First-principles nanoplasmonics on metal-clusters dimers

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Introduction and objetives

- **Metal-cluster dimers** are a prototypical scenario for quantum plasmonics. The well-known hybridization of localized surface plasmons (LSPs) is strongly affected by the appearance of light-induced currents between the nanoparticles, breaking down the predictions of classical optics [1].

Absorption cross section of metallic-cluster dimer (arb. units)
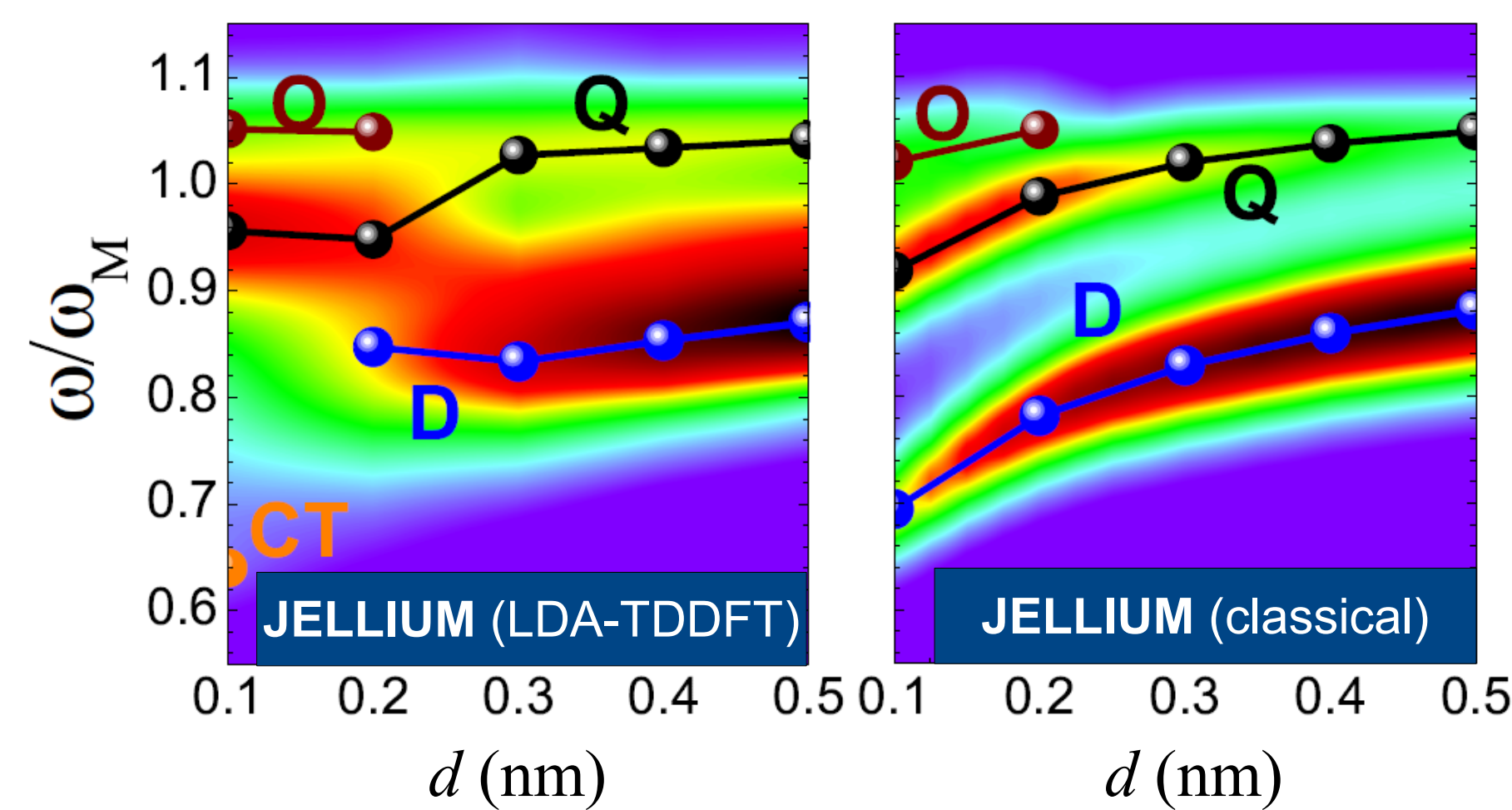
- The main trends can be well understood using the jellium model and time-dependent density functional theory (TDDFT). However, atomic structure has to be consider to have results with enough predictive accuracy [2].

- In this work we provide further insights on the importance of the atomic structure, including effects due to the relative orientation of the atoms and relaxation of the atoms in the gap region.

Setup and method

- We analize the optical response of Na_{297} icosahedral clusters dimers with two different relative orientations, edge-to-edge (E2E) and face-to-face (F2F), varying the distance between them. The structure of the atoms around the gap region is optimized in the E2E case.
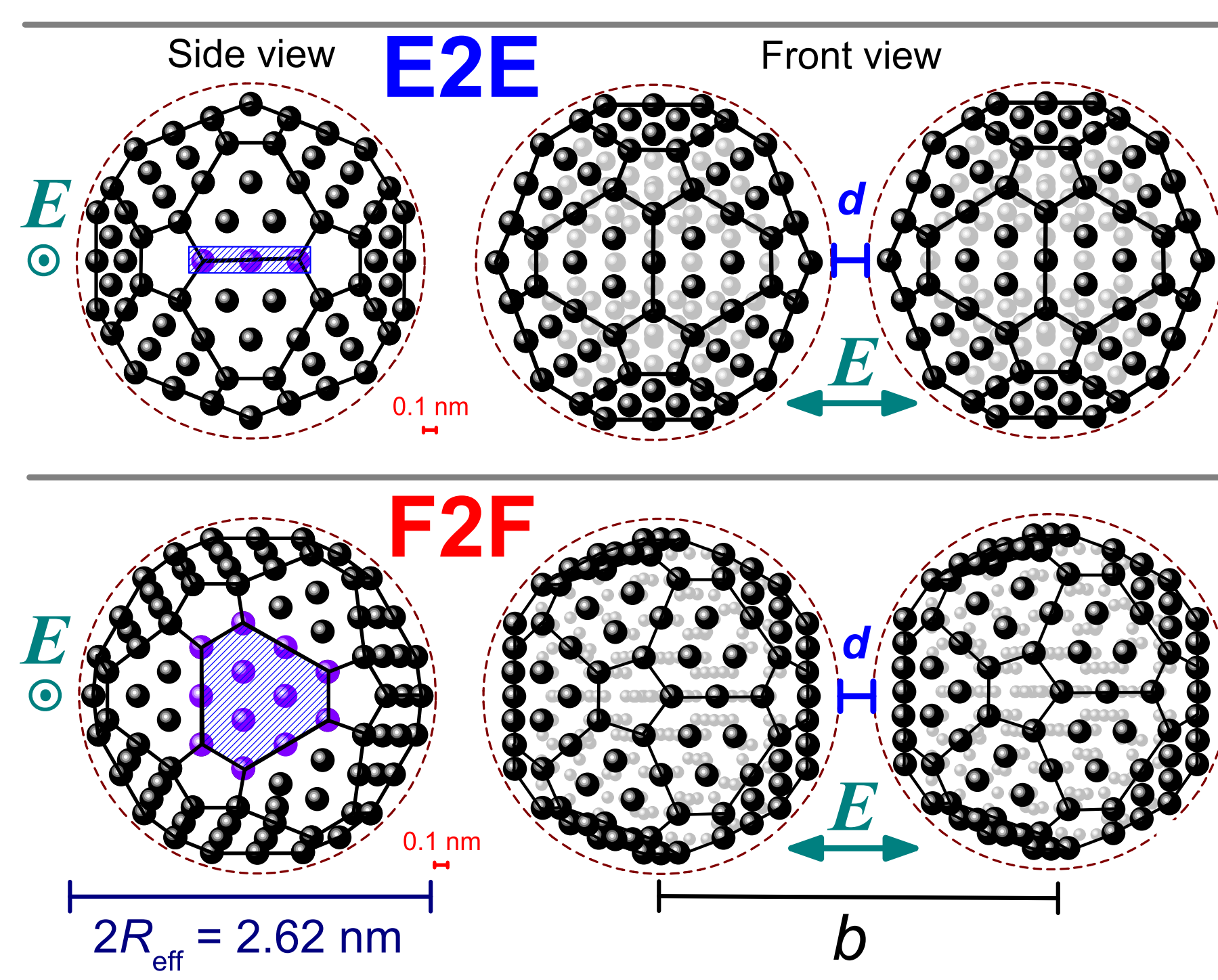

- We define the distance between the clusters as $d = b - 2R$, where b is the distance between the center of the clusters, and $2R = 2.62$ nm is an effective cluster diameter. We focus on the range $d \leq 0.6$ nm, where charge transfer (CT) between the clusters is not negligible.

- The optical response is evaluated using TDDFT under the adiabatic local density approximation (LDA). Only the $3s$ conduction electrons are explicitly included in the calculations by using standard norm-conserving Troullier-Martins pseudopotentials. The calculations were performed in real space and real time using the Octopus [3] code.

Optical absorption

- First we evaluate the **optical absorption spectra** for both F2F and E2E orientations.

a) *Minor differences:* $d \geq 0.6$ nm.

b) *Minor differences:* $d \leq 0.1$ nm.

c) *Orientation matters:* 0.1 nm $< d < 0.6$ nm.
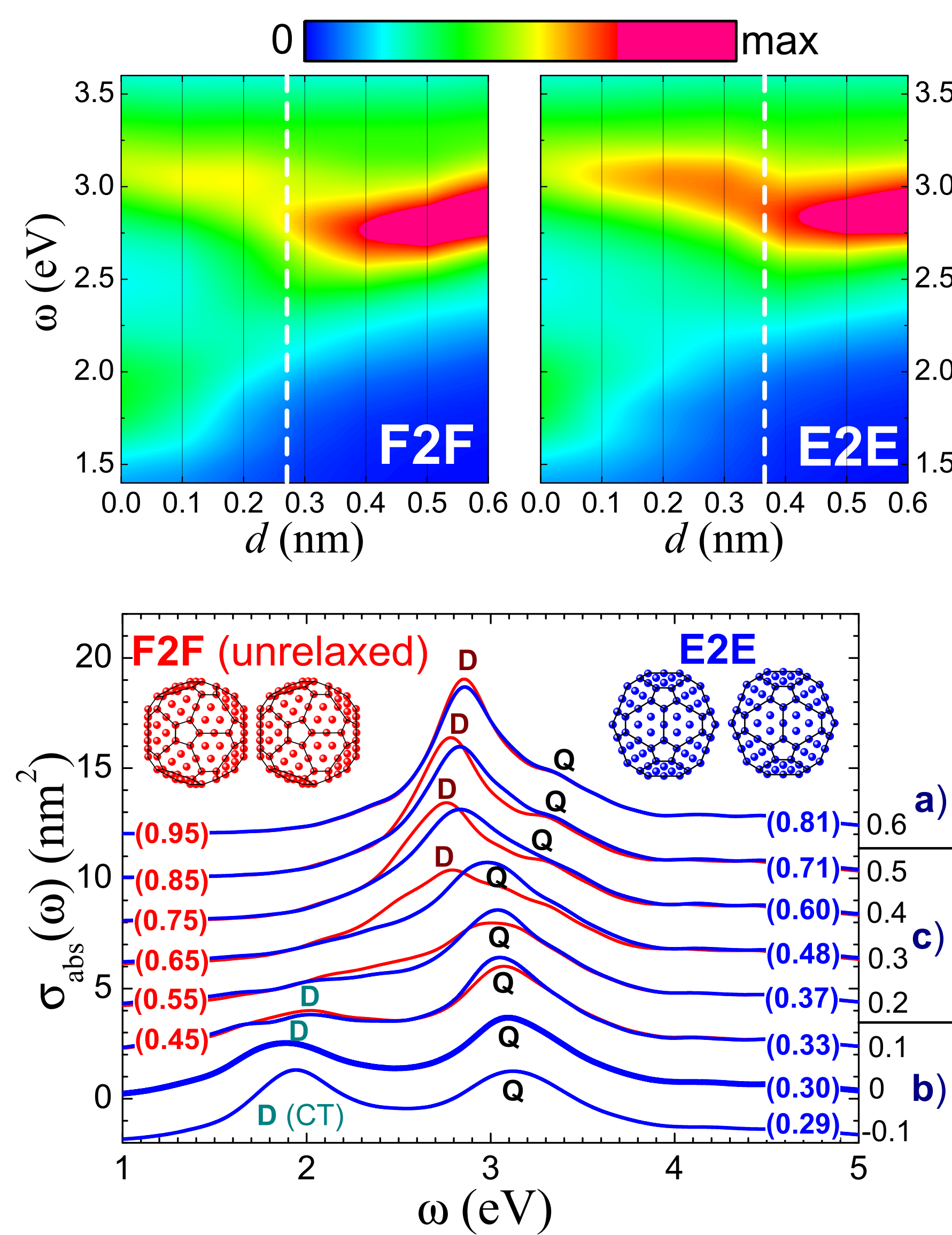
Optical absorption vs distance

* **a):** Negligible CT. The relative orientation does not affect the hybridization.

* **b):** Overlap of ground-state densities. The system behaves as a single "peanut-like" nanoparticle.

* **c):** Changes in the CT-current intensities and in the near fields. The D mode is dominant in the F2F (E2E) orientation if $d > 0.3$ nm (0.4 nm). **This can be only predicted after a full account of the atomic structure in the gap region.**
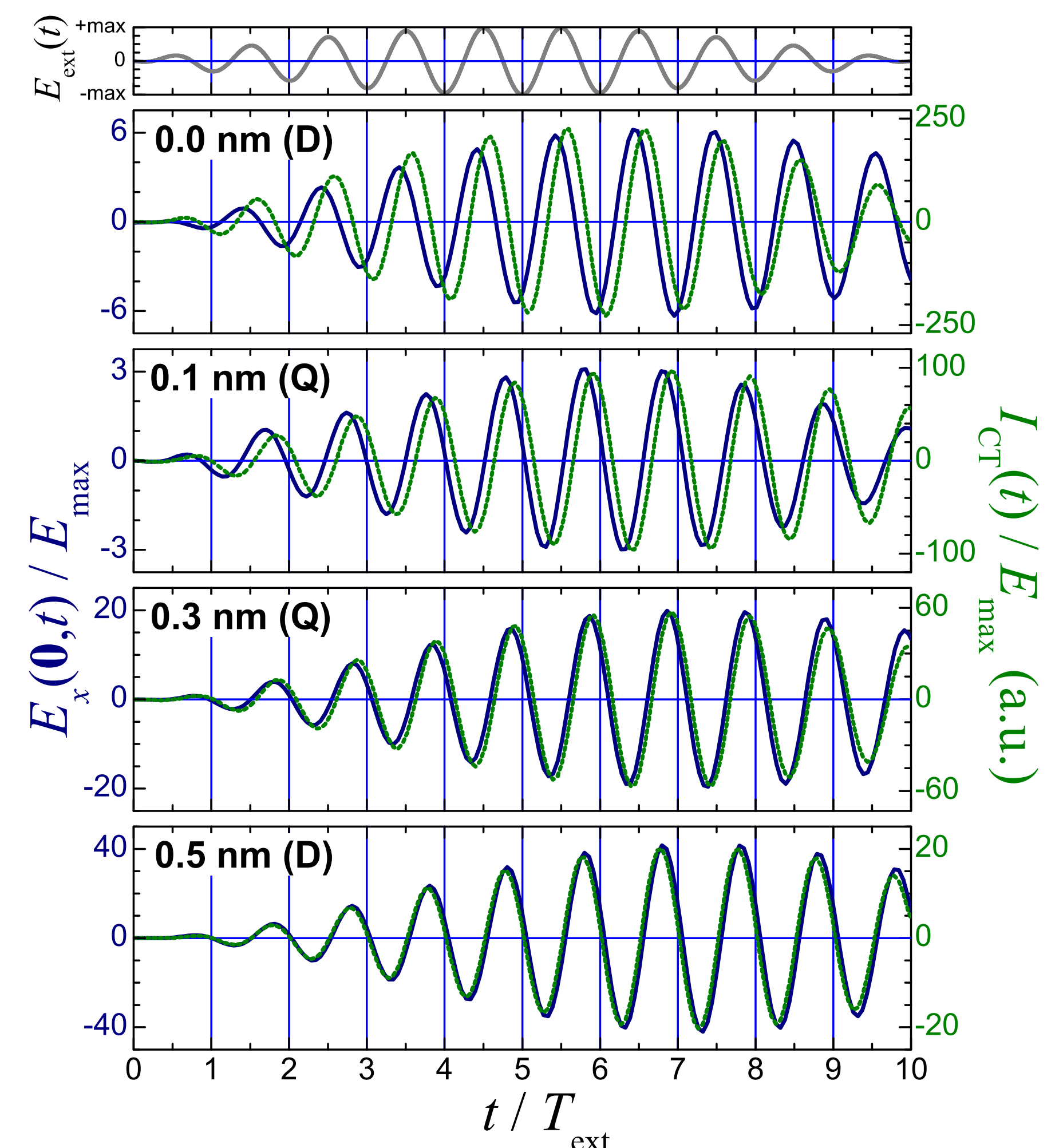
$d = 0.1$ nm (D)

$d = 0.1$ nm (Q)
$d = 0.4$ nm (D)

maximum I_{CT} $I_{CT} = 0$
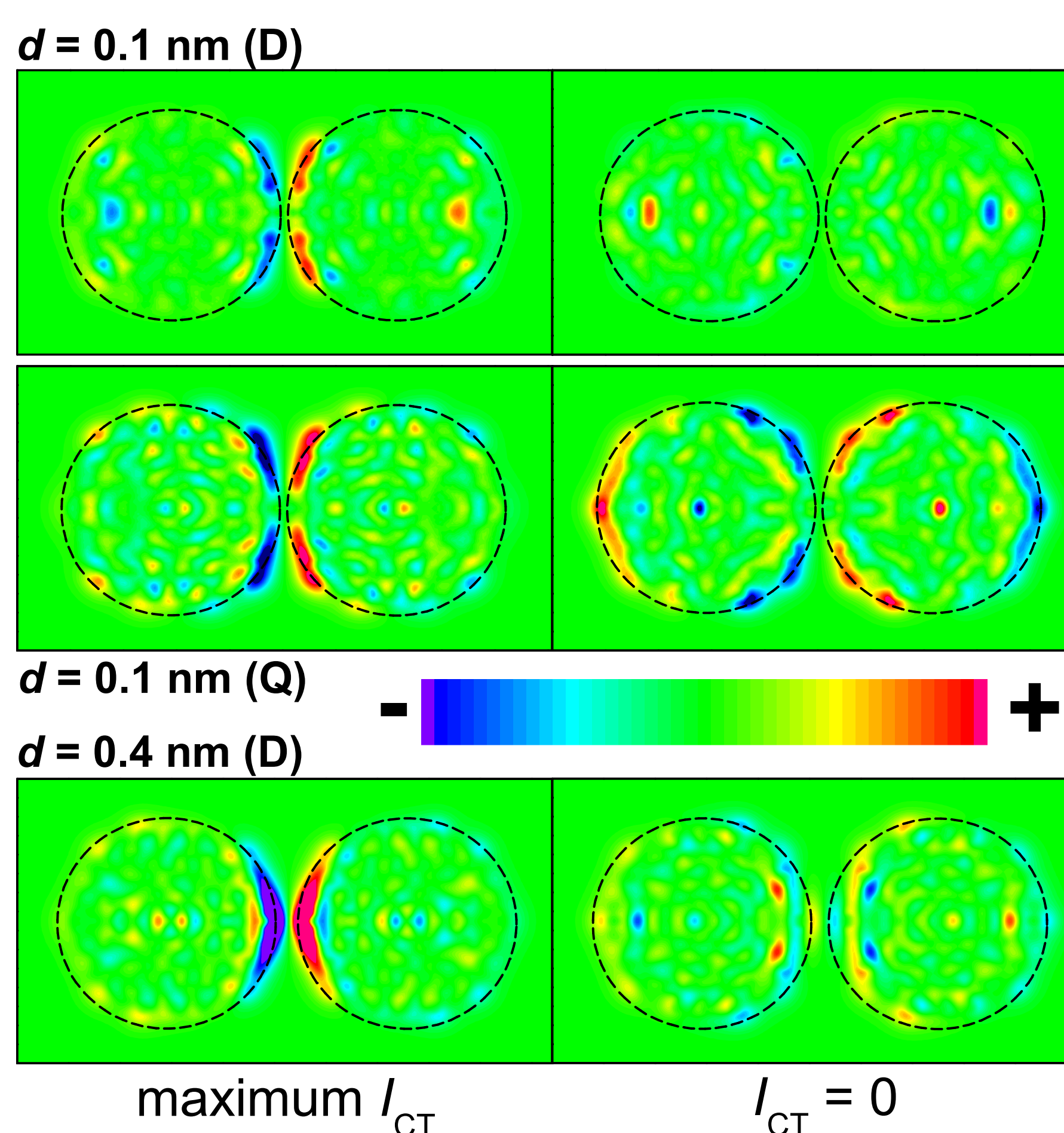
Snapshots of driven induced densities (E2E)

CT current and E field

- We now analyze the resonant **CT intensities** and the **E-field enhancement** for selected modes.

a) Charge-transfer modes (D,Q) $[d \leq 0.1$ nm$]$.

b) "Tunnelling" mode (Q) $[d = 0.3$ nm$]$.

c) Coupled D mode (weak CT) $[d = 0.5$ nm$]$.

CT intensities and total E field at O (E2E)

* In **a):** Conductive charge transfer. Note the different phase shifts in D and Q.

* In **b):** Main Q mode after the quenching of the D mode. The dynamics are strongly linked with the induced tunnel current.

* In **c):** Main D mode slightly influenced by weak tunnelling.

The different atomic arrangement (E2E and F2F) are manifest in case **b).** At that distance the main mode is D for the F2F orientation.

Conclusions

By using *ab initio* TDDFT calculations we analyze the optical response of metal nanoparticle dimers, demonstrating that the relative orientation of the clusters play a key role in the absorption cross section when 0.2 nm $\leq d \leq 0.5$ nm. This sensitivity to the atomic arrangement in the nanojunction paves the way to further studies relevant for molecular optoelectronics and nanosensing.

Acknowledgments

References

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