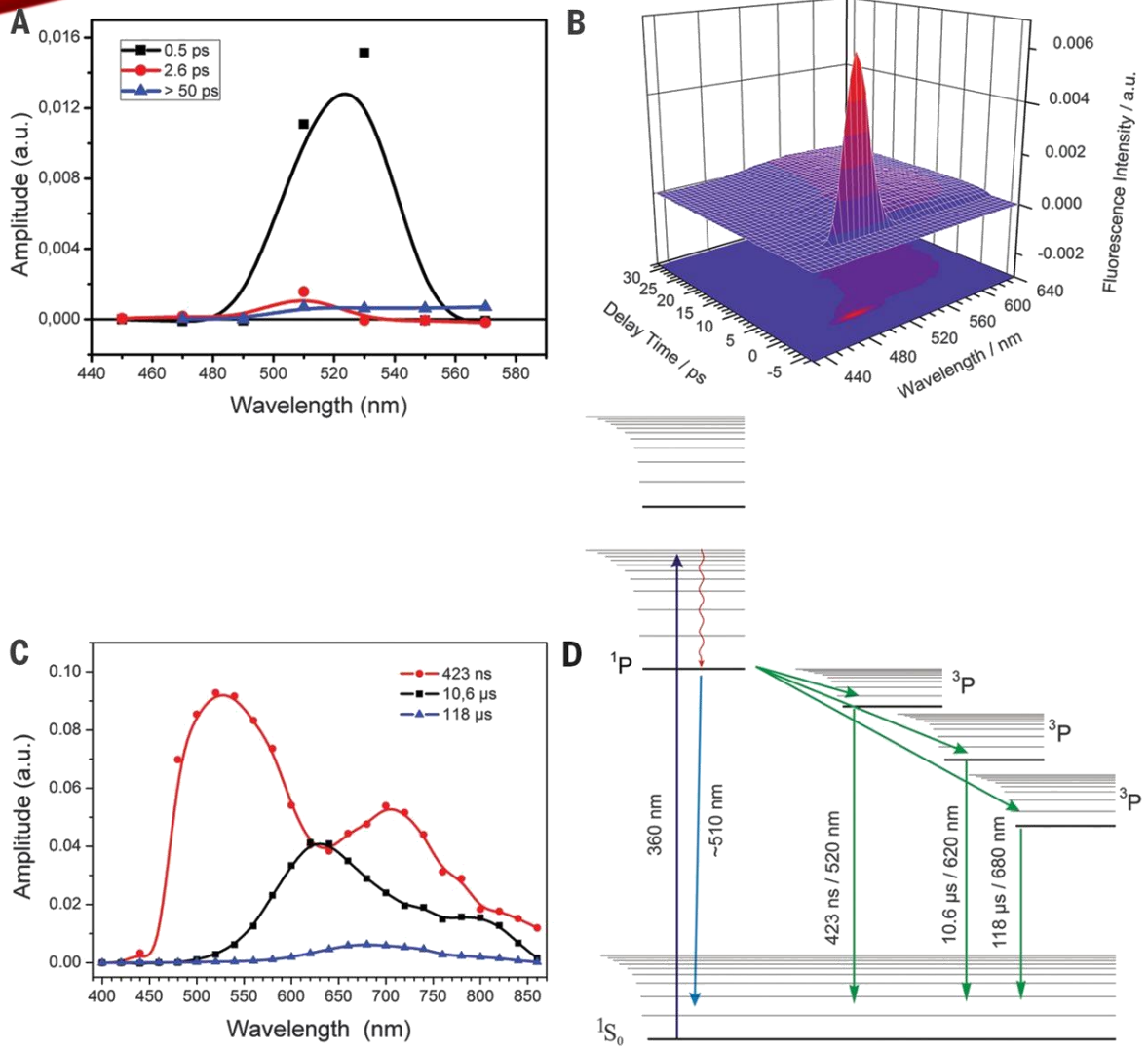
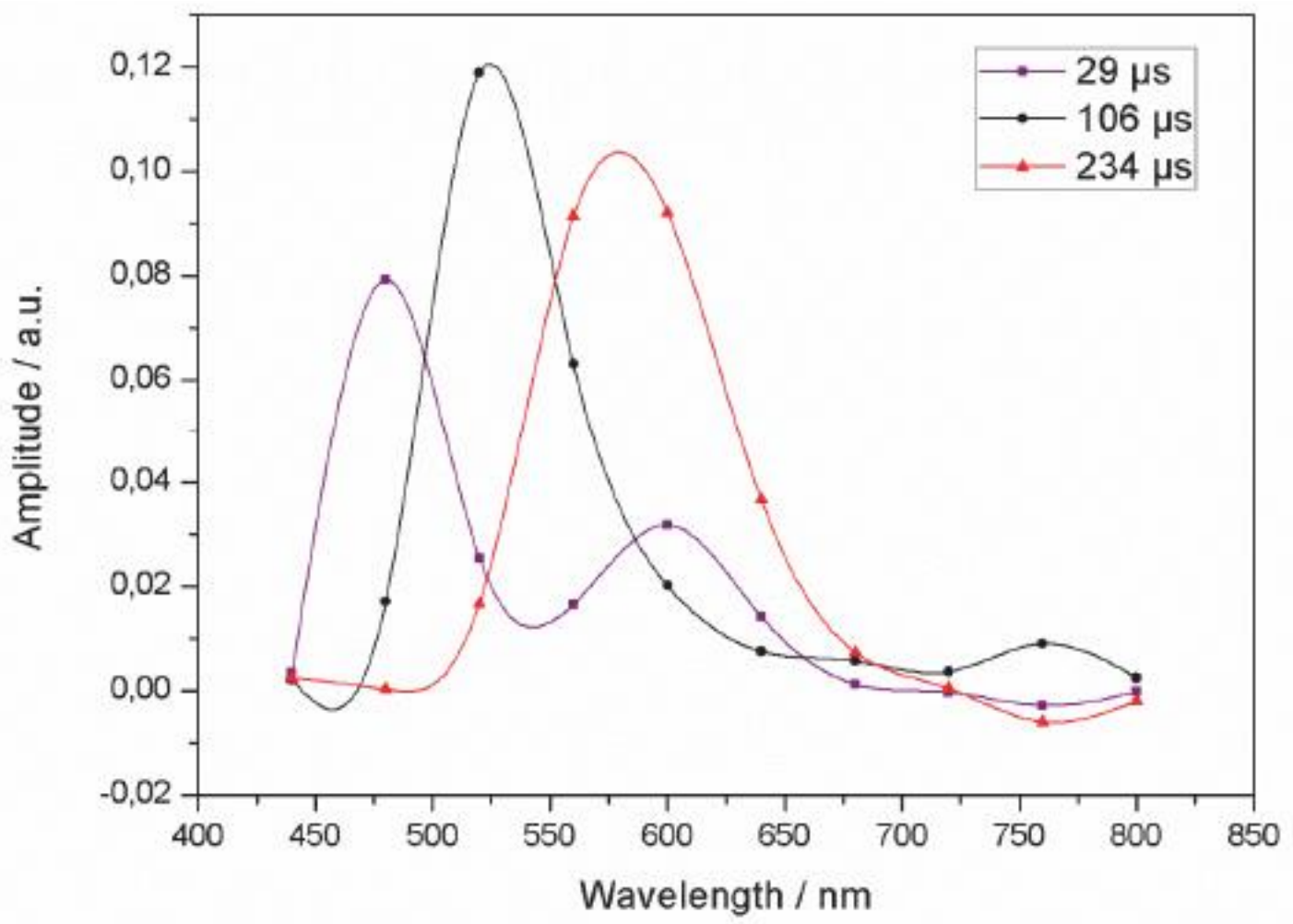


Time-resolved spectroscopy of Ag_3K_9-LTA. (A and B) AWD 3D time-resolved fluorescence emission spectra in 50-ps time window obtained with (C) femtosecond fluorescence up-conversion, in 1-ms time window through nanosecond luminescence. (D) Schematic illustration of the main electronic states involved as a function of energy (on the vertical axis).



Amplitude-to-wavelength dependence obtained by the ns luminescence technique for Ag_3K_9LTA at 77 K in a 1 ms time window.

CONCLUSION

- XEOL-XAFS has allowed the unambiguous identification of the local structure of the emissive Ag clusters in partially exchanged LTA zeolites.

- DFT modeling based on these detailed structures showed that water ligand molecules of double positively charged $Ag_4(H_2O)_4$ and $Ag_4(H_2O)_2$ clusters can modulate the HOMO-LUMO gap.

- They behaved as confined two electron helium or alkaline earth–like superatom quantum systems that mainly emit via their longlived lowest-lying ^3P triplet excited state, as confirmed with time-resolved optical spectroscopy.

- This is likely the case for Ag clusters confined in fully exchanged LTA or in FAU zeolites that possess very similar structural and luminescent properties.

UNMASKING THE GLOW OF SILVER CLUSTERS