Influence of the atomistic structure on the electric field enhancement in plasmonic nanostructures

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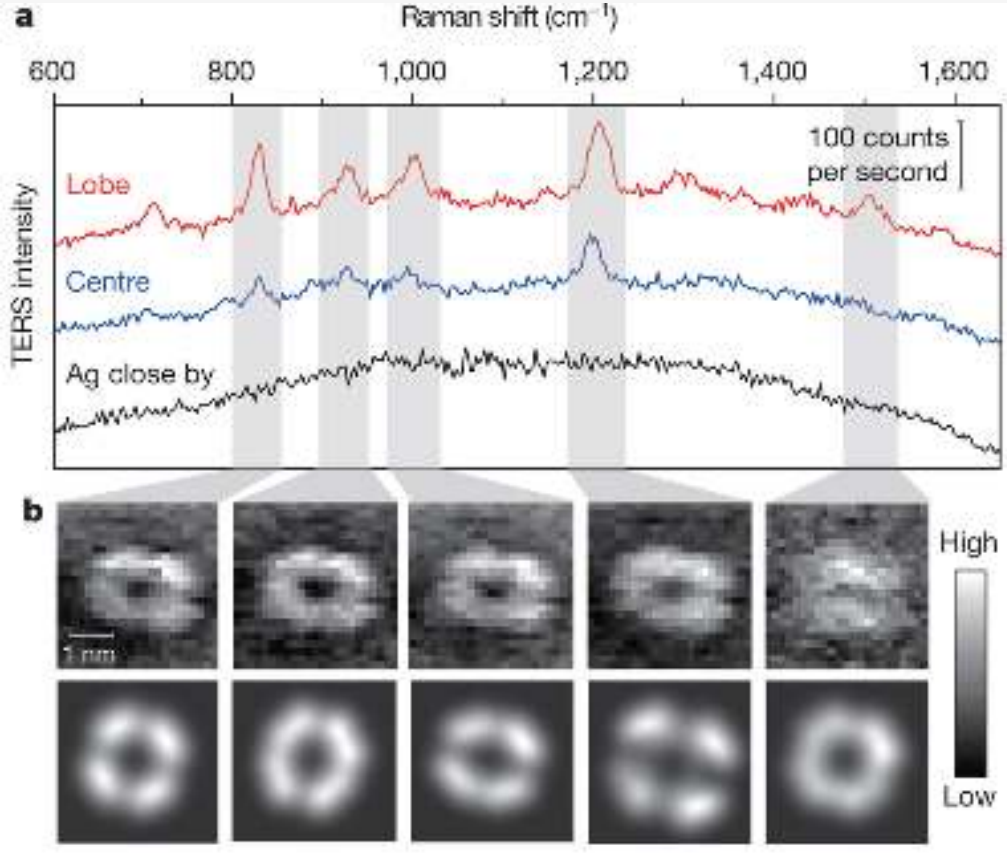
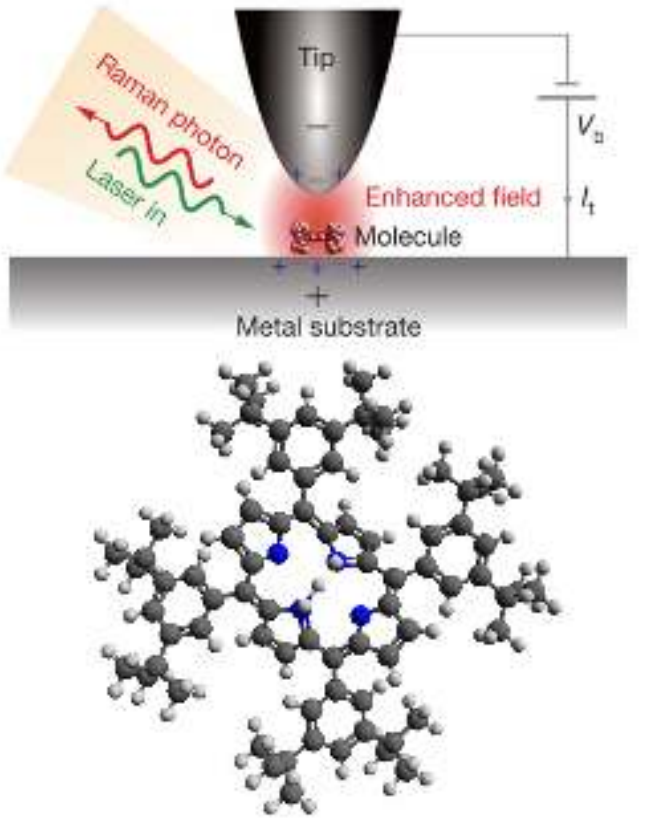
Single Molecule Mapping





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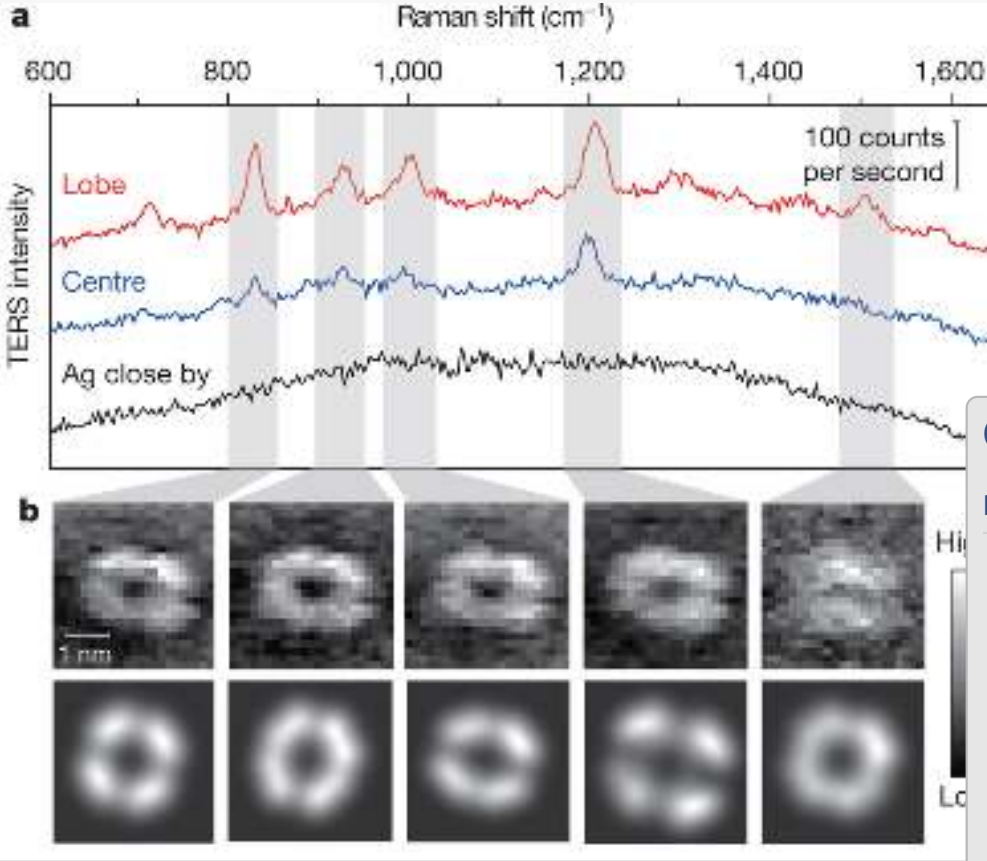
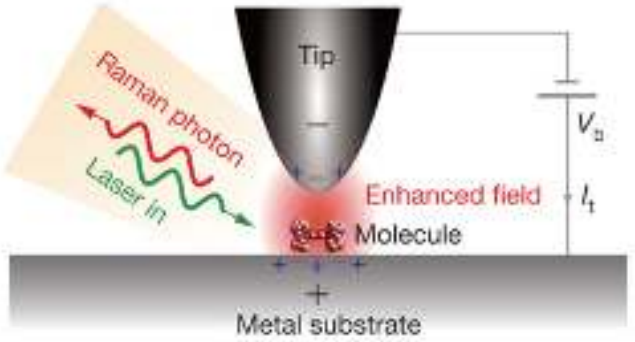




Chemical mapping of a single molecule by TERS[1]:

- Raman spectrum of a single H_2TBPP molecule on Ag(111).
- Intra-molecular features, resolution below 1nm!!

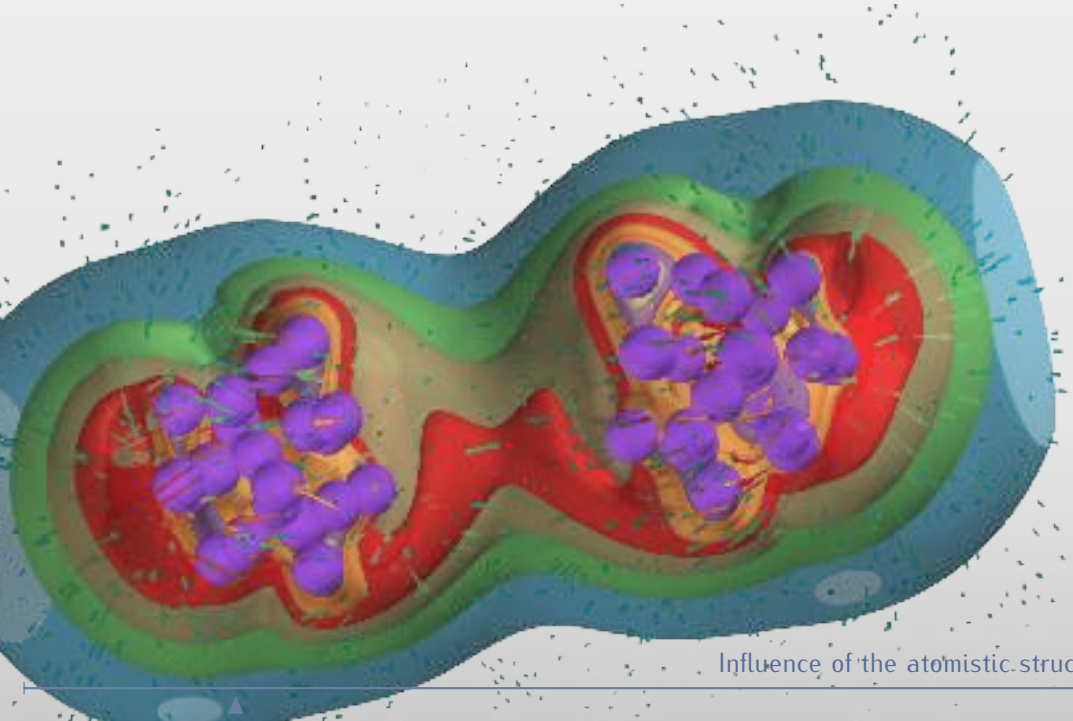
[1] R. Zhang et al. NATURE 498, 82-86 (2013)

Field enhancement from quantum mechanics calculation

Density change and Induced electric field

$$[1 - \chi_0(\omega)K(\omega)]\,\delta n_\mu(\omega) = \chi_0(\omega)d^\nu$$

$$E_{ind}(r,\omega) = -\nabla r \int \frac{\delta n(r',\omega)}{|r-r'|} d^3 r'$$



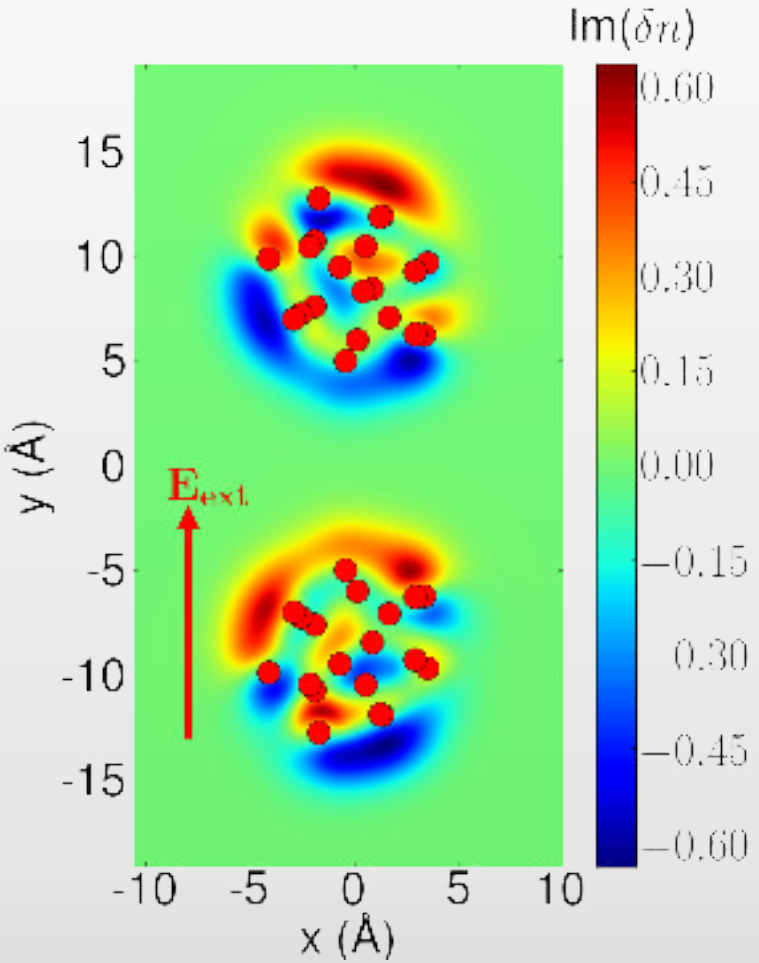
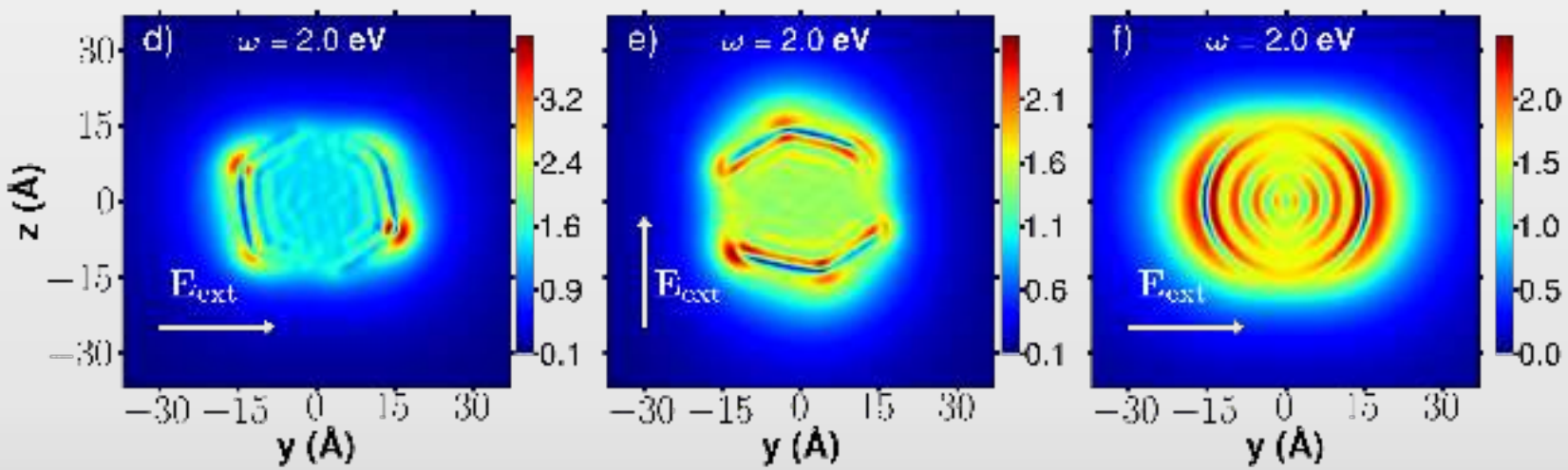


Figure : Density distribution of a Na_{20} dimer

TDDFT calculations with atomic-scale resolution: Atomic-scale lightning rod effect for Na_{380}[1].



[1] M. Barbry et al, NanoLetters, 15, 5 (2015).

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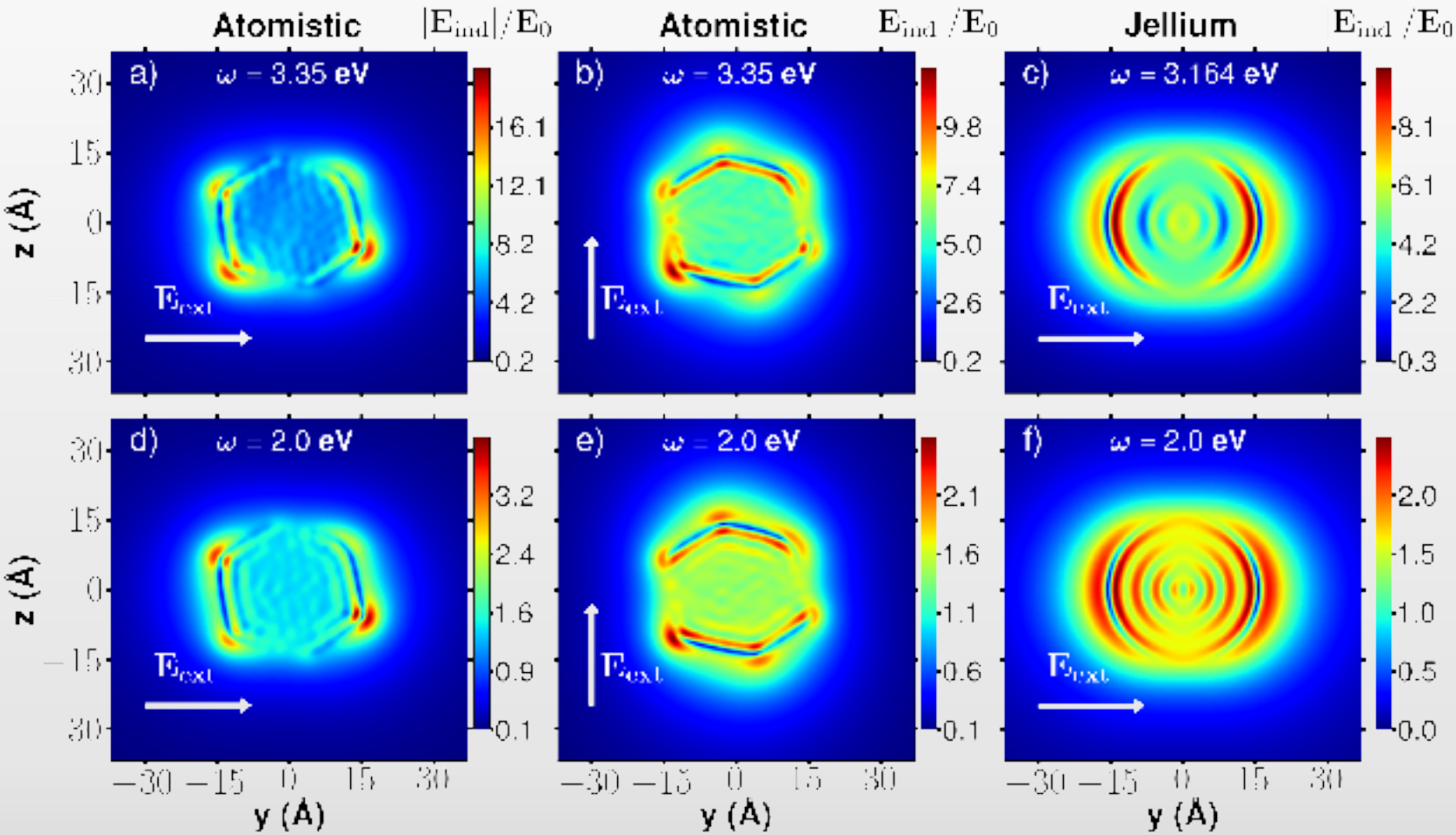

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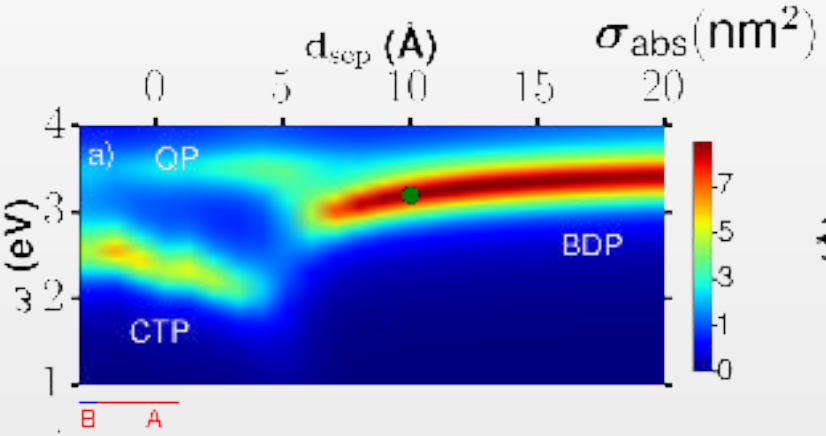
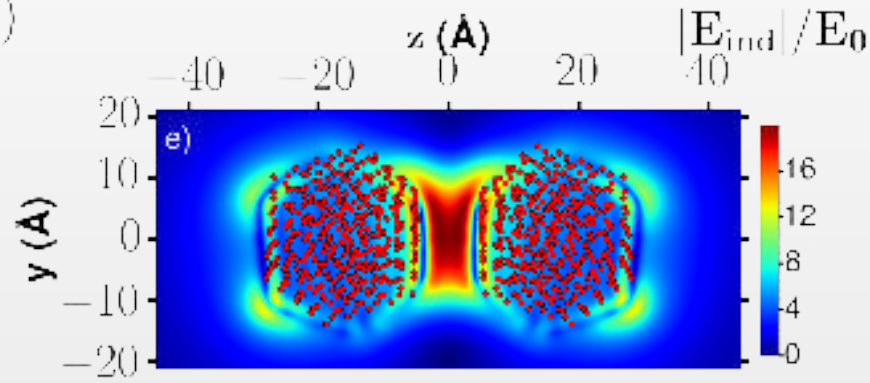
Far field and near field for Na_{380}





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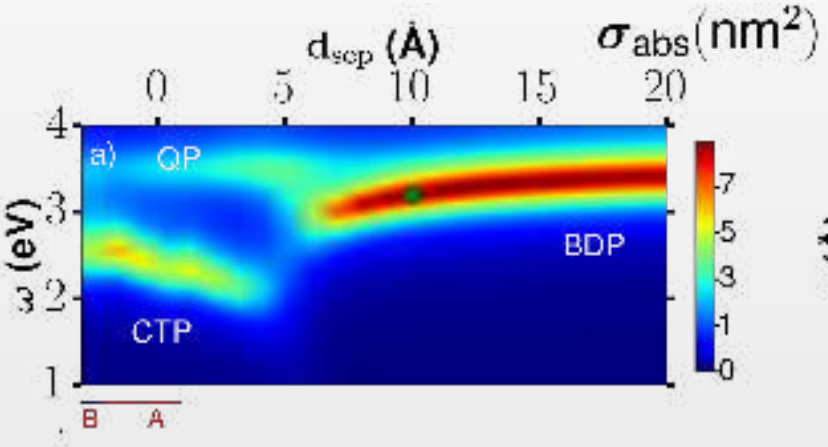

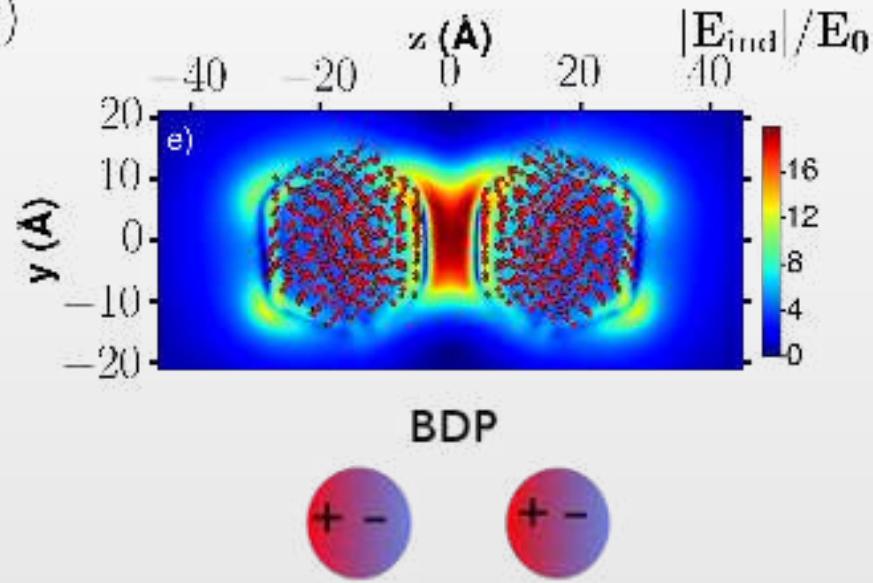

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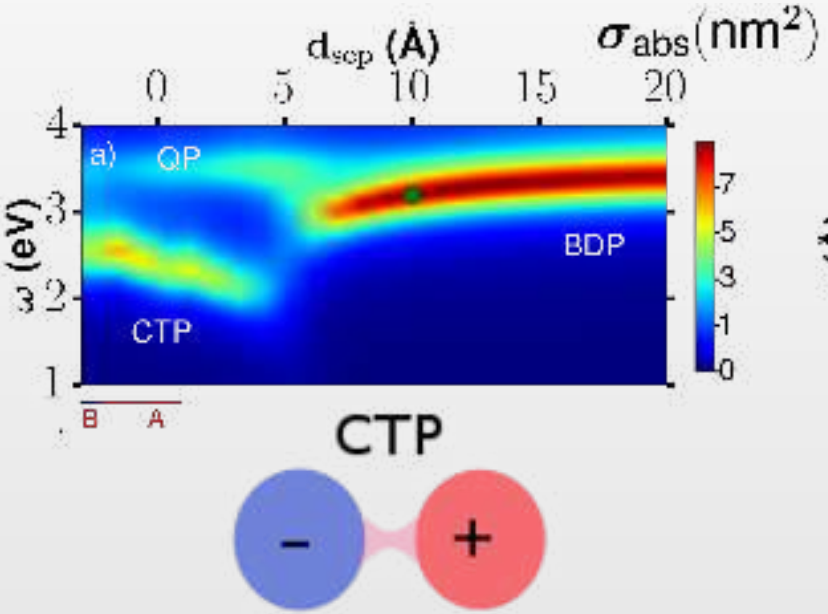

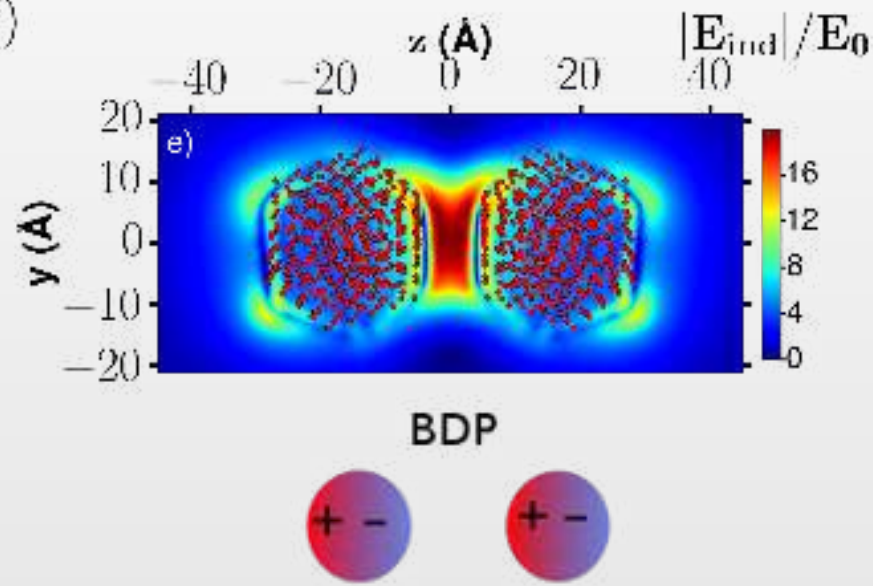

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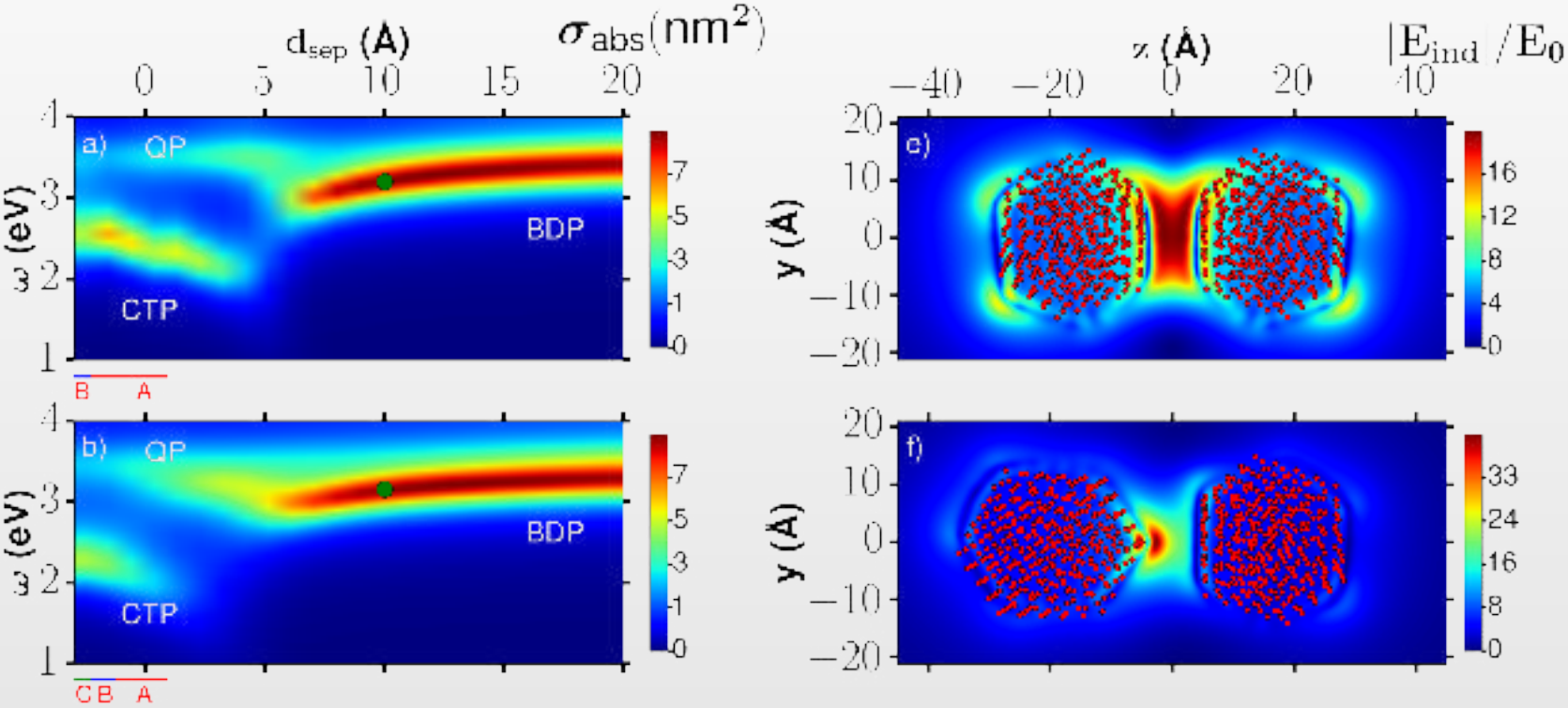
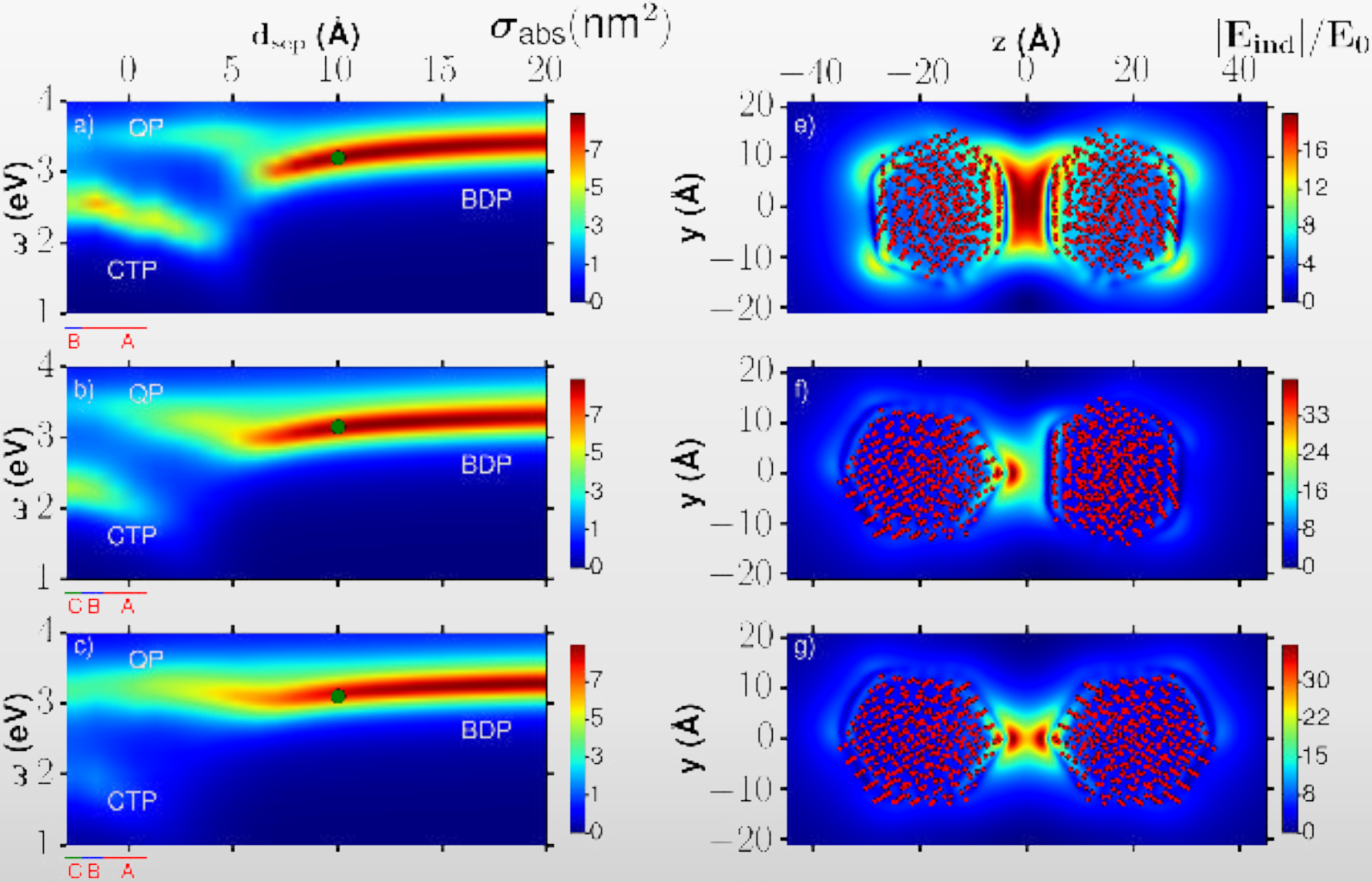
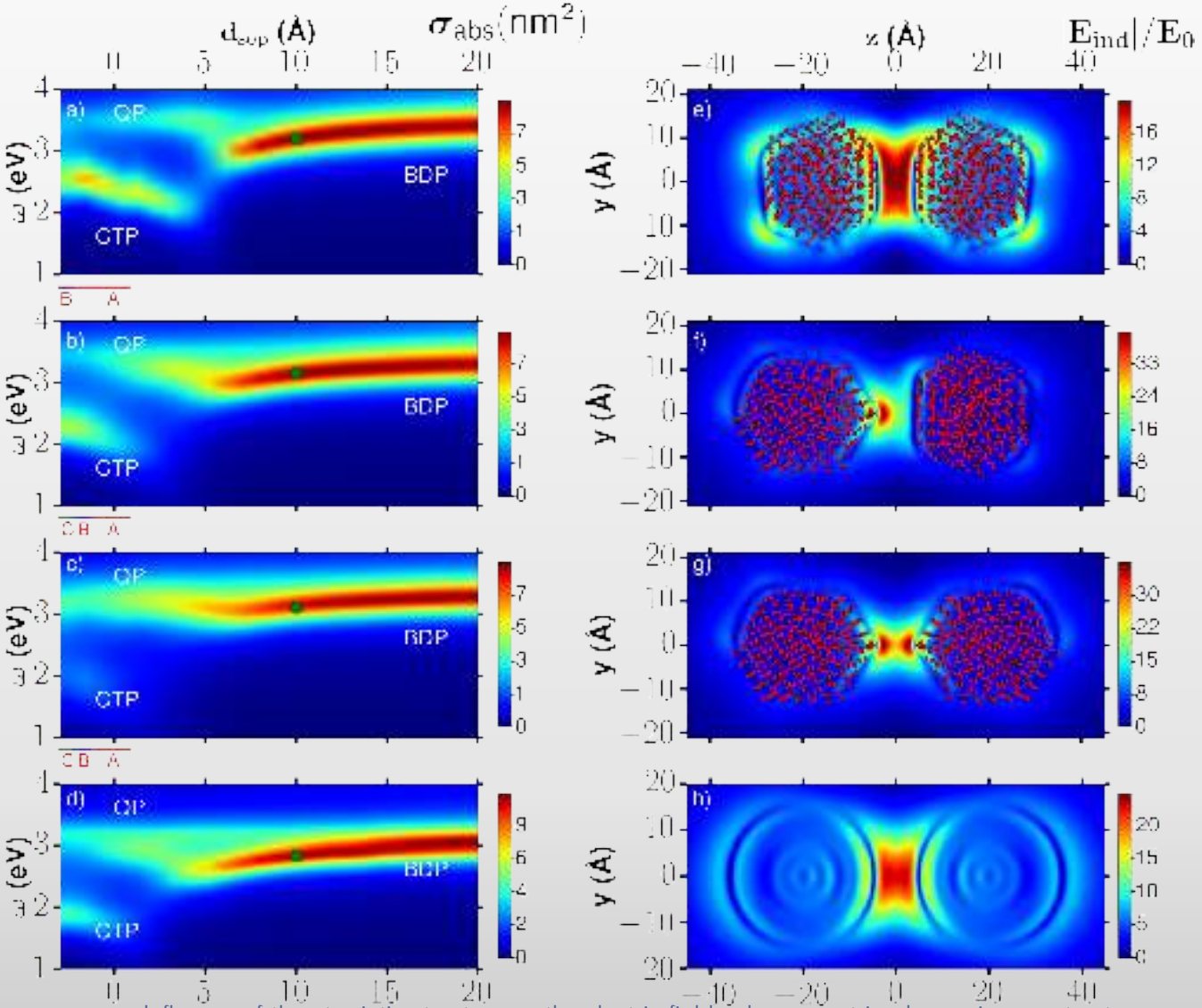


Far field and near field for Na_{380} [1]

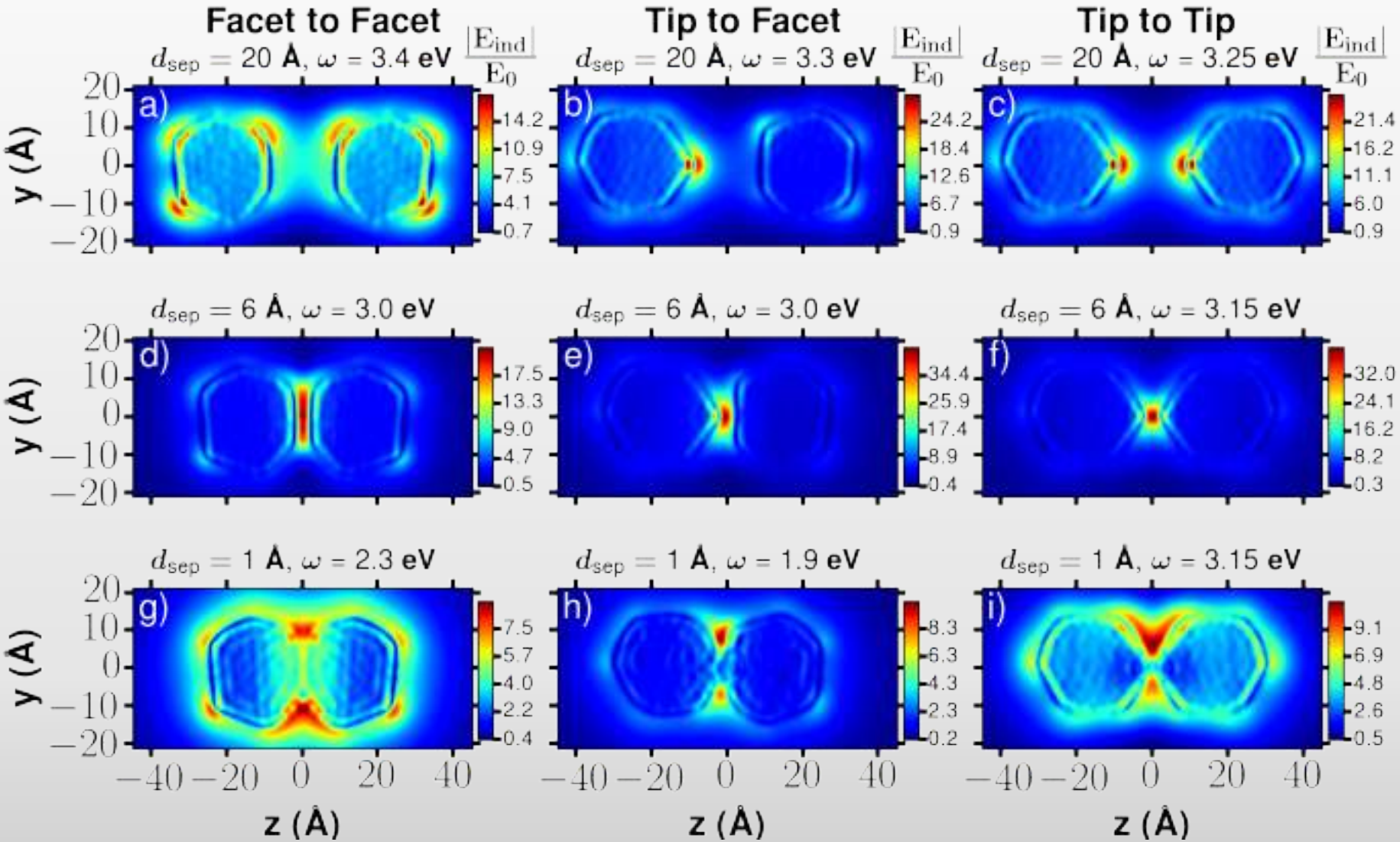


Far field and near field compared to Jellium for Na_{380}

- Facet to facet
- Tip to facet
- Tip to tip
- Jellium



The near field dependence of the Na_{380} with the clusters separation



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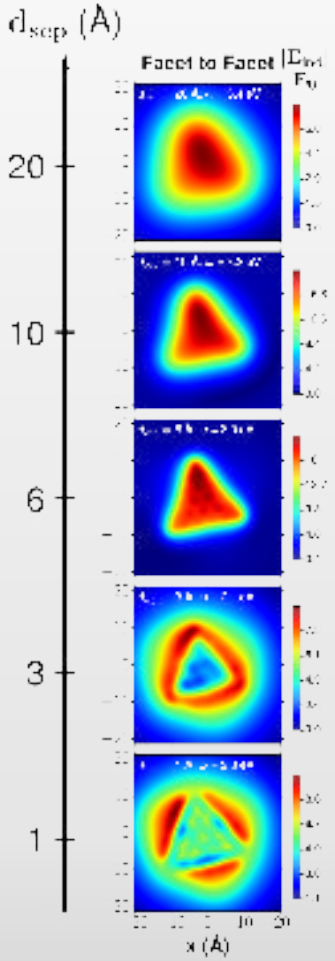

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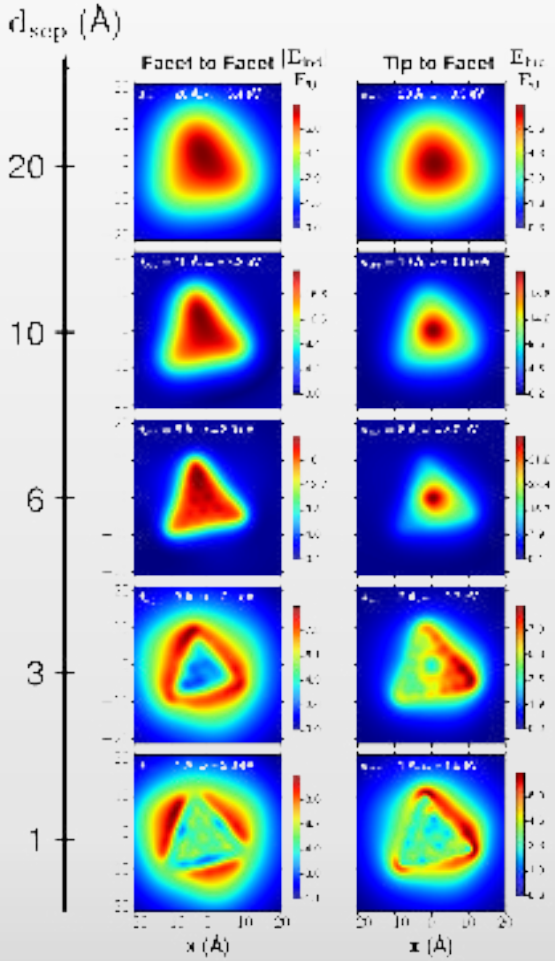

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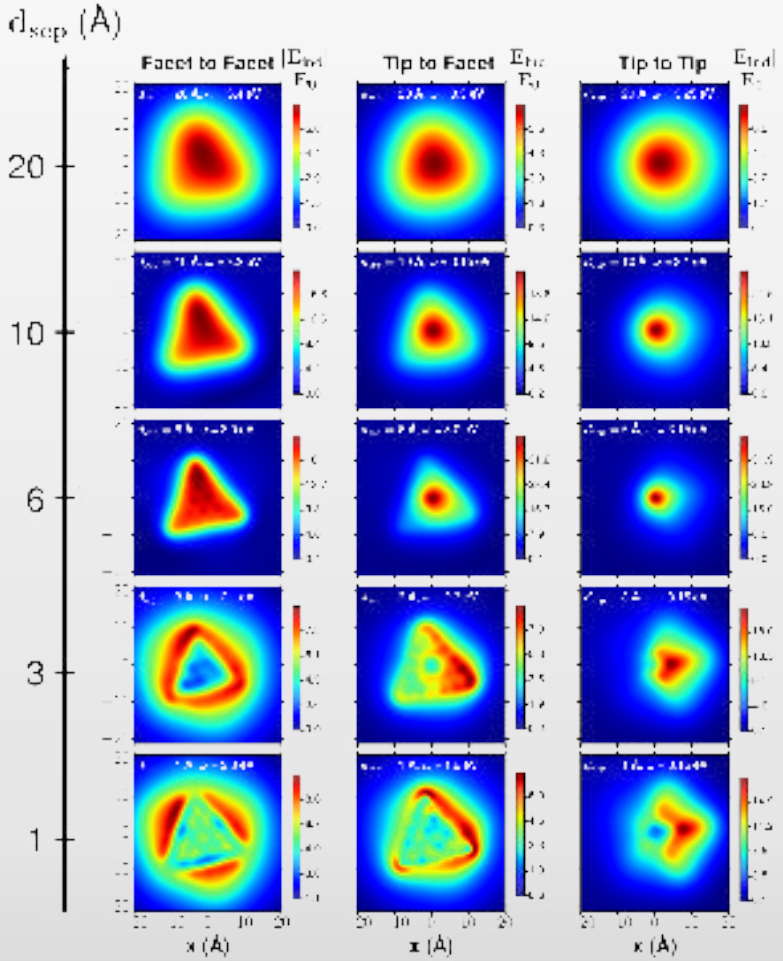

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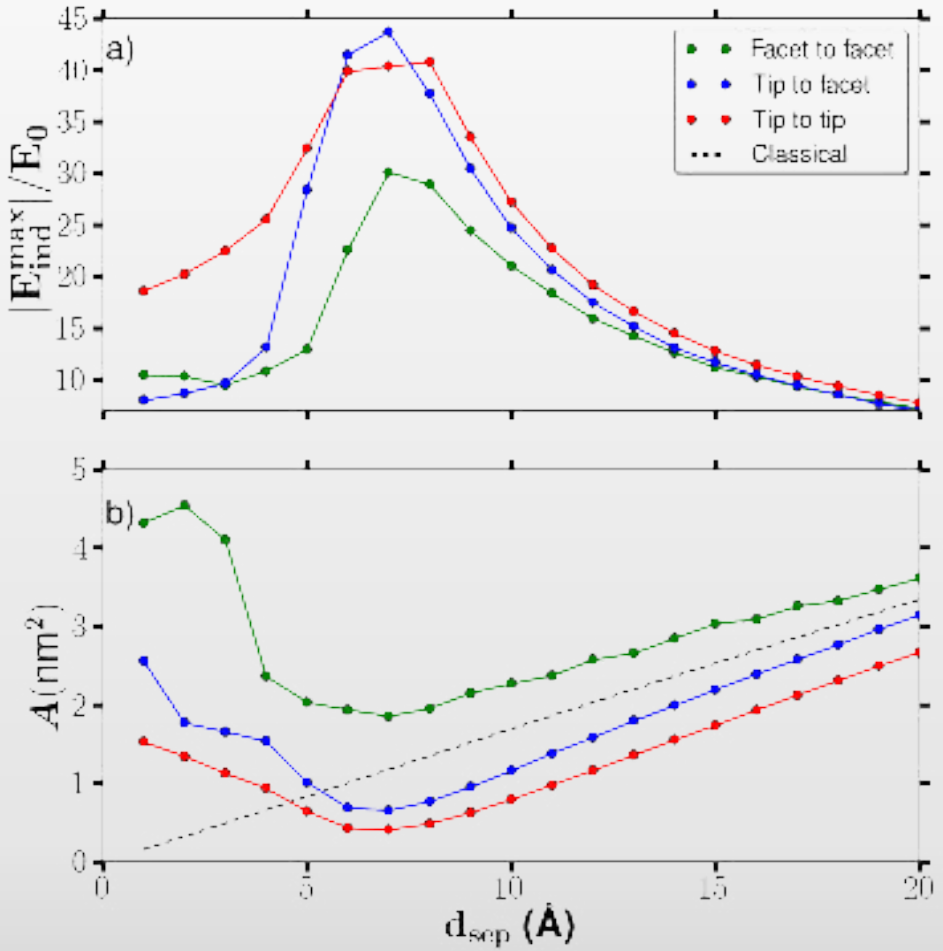
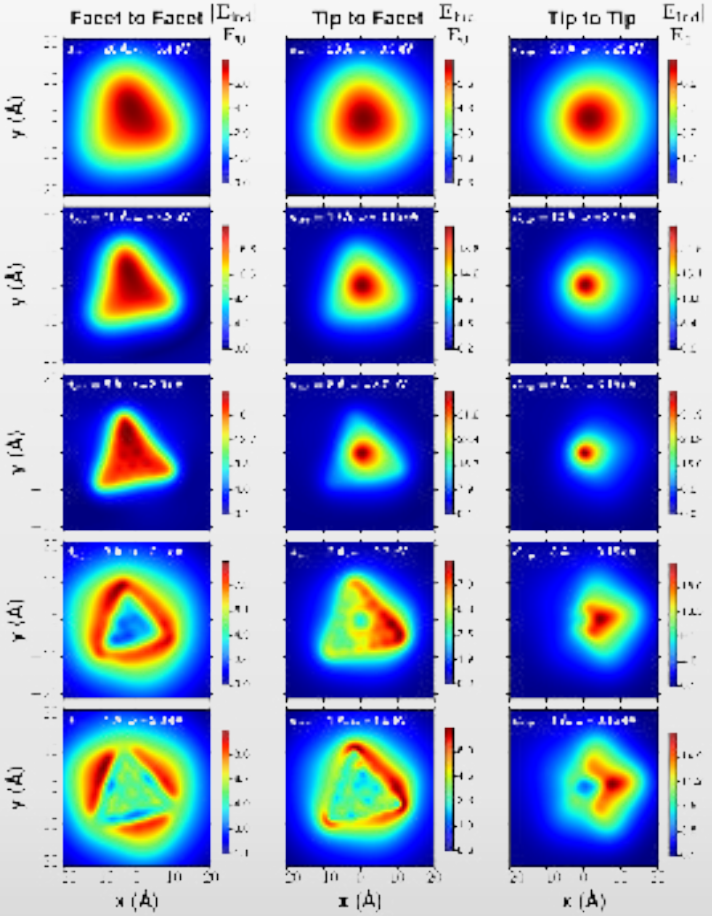
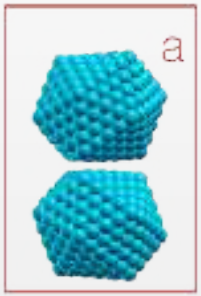
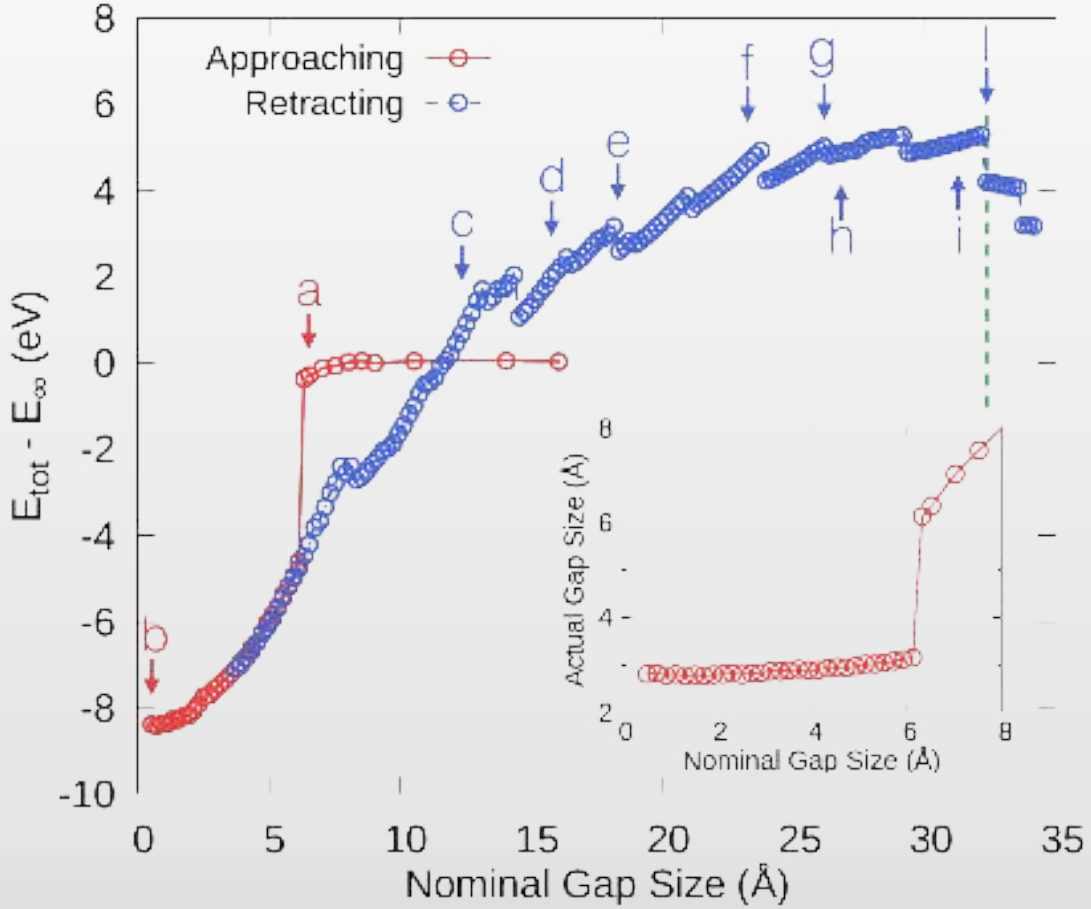
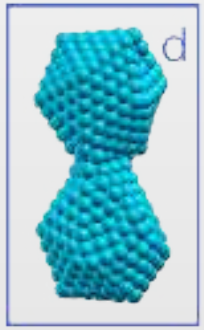




Clusters relaxation: jump to contact[1]







[1] F. Marchesin et al. ACS Photonics (2016)

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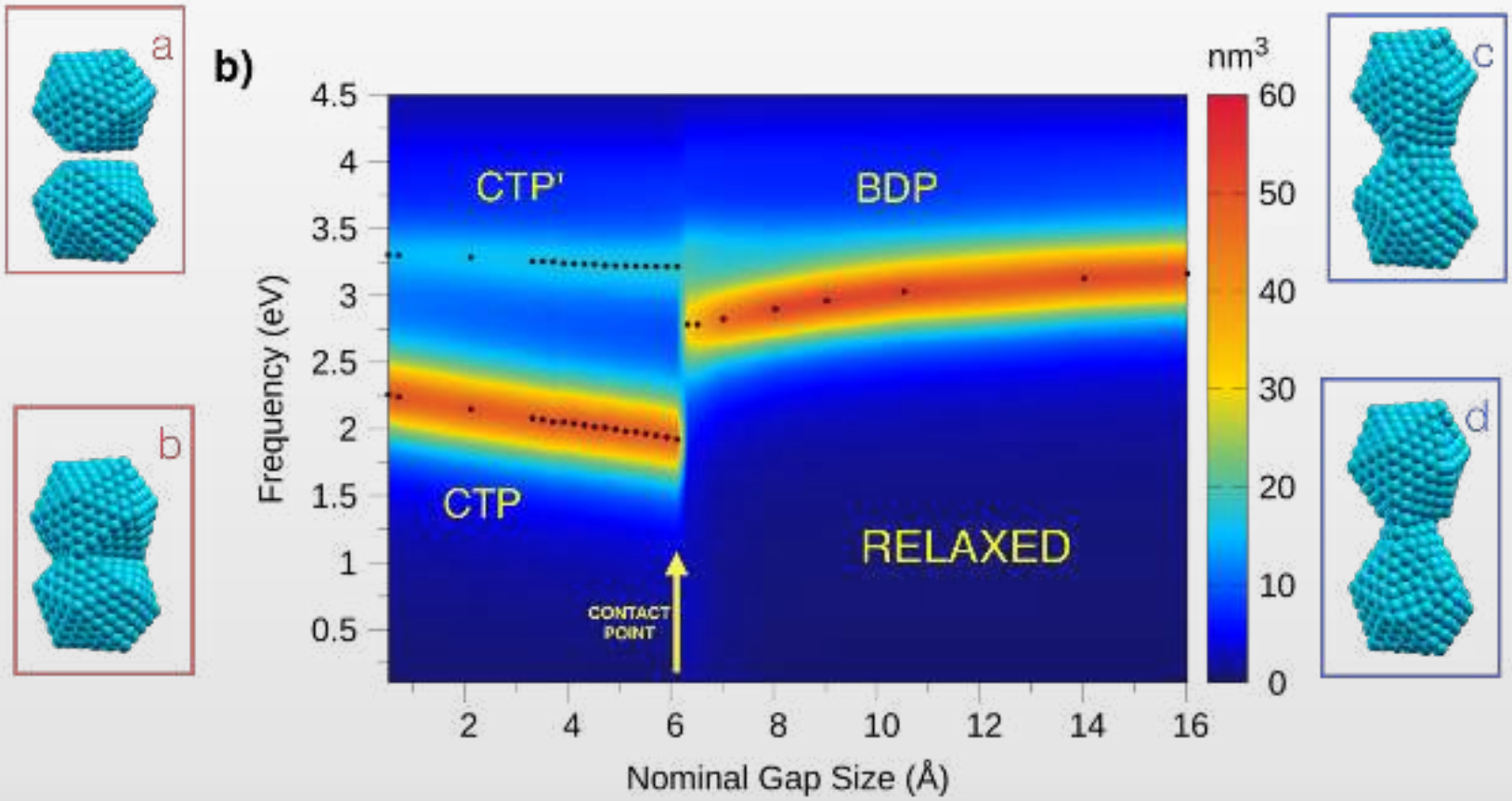

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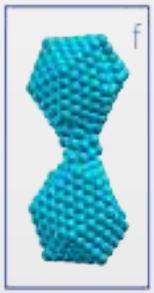
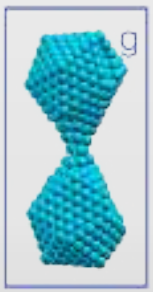
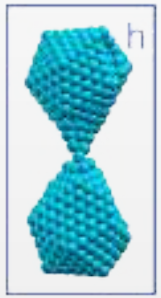
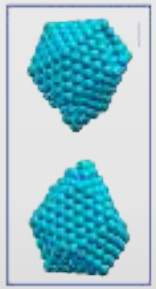
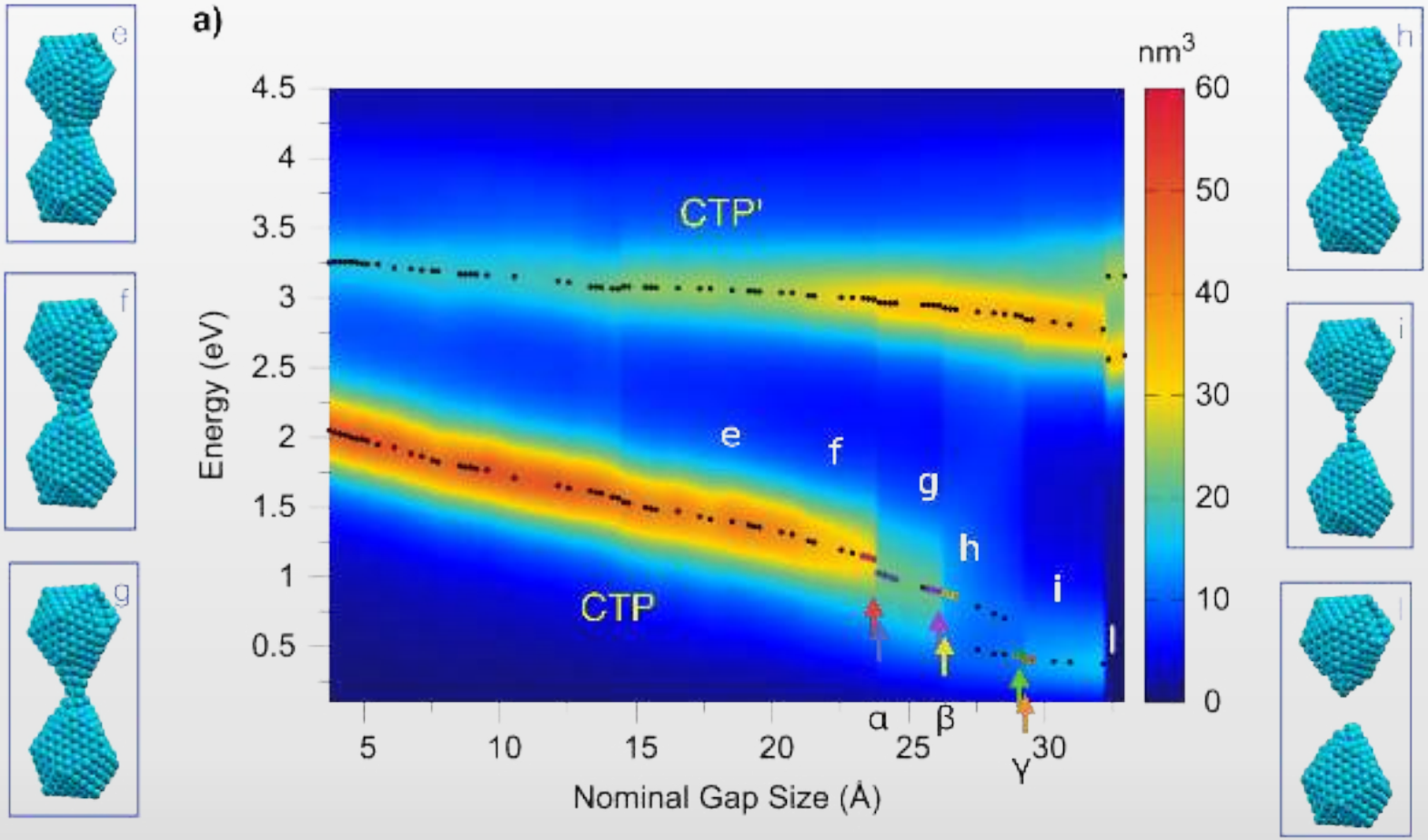








Clusters relaxation: cross section



Conclusion

Ab initio TDDFT calculations of realistic models for a plasmonic nanogap:

- Our model provides quantum mechanic atomic-scale resolution of the electric field enhancement in contrast to classic[1], jellium[2]and quantum corrected[3]models.
- Thanks to this resolution we demonstrate a large dependence of the electric field enhancement on the geometrical details of the nanogap.

Next Ideas:

- Introducing a molecule inside the dimer and perform Raman calculations.
- Performing EELS calculations based on the same model.

[1] Taylor, R. W. et al. ACS Nano 5, 3878-3887 (2011).

[2] Quijada, M. et al. Phys. Rev. A 75, 042902 (2007).

[3] Esteban R. et al. Nature comm. 3, 825 (2012)

[4] F. Marchesin et al. ACS Photonics (2016)

Acknolegements

THANK YOU



- Javier Aizpurua, Photonics group, Donostia
- Rubén Esteban , Photonics group, Donostia
- Andrei G. Borisov, Orsay, France

questions frame: TDDFT

Time-dependent Kohn-Sham equations

$$\left[-\frac{1}{2}\nabla^2 + V_{\text{eff}(r,t)}\right]\varphi_i(r,t) \quad = \quad i\frac{\partial}{\partial t}\varphi_i(r,t),$$

with the effective time-dependent potential,

$$V_{\text{eff}}(r,t) \quad = \quad V_{\text{ext}}(r,t) + \int \frac{n(r',t)}{|r-r'|}dr' + V_{\text{xc}}(r,t)$$

Fast Fourier Transform

$$E_{ind}(r,\omega) \quad = \quad -\text{FT}^{-1}\left(\text{FT}\left[\frac{r}{|r|^3}\right]\text{FT}\left[\delta n(r,\omega)\right]\right)$$

questions frame: Cross section and polarizability in linear response TDDFT

Cross section σ

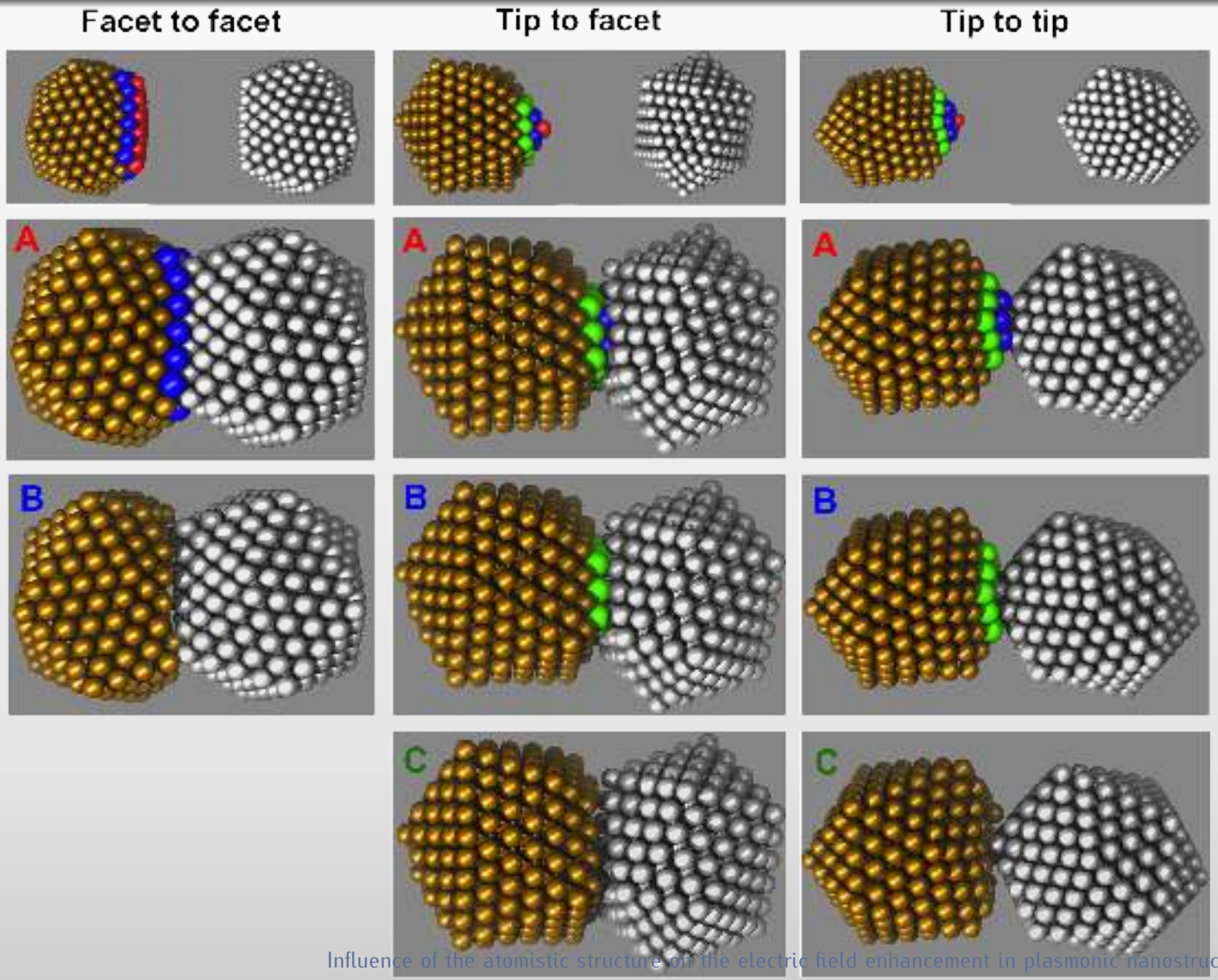
$$\sigma(\omega) = -\frac{4\pi\omega}{3c}\,\mathrm{Im}\left[P_{xx}(\omega) + P_{yy}(\omega) + P_{zz}(\omega)\right]$$

$$\text{with} \quad P_{ij}(\omega) = \int r_i \chi(r, r', \omega) r'_j \, dr dr'$$

Confinement A

$$A = \int_S \frac{|E_{\mathrm{enh}}(x, y_0, z)|^2}{|E_{\mathrm{enh}}^{\max}|^2} dx dz$$

questions frame: Interpenetration of the clusters



questions frame: Comparison to classical model