A time-dependent functional theory study of the interaction between molecules and the electronically excited materials

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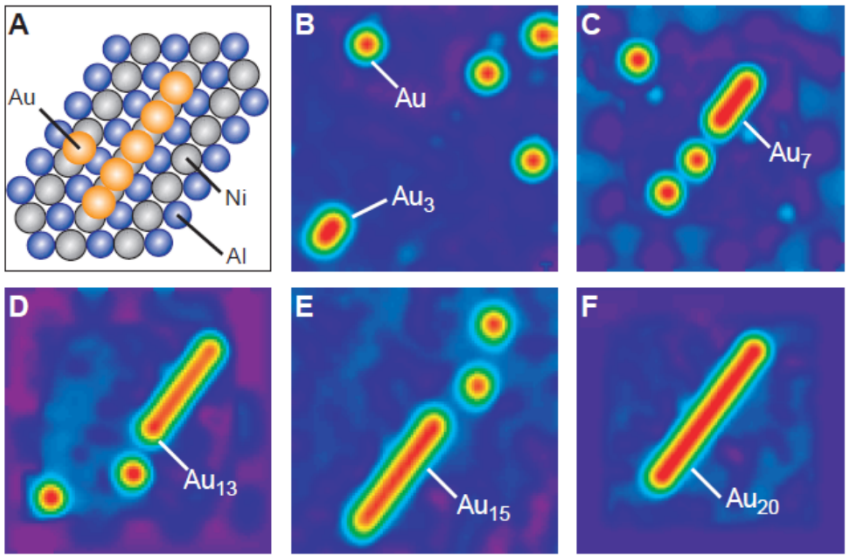
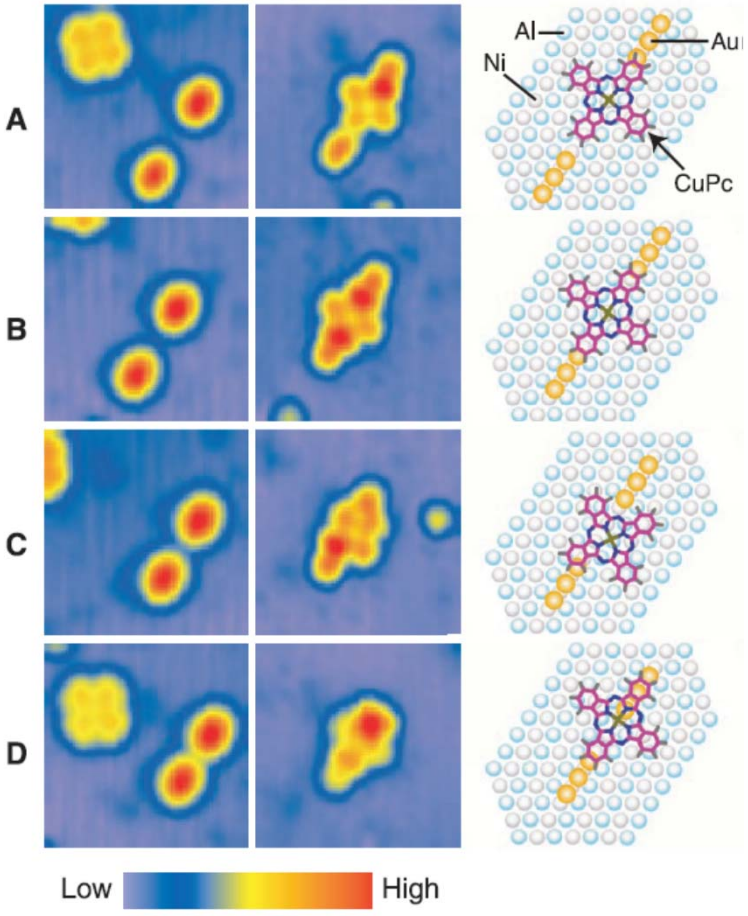
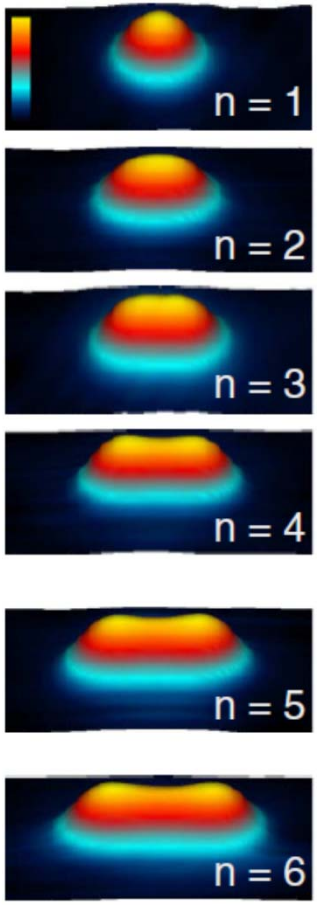
Recent progress of atomic manipulation techniques



W. Ho et al, Science 297, 1853 (2002)



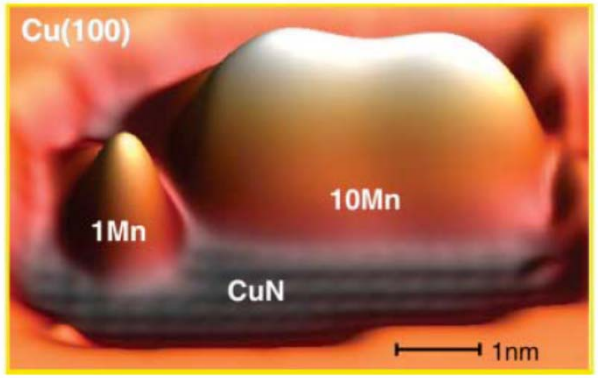
W. Ho Science 302, 77 (2003)



Neel et al, PRL 107,106804 (2011)

CoCunCo

Kondo effect



Hirjibehedin et al. Science 312, 1021 (2006)

Possible applications of atom manipulation techniques to optical properties of molecules

Enhanced absorption of molecules near Metal clusters

Surface enhanced electronic excitations
Surface enhanced IR absorption

Surface enhanced fluorescence

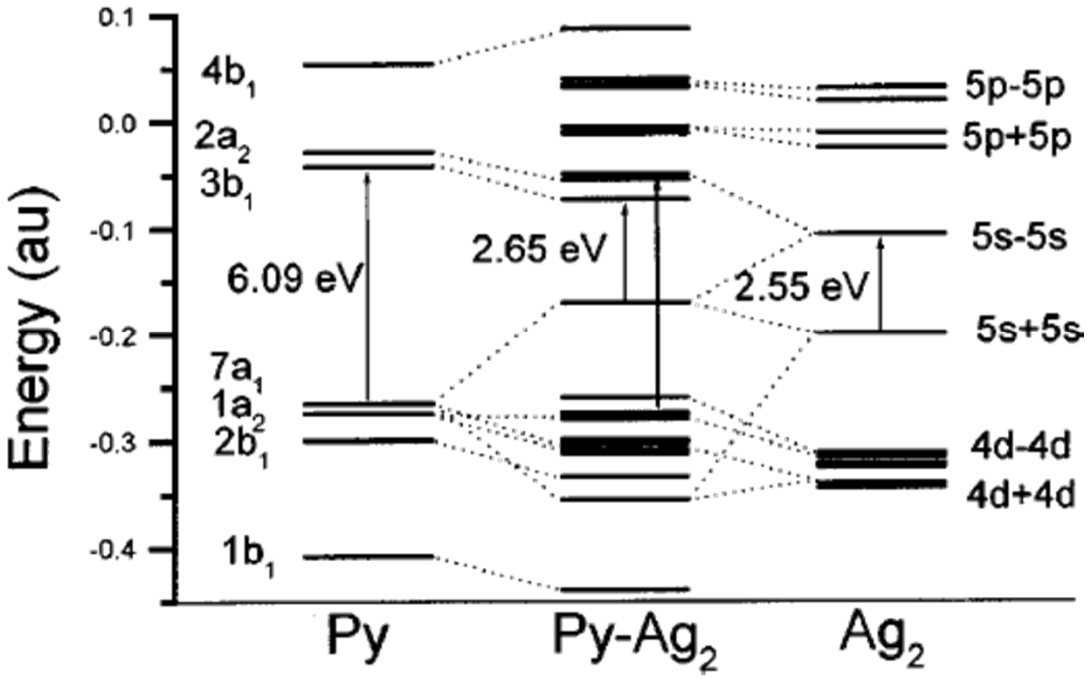
Surface enhanced Raman scattering

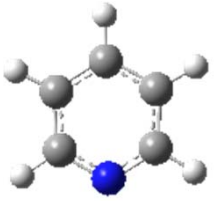
Surface enhanced nonlinear optical properties

L. Jensen et al. Chem. Rev. 111, 3962, (2011)

Molecule-metal atom chain interactions

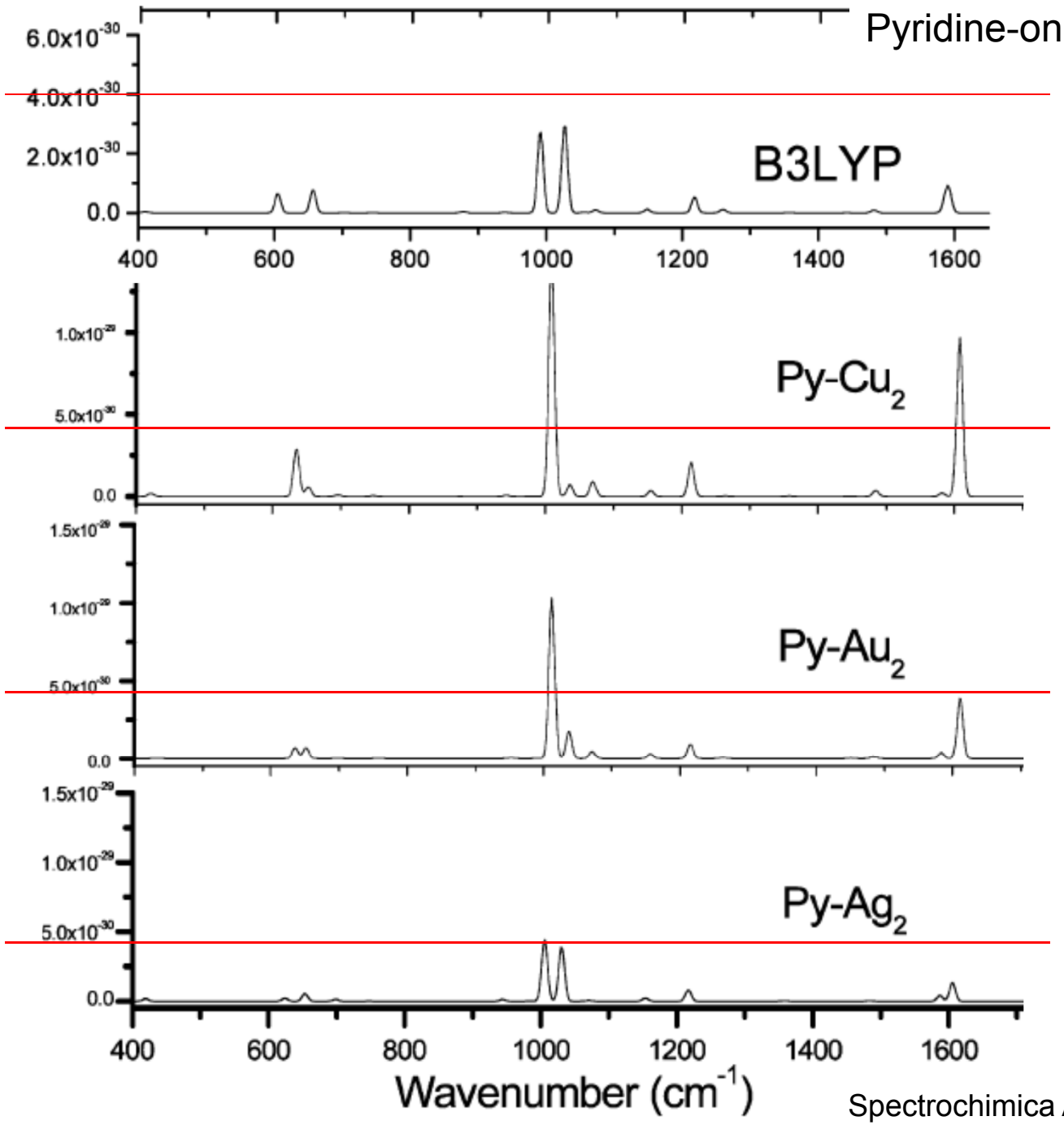
Indication of formation of charge–transfer states

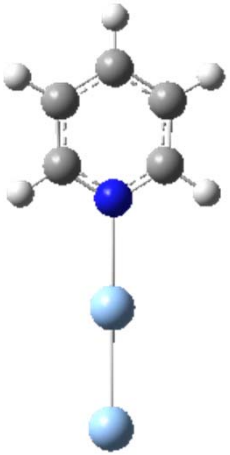




Pyridine

JCP 118, (**2003**) 4073





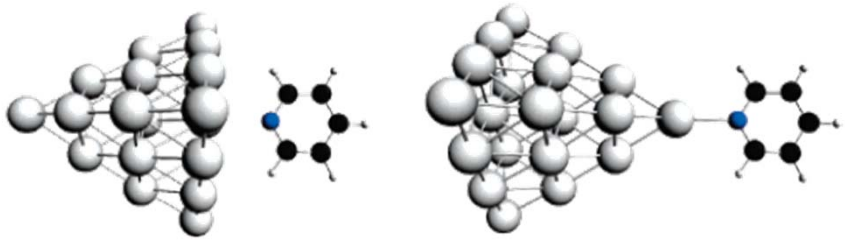
"Static"-Raman

Spectrochimica Acta Part A 60 (**2004**) 137

George C. Schatz

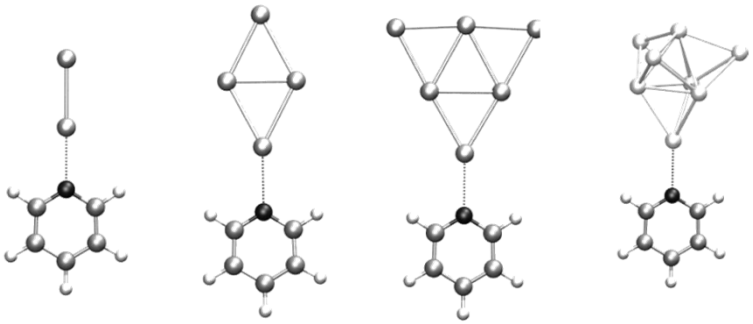
JACS **2006**, 128, 2911, Nano letters **2006**, 1229

Ag_{20}



SERS
10^5 enhancement
TDDFT with
short time appro.
Raman

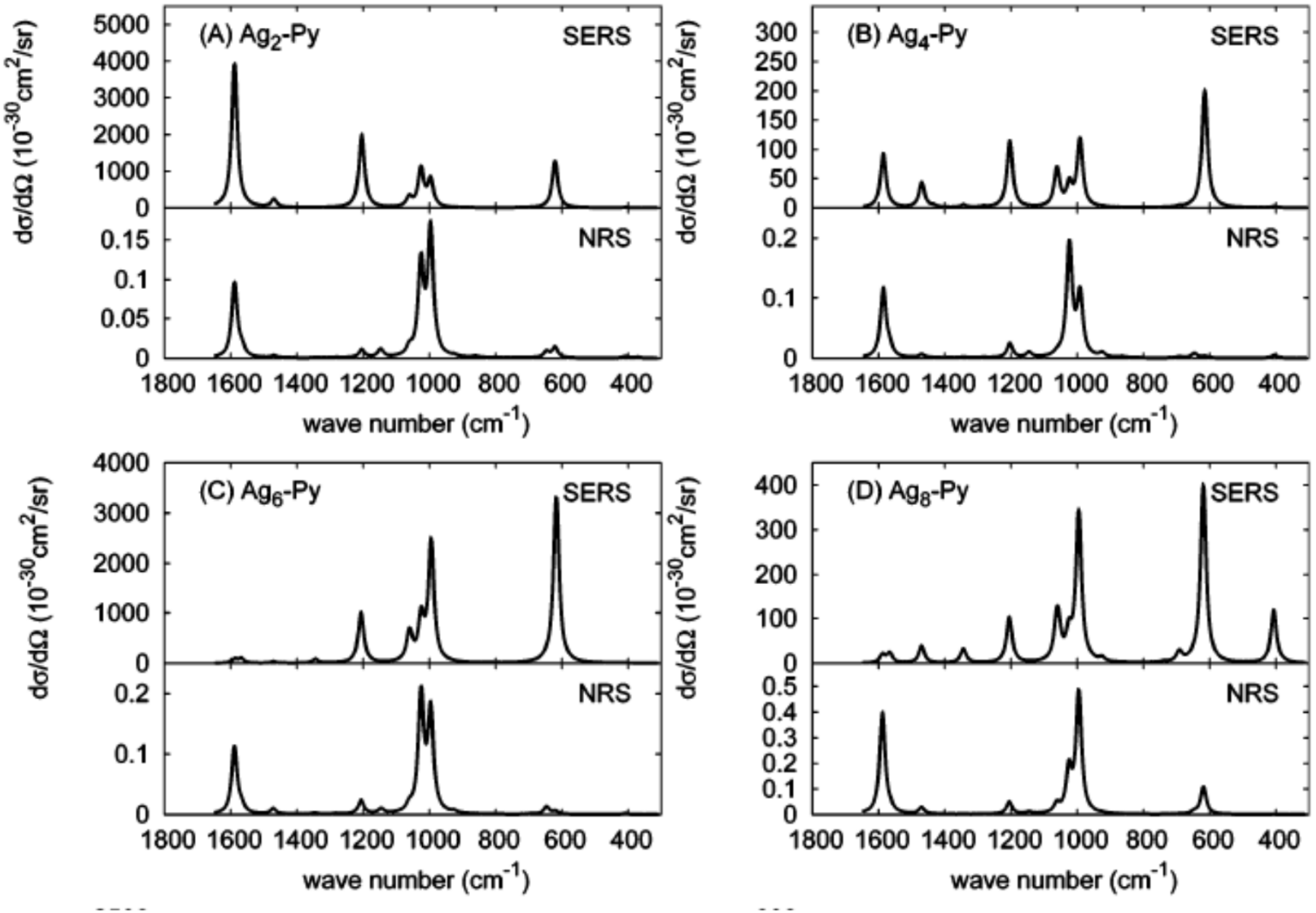
J. Phys. Chem. C **2007,** *111,* 4756



SERS
10^4 enhancement
TDDFT with
short time appro.
Raman

J. Phys. Chem. C **2008,** *112,* 11272–11279

Electronic excitation of Ag_n 10, 20, 35, 56, 84,120 (Tetrahedral Clusters)



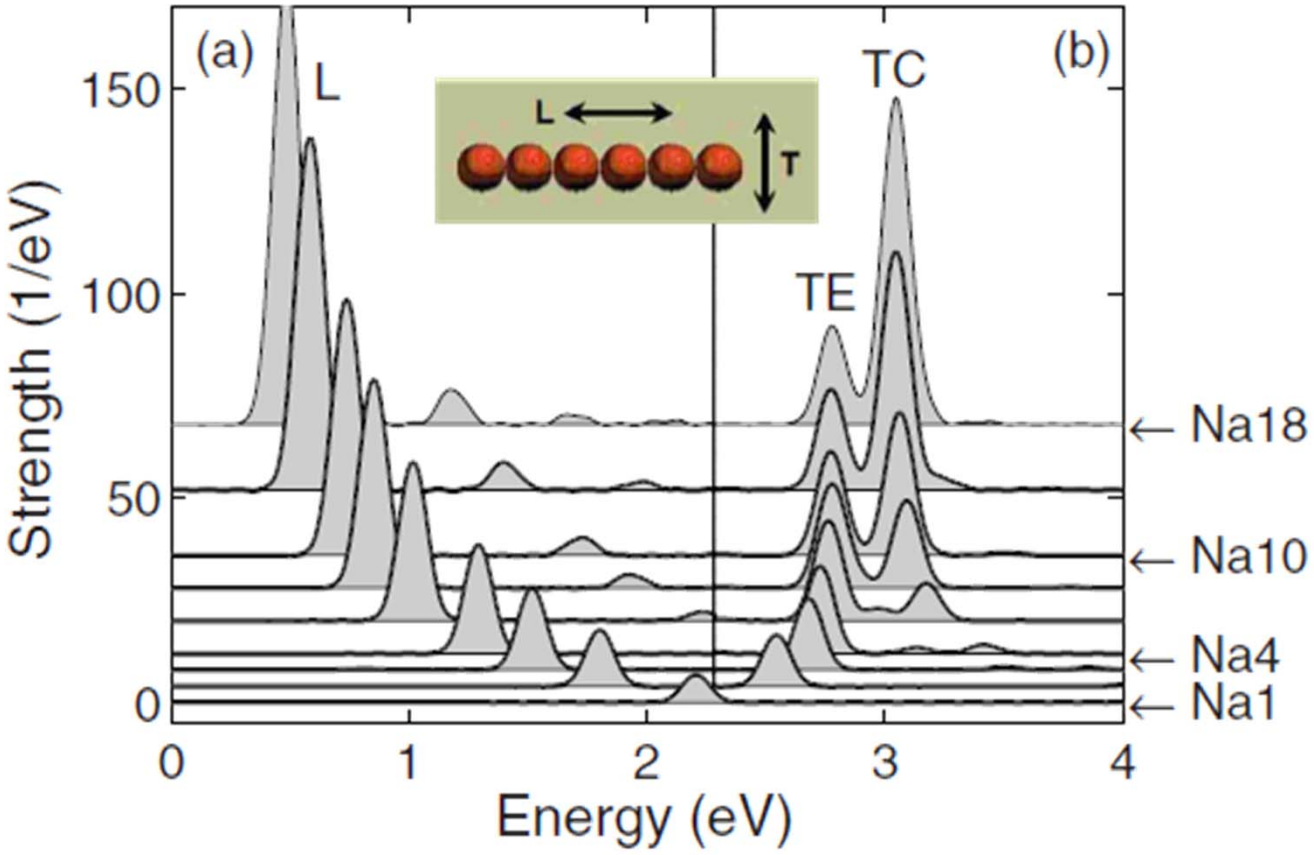
10^4-10^5 enhancement

Fundamental understanding of how plasmonic excitations of metal clusters affect Raman intensity of the molecule is not clear.

Collective or non-collective?

What is the plasmonic excitations of “finite systems”?

End and Central Plasmon Resonances in Linear Atomic Chains

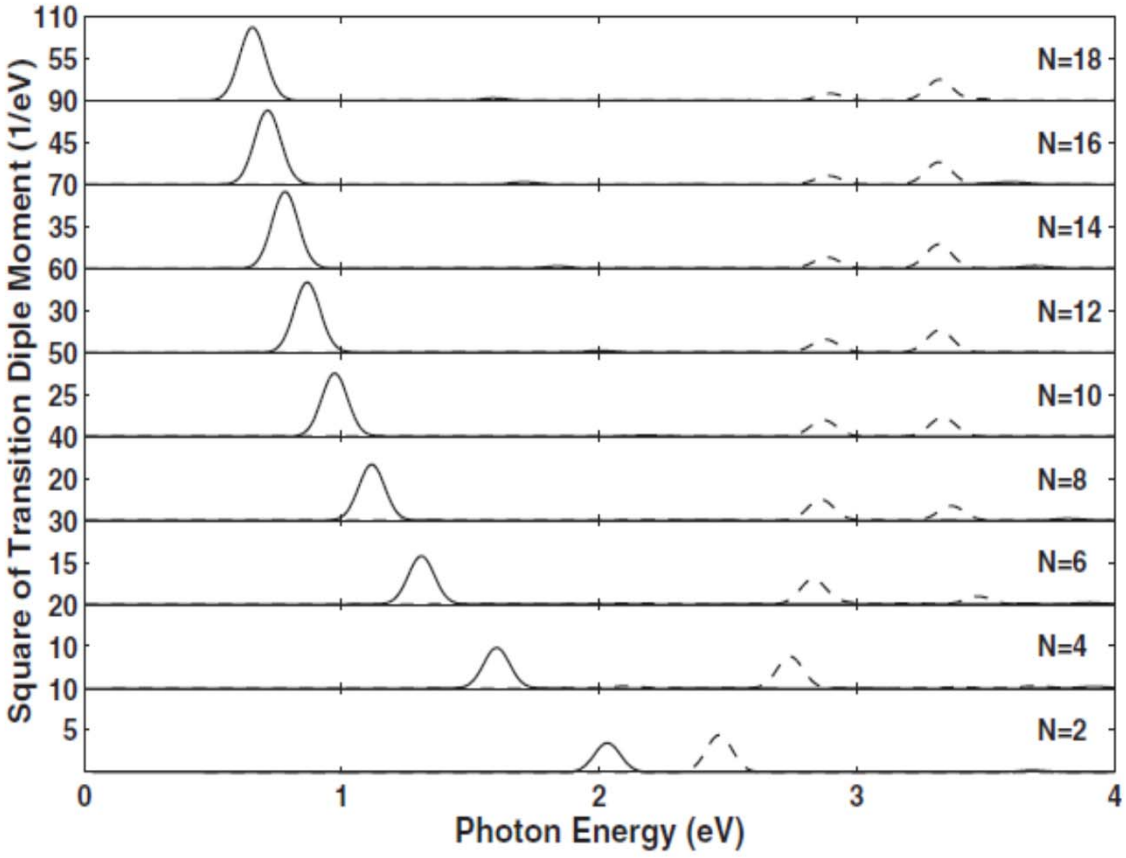


J. Yan and S. Gao PRB 78 (2008)
J. Yan, Z. Yuan, S. Gao, PRL 98 (2007)

TDDFT in real time & real space

Institute of Physics, Chinese Academy of Sciences

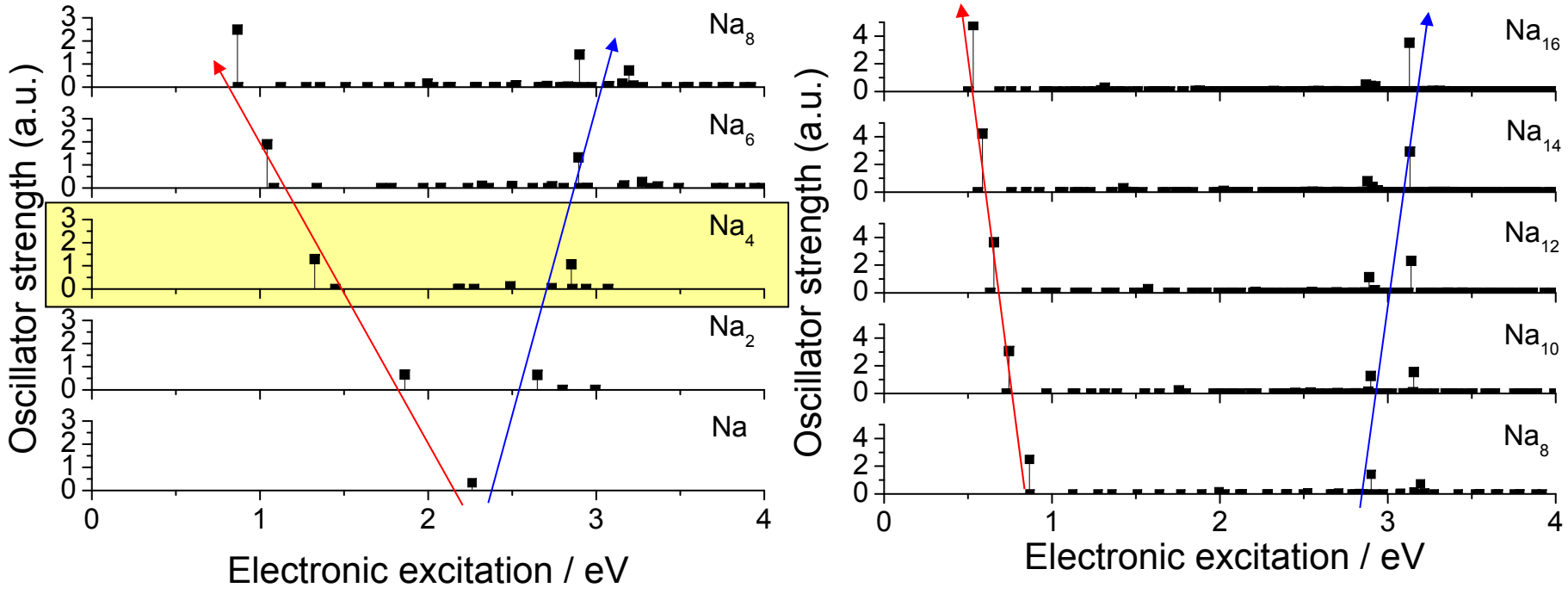
Optical absorption of Na chain clusters



Linear-response theory-TDDFT PW91,LANL2DZ

K.-Y. Lian, P. Sałek,.M. Jin, D. Ding, J. Chem. Phys. **130**, 174701 (2009)

Formation of plasmon-like excitation

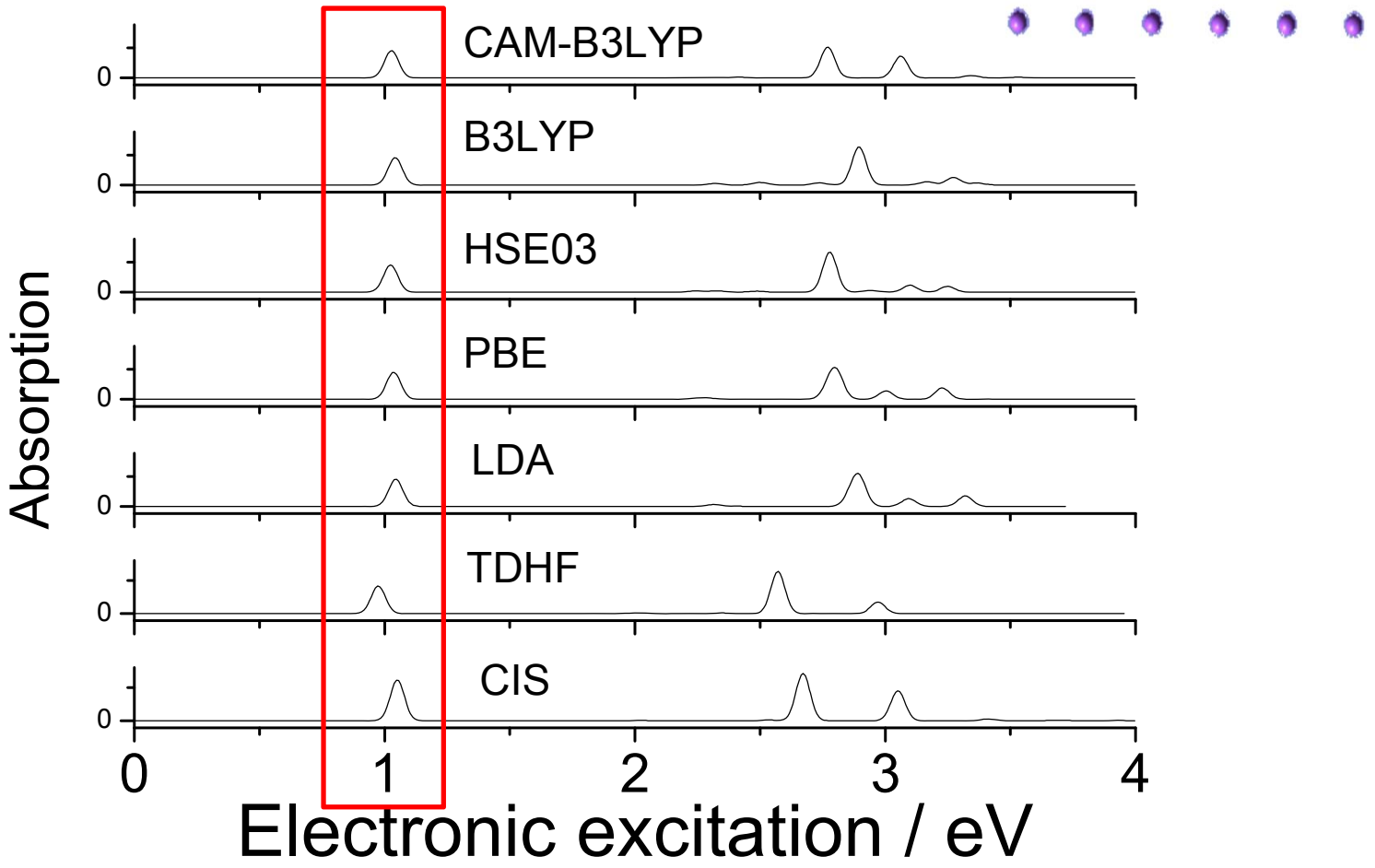


Chain-Na_n n=1,2,4,6,8,10,12,14,16

LRT-TDDFT equation

Optical absorption of Na chain clusters

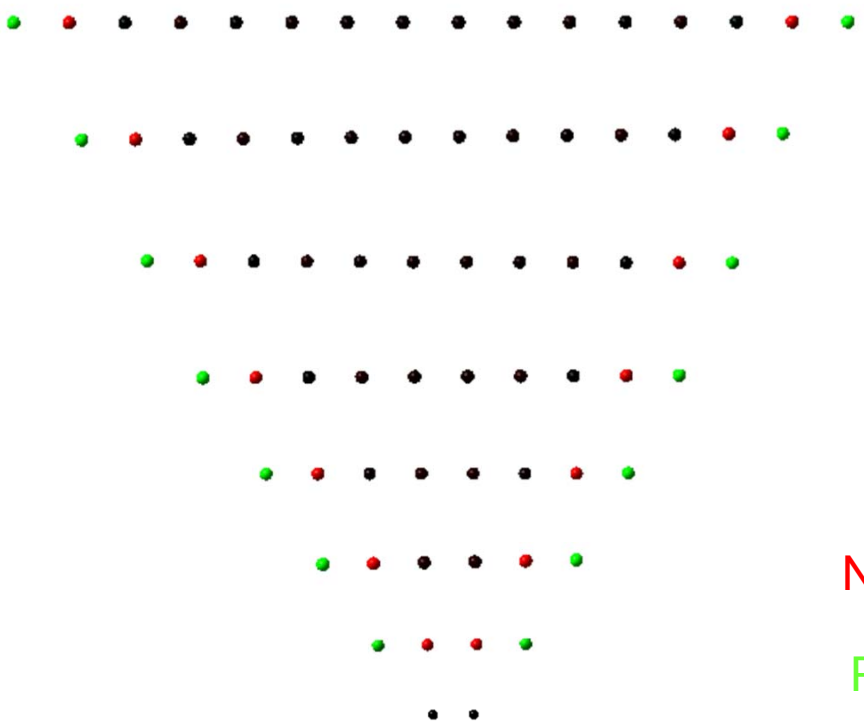
Na_6



The first excitation is almost independent of functionals or theory levels.

Charge distribution in Na_n chain clusters

n=16



Negative

Positive

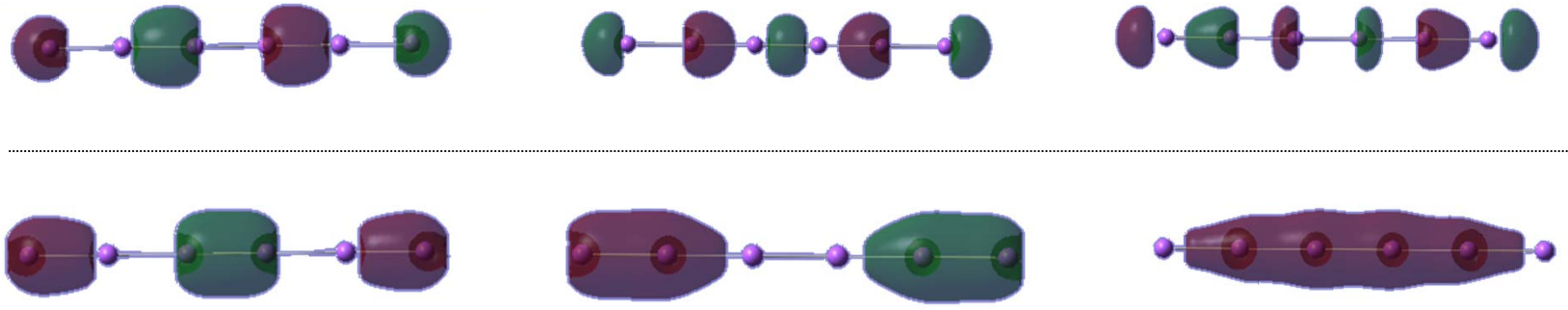
n=2

Electronic ground state property

Natural transition orbital analysis

1th excitation
(1st strong peak)

electron



0.95 0.044 0.0057

hole

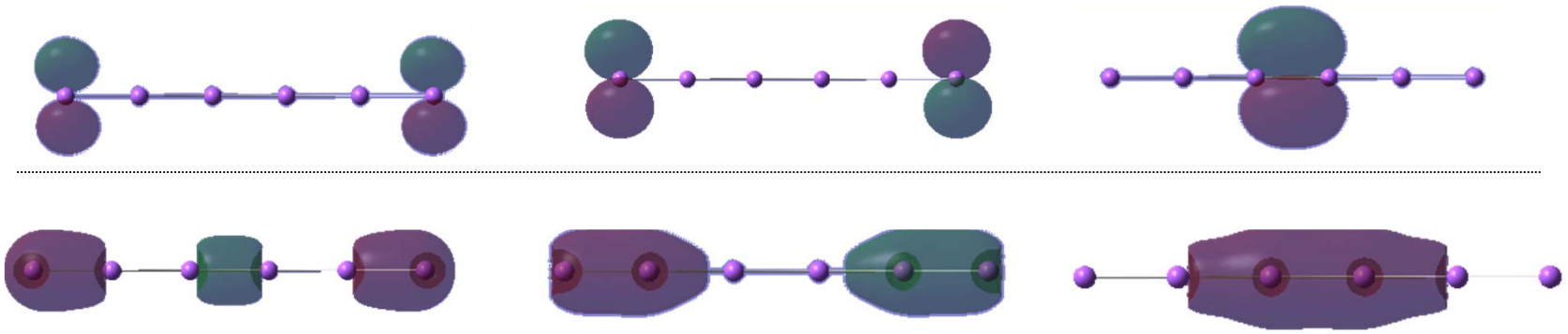
Collectivity index ~1.1

n = 1.1 ~ one e-h (or h-e) pair contribution.

Yasuike et al. Phys. Rev. A (2011)

12th excitation
(2nd strong peak)

electron



0.73

0.23

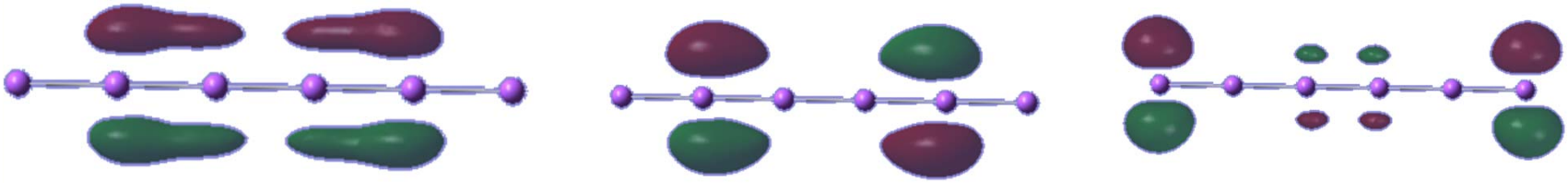
0.031

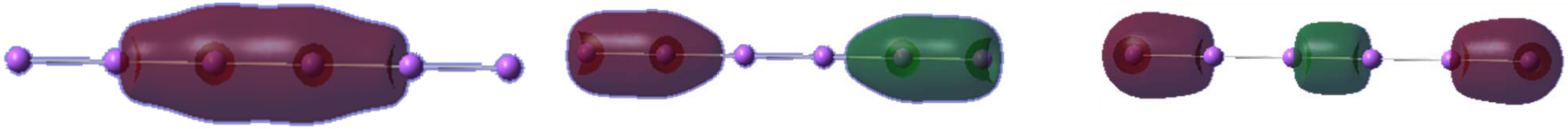
hole

Collectivity index ~1.17

19th excitation
(3rd strong peak)

electron



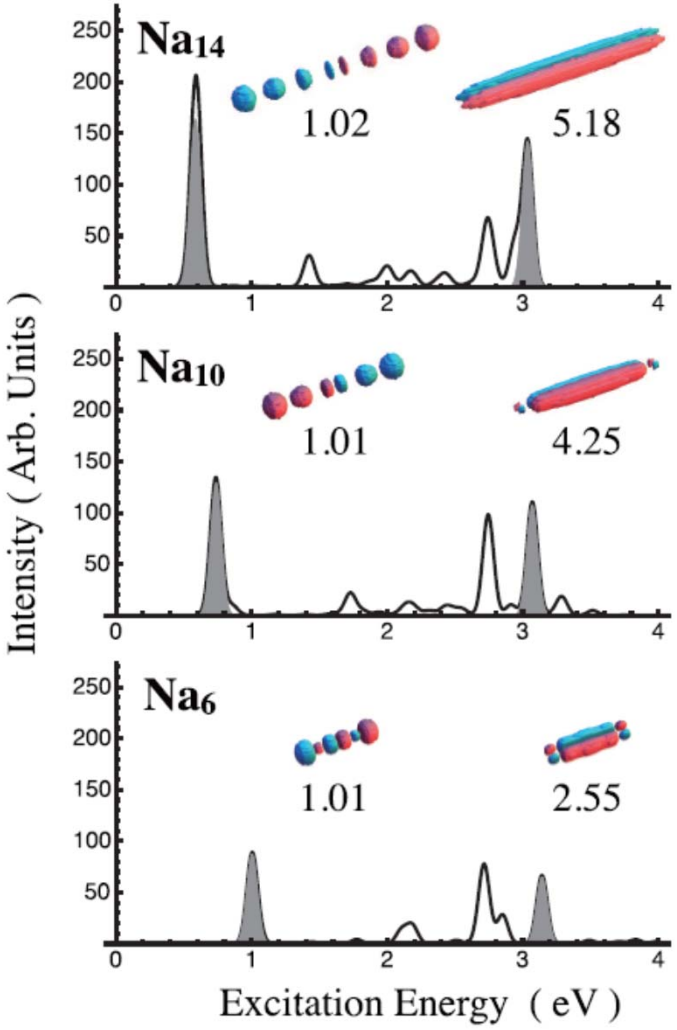


0.59 0.36 0.053

hole

Collectivity index ~2.1

A more rigorous analysis shows

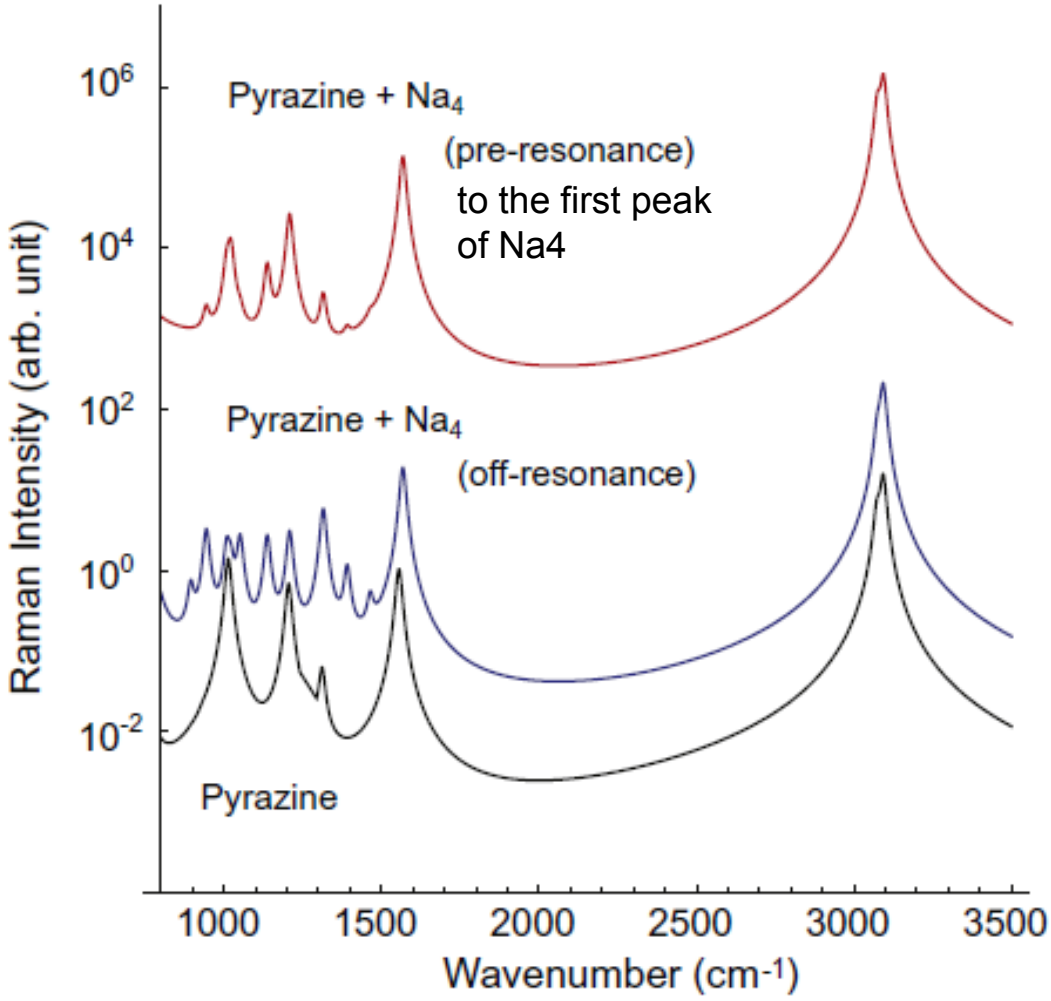


	Collectivity index		
	Lower	Higher	Fully collective
Na_{14}	1.02	5.18	7
Na_{10}	1.01	4.25	5
Na_6	1.01	2.55	3

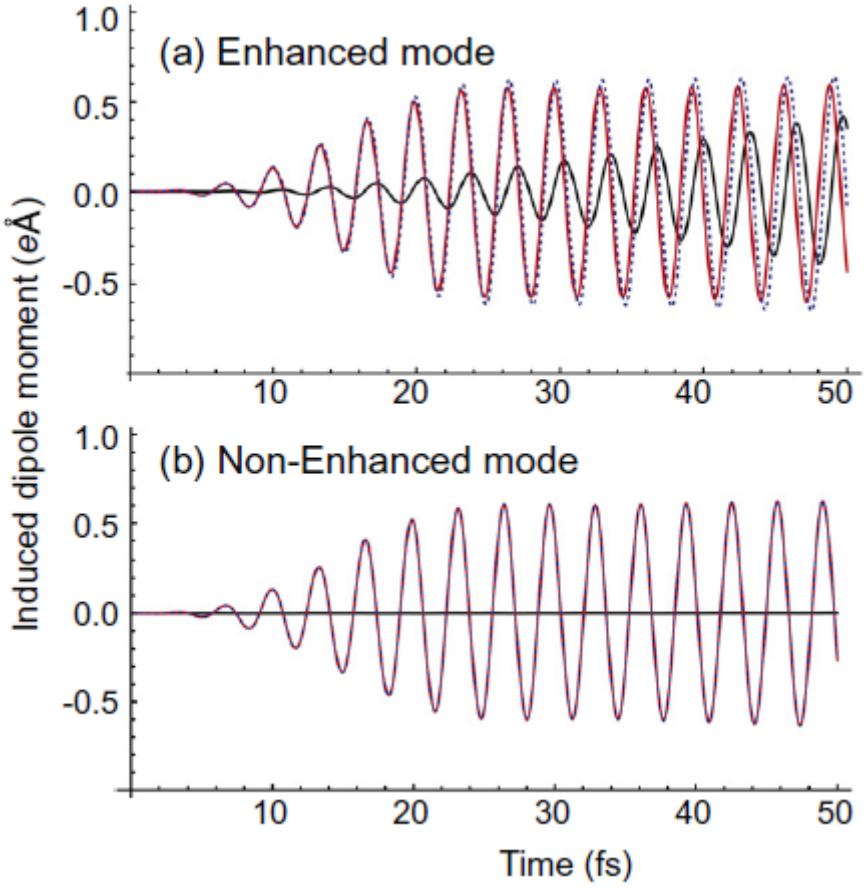
n^* = 1.01 ~ one e-h (or h-e) pair contribution.

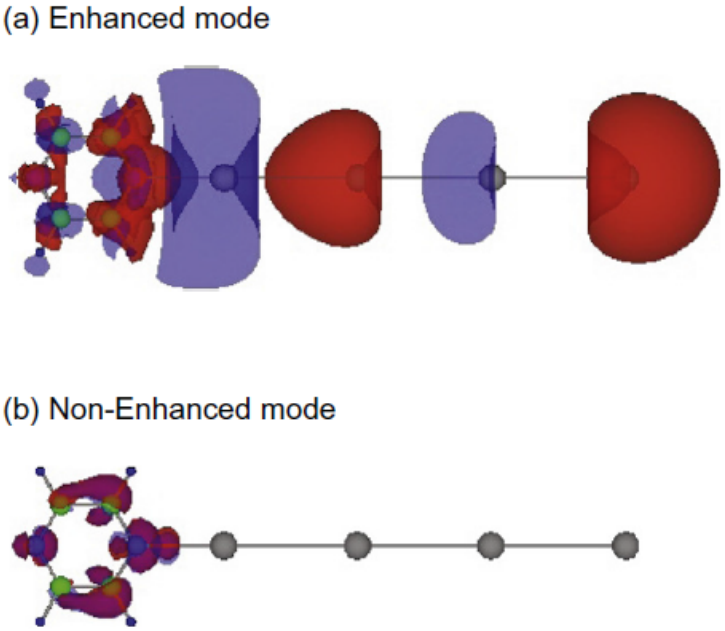
Yasuike et al. Phys. Rev. A (2011)

Plasmonic Enhanced Raman



Real-time dependent DFT

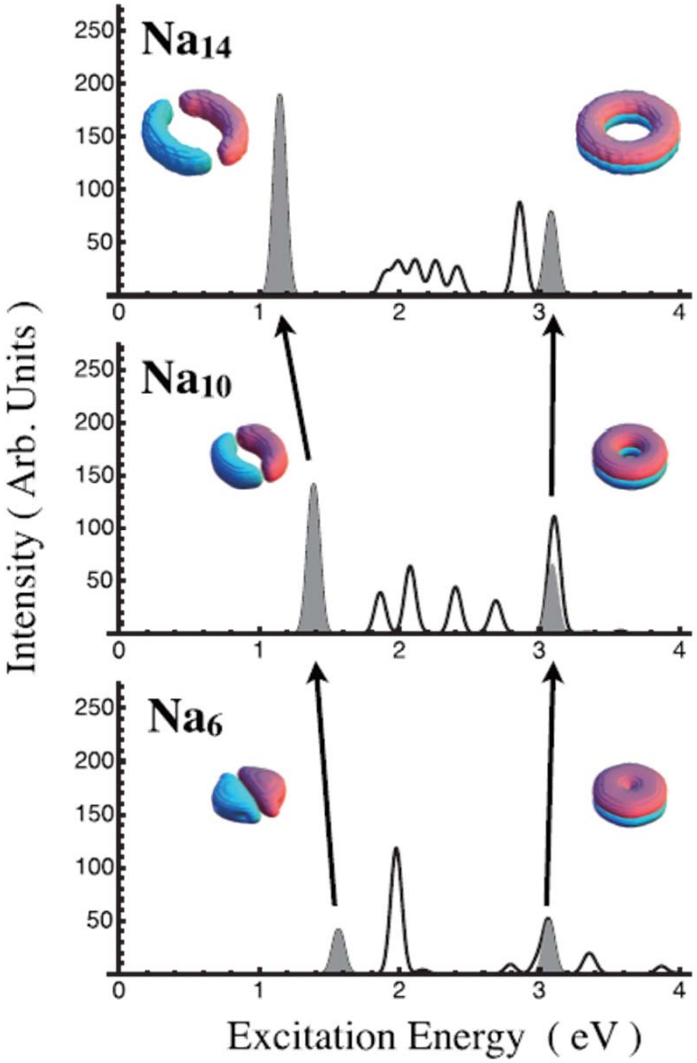




CPL (2012)

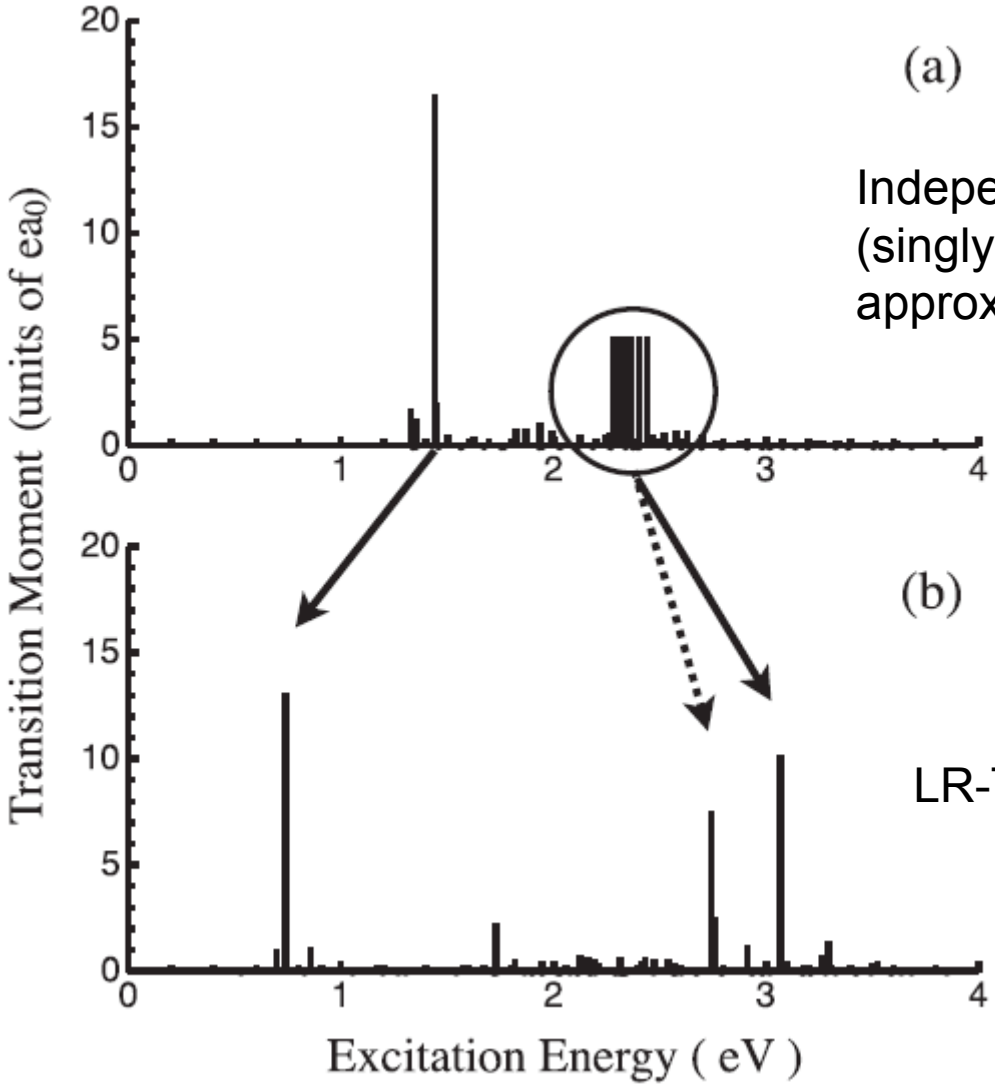
Ring structure

Collectivity index of the electronic excitation of ring structures



	Collectivity index		
	Lower	Higher	Fully collective
Na_{14}	2.01	7	7
Na_{10}	2.04	4.99	5
Na_6	1.78	2.91	3

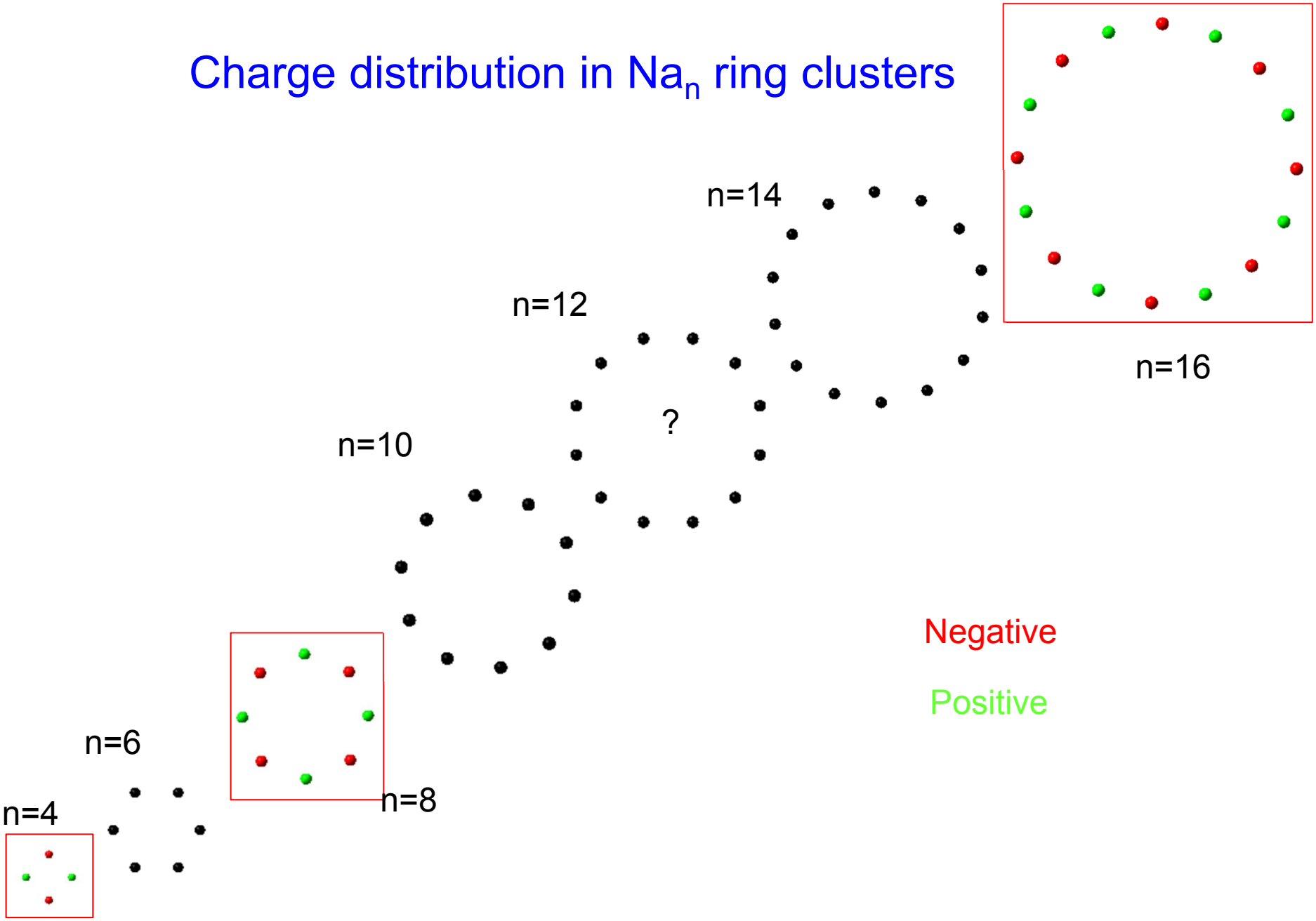
Yasuike et al. Phys. Rev. A (2011)



Independent particle
(singly excited configuration)
approximation

LR-TD-DFT

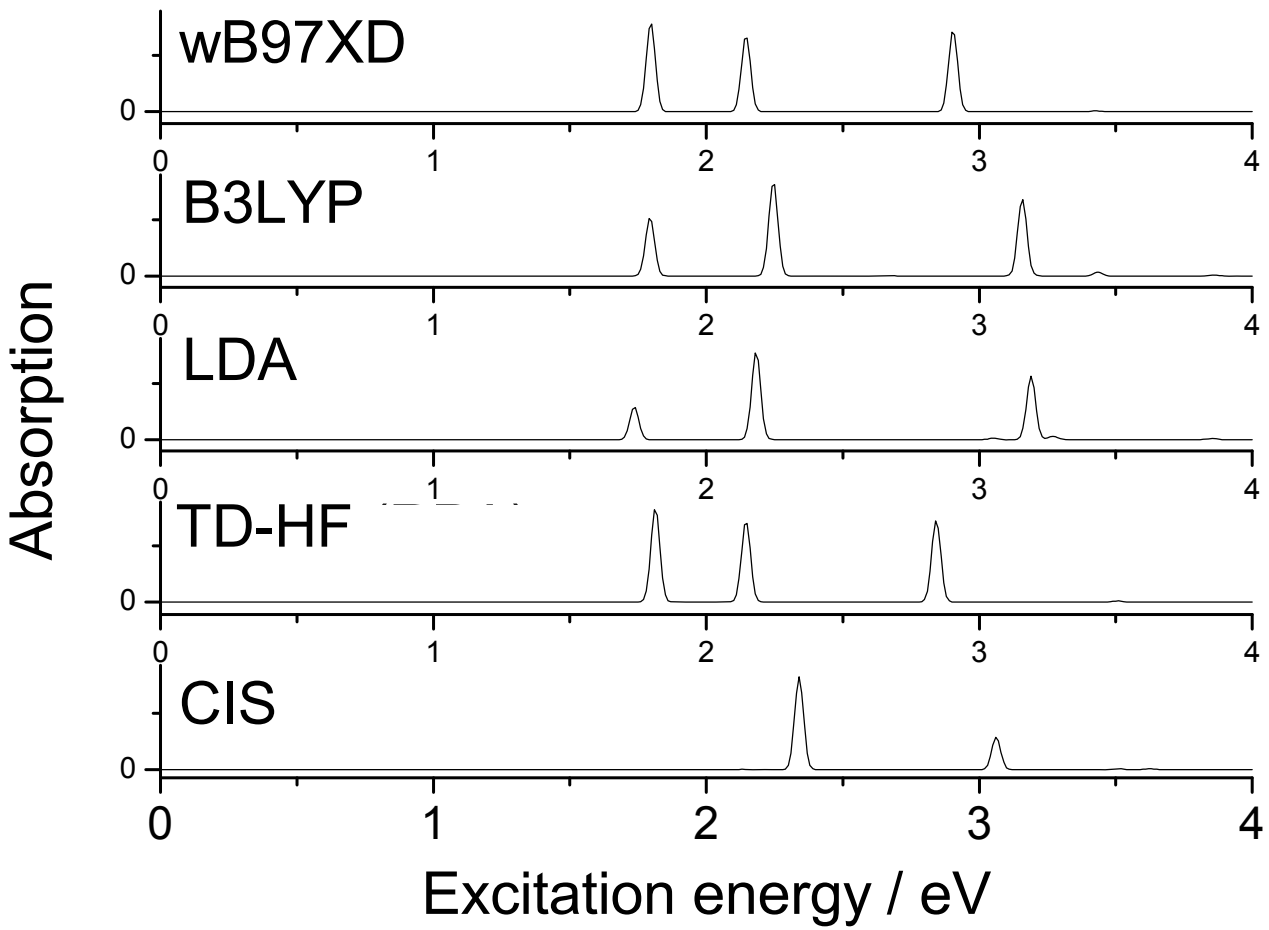
Charge distribution in Na_n ring clusters



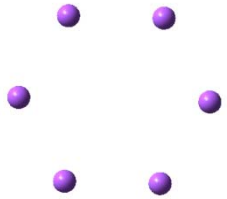
Electronic ground state property

Na_6 ring cluster

LRT-TDDFT



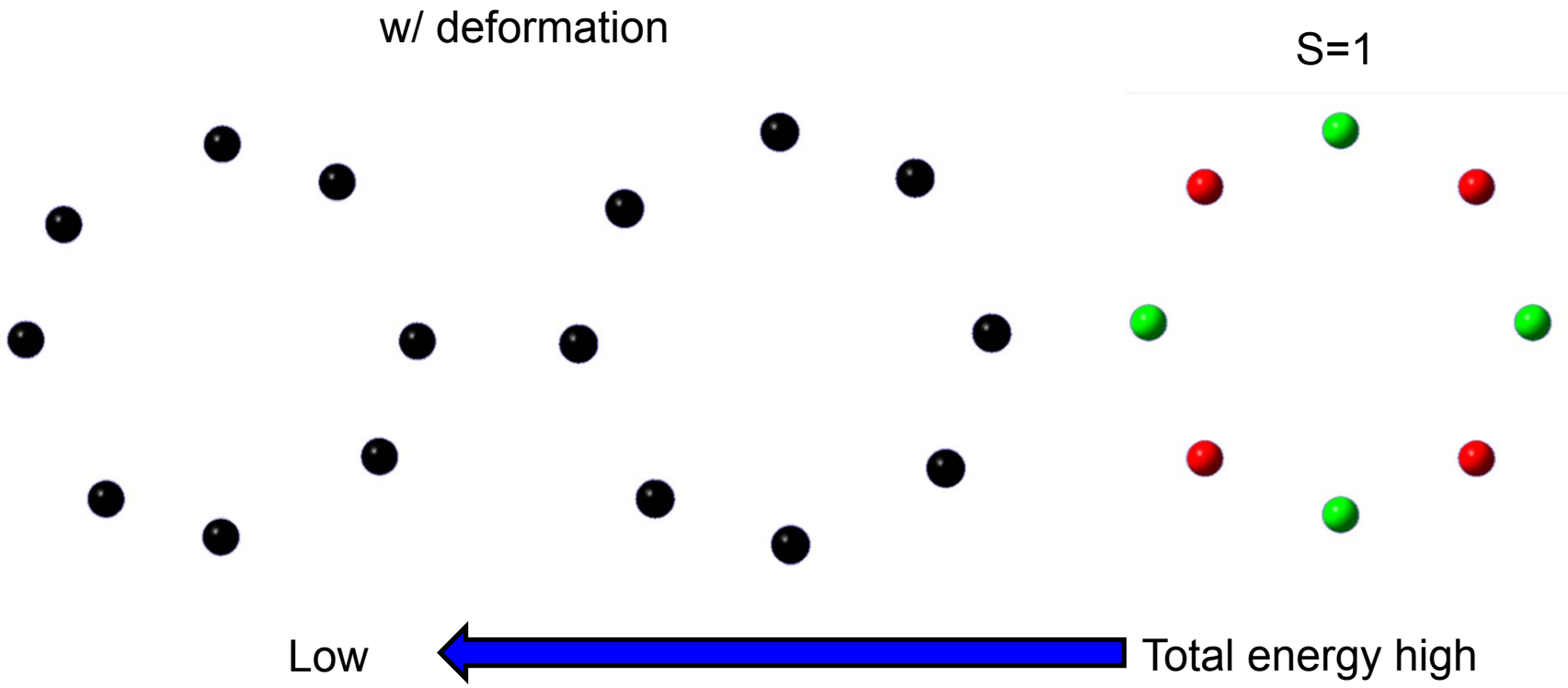
Na_6



The first excitation depends on the functionals or theory levels.

Charge ordering (n=4m+4)

Wild guess (analogy to one dimensional system)



LR-TDDFT
forms stable
electronic excitations

LR-TDDFT
does not form stable
electronic excitations

Time-dependent Hartree-Fock (TDHF)

Time-dependent HF equation

$$\begin{bmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{bmatrix} \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix} = \omega \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix}$$

where

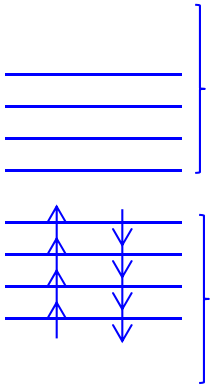
$$\begin{aligned} \mathbf{A}_{ia,jb} &= \delta_{ij}\delta_{ab}(\varepsilon_a - \varepsilon_i) + (ia \,\|\, jb) \\ &= \delta_{ij}\delta_{ab}(\varepsilon_a - \varepsilon_i) + (ia \,|\, jb) - (ij \,|\, ab) \end{aligned}$$

$$\begin{aligned} \mathbf{B}_{ia,jb} &= (ia \,\|\, bj) \\ &= (ia \,|\, bj) - (ib \,|\, aj) \end{aligned}$$

Antisymmetrized two-electron integral

$$(ia \parallel jb) = \int\int d\vec{r}\, d\vec{r}\,' \times \left[\frac{\phi_i(\vec{r})\phi_a(\vec{r})\phi_j(\vec{r}\,')\phi_b(\vec{r}\,') - \phi_i(\vec{r})\phi_j(\vec{r})\phi_a(\vec{r}\,')\phi_b(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|} \right]$$

ϕ HF orbital



Unoccupied orbitals $(\phi_a, \phi_b, \cdots)$

Occupied orbitals $(\phi_i, \phi_j, \cdots)$

Local and nonlocal transition densities

Local transition density Non-local transition density

$$(ia \parallel jb) = \int\int d\vec{r}\, d\vec{r}\,' \times \left[\frac{\rho_{ia}(\vec{r})\rho_{jb}(\vec{r}\,') - \rho_{ia}(\vec{r},\vec{r}\,')\rho_{jb}(\vec{r},\vec{r}\,')}{|\vec{r} - \vec{r}\,'|} \right]$$

e-h interaction

Configuration Interaction Single (CIS) = Tamm-Dankoff approximation (TDA)

$$\mathbf{B}_{ia,jb} = 0$$

$$\mathbf{AX} = \Omega\mathbf{X}$$

Independent particle

e-h interaction

$$E_{cis} = E_{HF} + \sum_{ia} (c_i^a)^2(\varepsilon_a - \varepsilon_i) + \sum_{ia}\sum_{jb} c_i^a c_j^b (ia \,\|\, jb)$$

$$\Psi_{cis} = \sum_{ia} c_i^a \Phi_i^a$$

$$\left\langle \Phi_i^a \middle| H \middle| \Phi_{HF} \right\rangle = 0$$

Brillioin's theorem)

Beyond TDA approximation in TDHF

$$\mathbf{B}_{ia,jb} \neq 0$$

De-excitation components will be involved in excitation

$$\Phi_{HF} \Rightarrow \Phi_{NEW}$$ (final state interaction)

Ground state energy can be expanded in terms of the excitation configurations

$$E = E_{HF} + E_1 + E_2 \cdots$$

$$E_1 = 0$$

$$E_2 = \frac{1}{2}[\mathbf{X} \quad \mathbf{Y}]\begin{bmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{bmatrix}\begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix}$$

The ground state of WF is stable if the matrix is positive semidefinite.

$$\begin{bmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{bmatrix}$$

JCP 1977 Seeger and Pople

Linear-Response Theory-Time-dependent DFT

$$\begin{bmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{bmatrix} \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix} = \omega \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix}$$

$$\mathbf{A}_{ia,jb} = \delta_{ij}\delta_{ab}(\varepsilon_a - \varepsilon_i) + (ia \mid jb) + (ia \mid f_{xc} \mid jb)$$

$$\mathbf{B}_{ia,jb} = (ia \mid bj) + (ia \mid f_{xc} \mid bj)$$

$$(ia \mid f_{xc} \mid jb) = \int\int d\vec{r}\, d\vec{r}\,' \, \tilde{\phi}_i^*(\vec{r})\tilde{\phi}_a(\vec{r}) \frac{\delta^2 E_{ex}}{\delta\rho(\vec{r})\delta\rho(\vec{r}\,')} \tilde{\phi}_b^*(\vec{r}\,')\tilde{\phi}_j(\vec{r}\,')$$

$\tilde{\phi}$ Kohn-Sham orbital

Tamm-Dancoff approximation (TDA)

$$\mathbf{B}_{ia,jb} = 0$$

$$\Rightarrow \quad \mathbf{AX} = \Omega \mathbf{X}$$

$$\Rightarrow \quad \Psi_{TDDFT-LR} = \sum_{ia} c_i^a \Phi_i^a$$

$$\mathbf{B}_{ia,jb} \neq 0$$

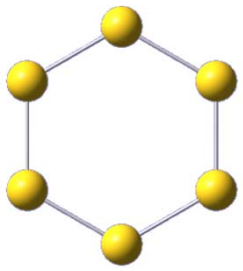
$\Rightarrow$ Does this mean that the ground state is not good?

Negative transition energies — **A**

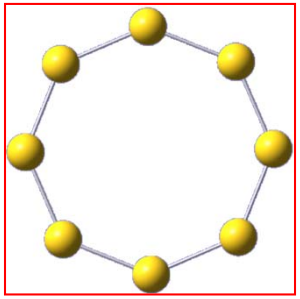
De-excitation components — **B**

JPC 1996 Bauernschmitt and Ahlrichs

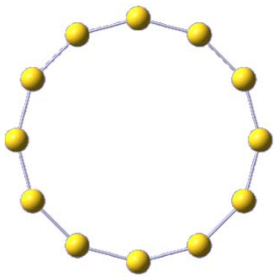
Au_n-ring



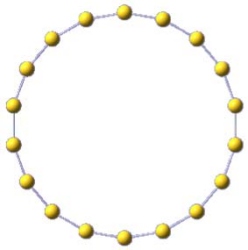
Au_6



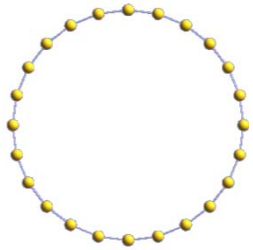
Au_8



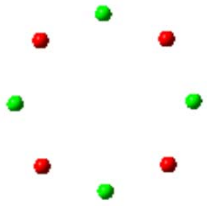
Au_{12}



Au_{18}

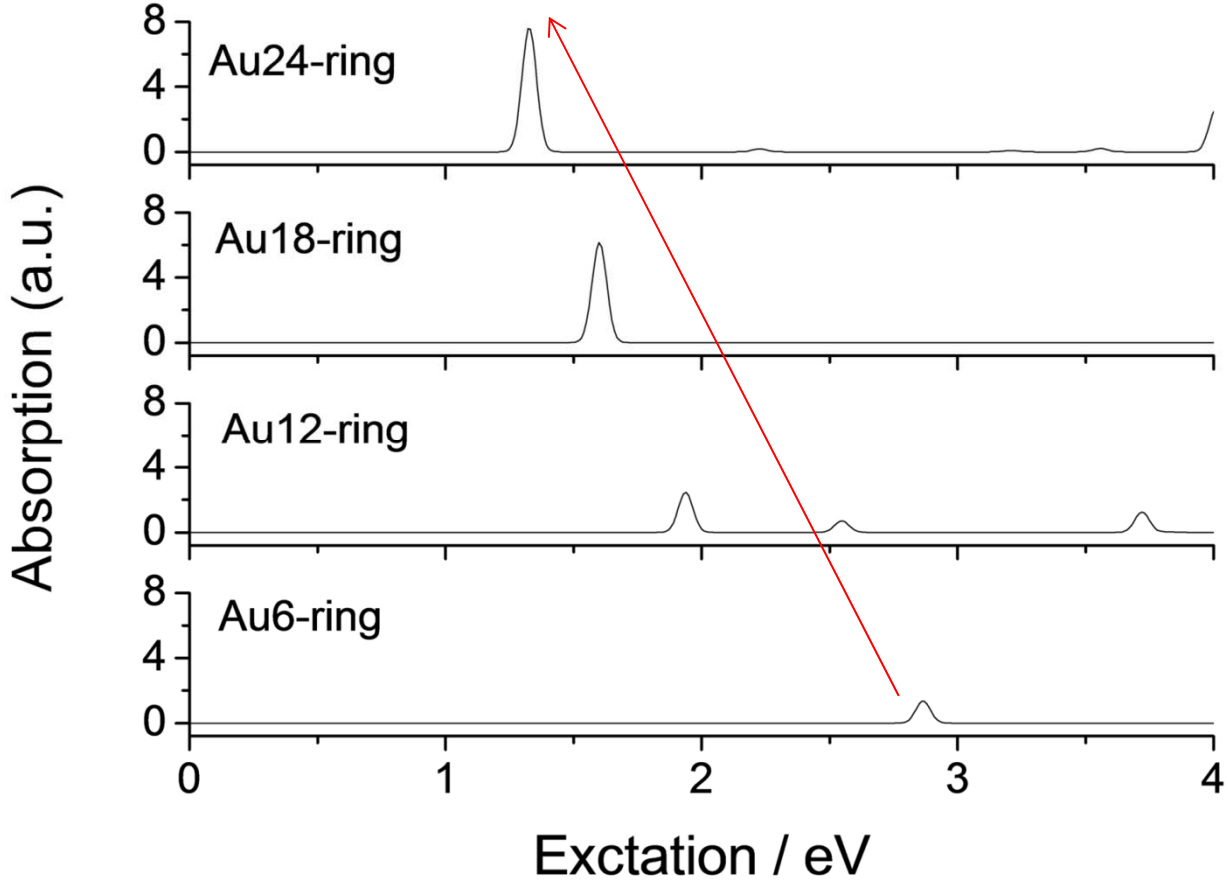


Au_{24}

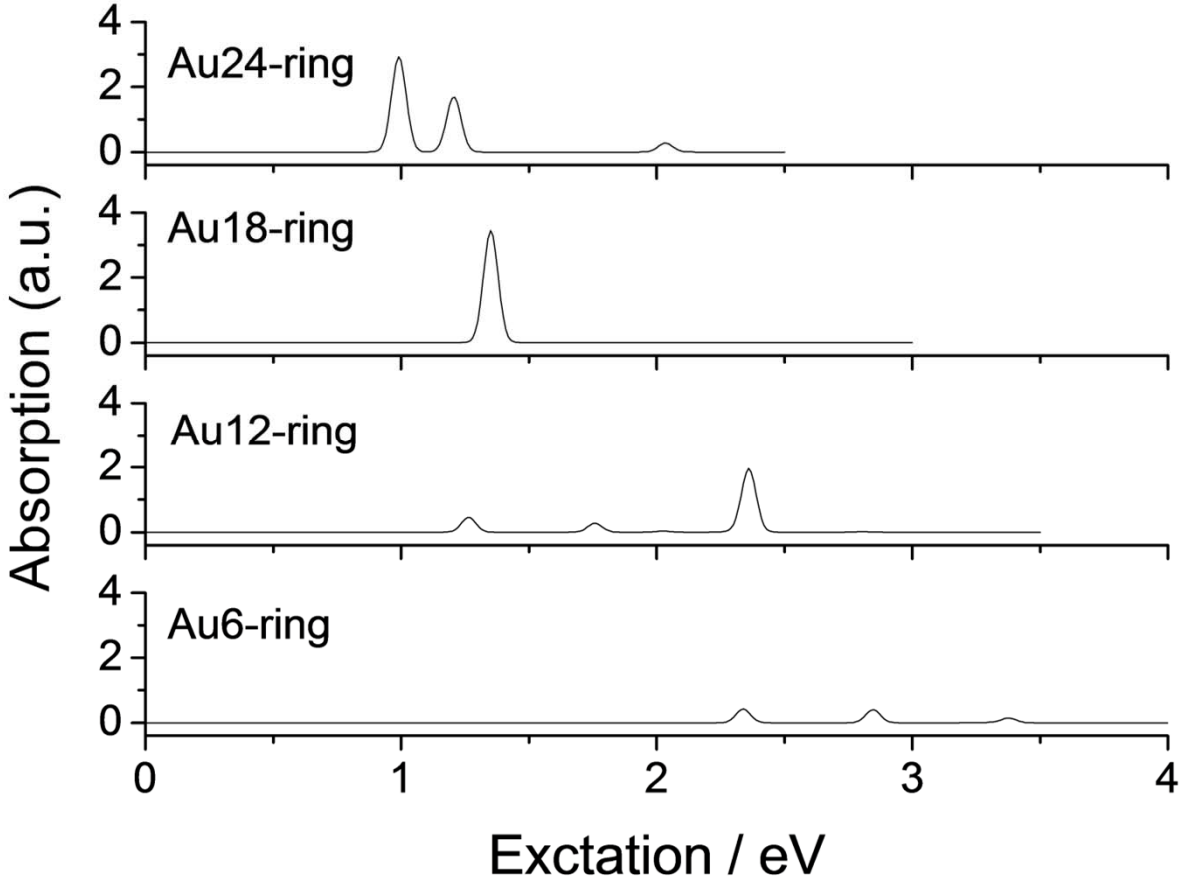


Na_8

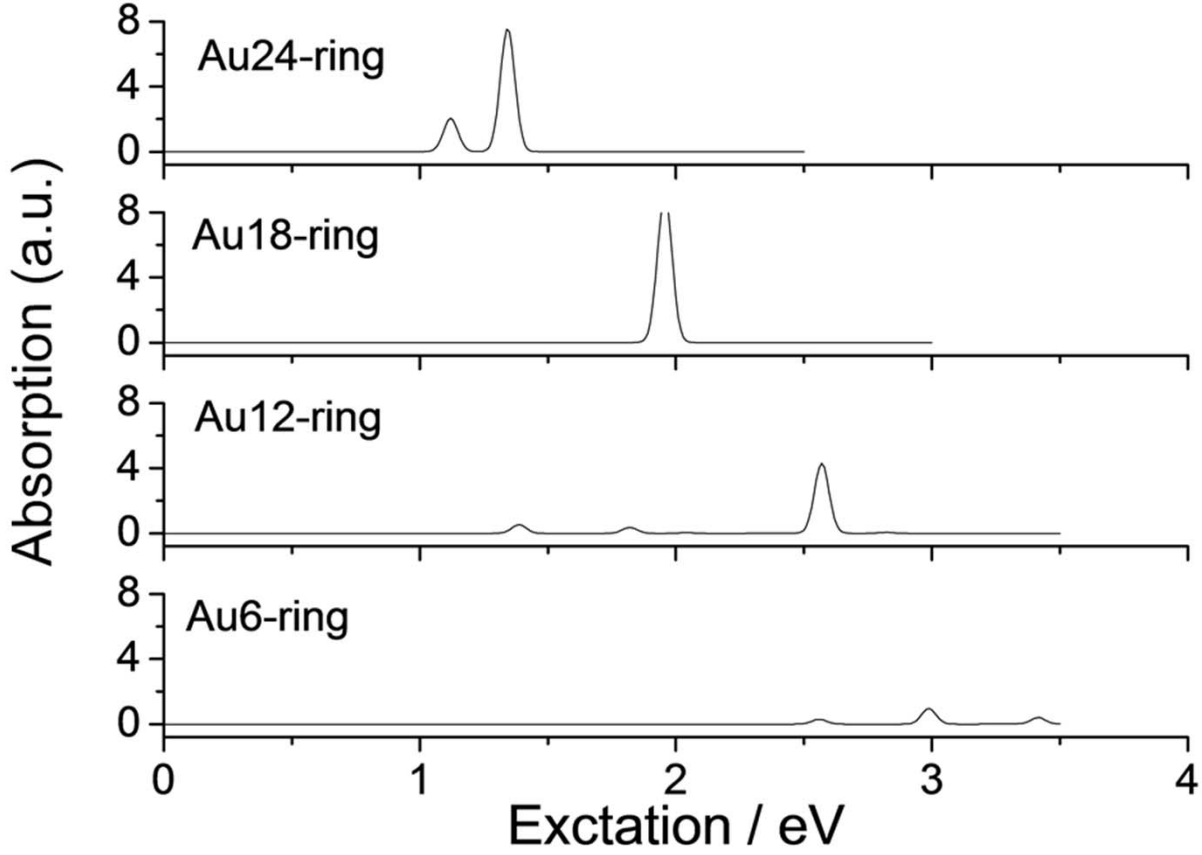
TD-HF


Au24-ring
Au18-ring
Au12-ring
Au6-ring
8
4
0
Absorption (a.u.)
0
1
2
3
4
Exctation / eV

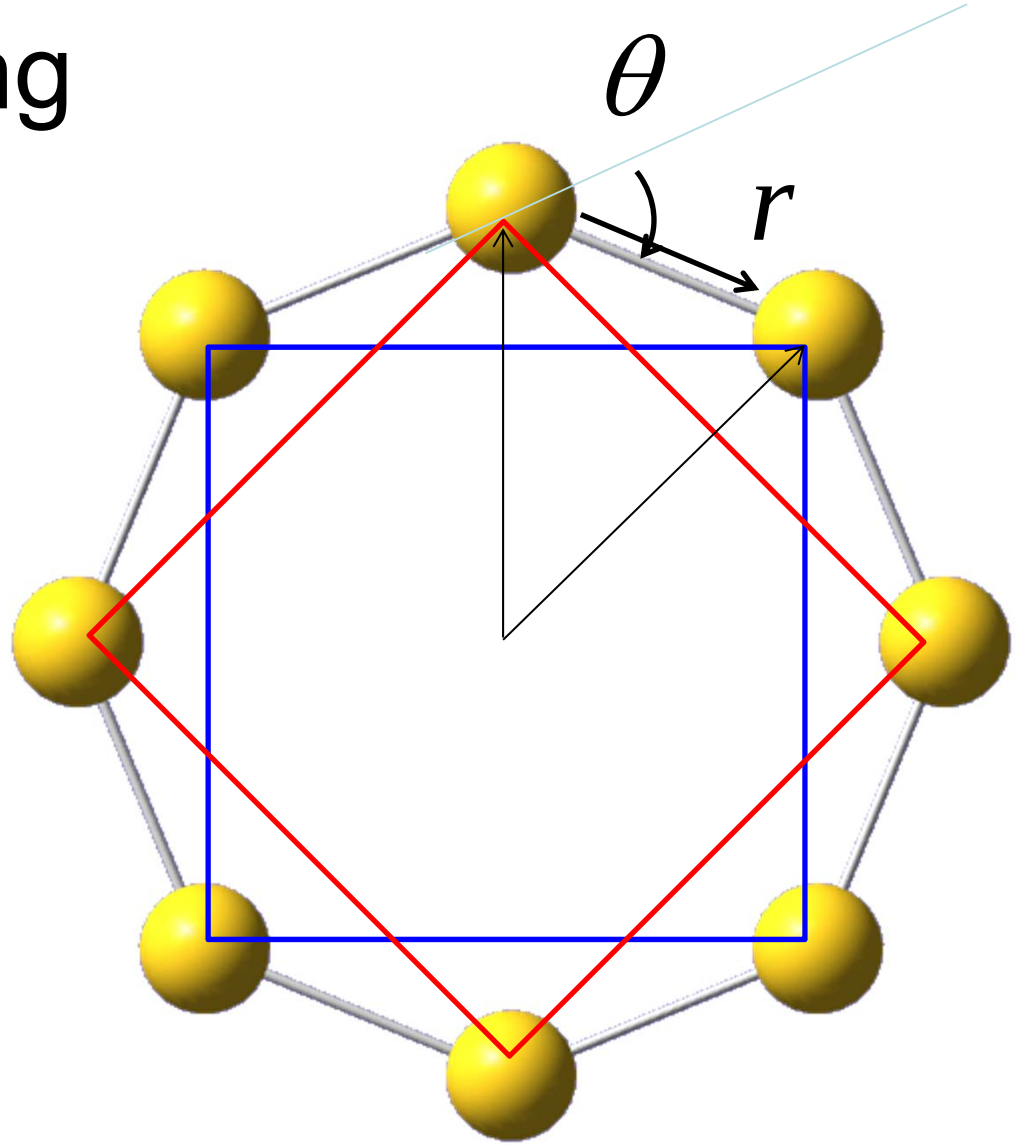
TD-CAM-B3LYP


Au24-ring
Au18-ring
Au12-ring
Au6-ring
Absorption (a.u.)
Exctation / eV
0
1
2
3
4

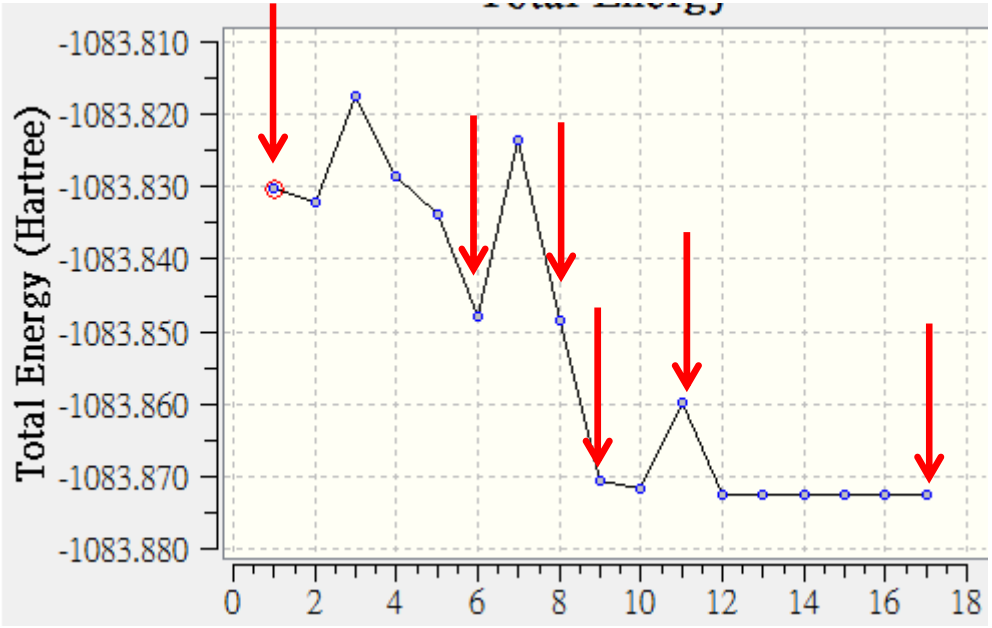
TDA-CAM-B3LYP



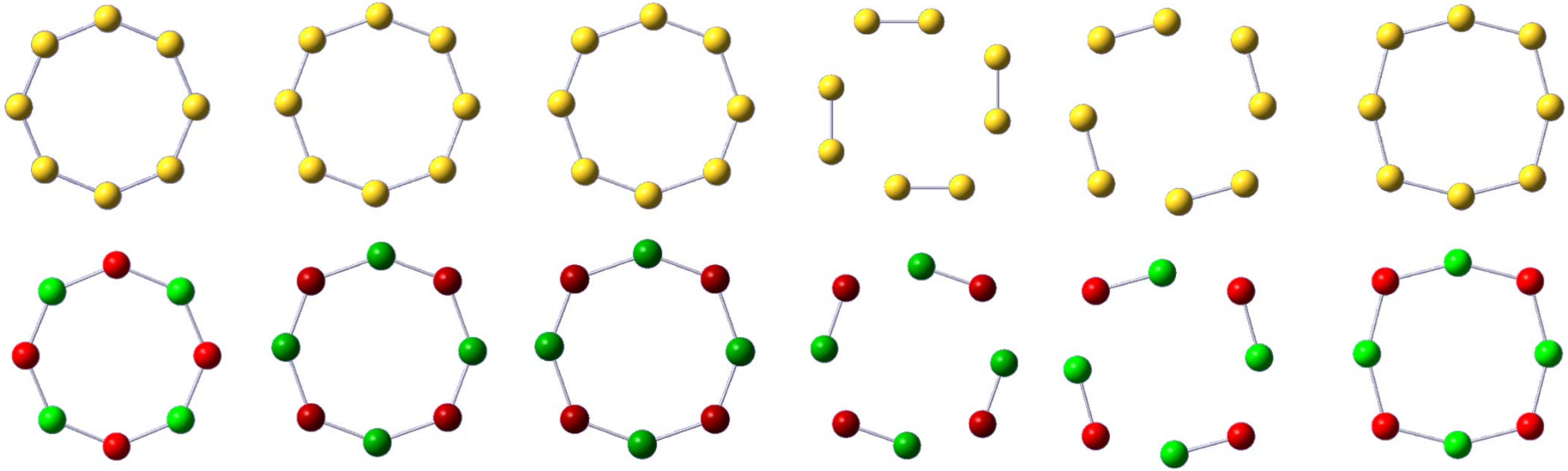
Au_8-ring



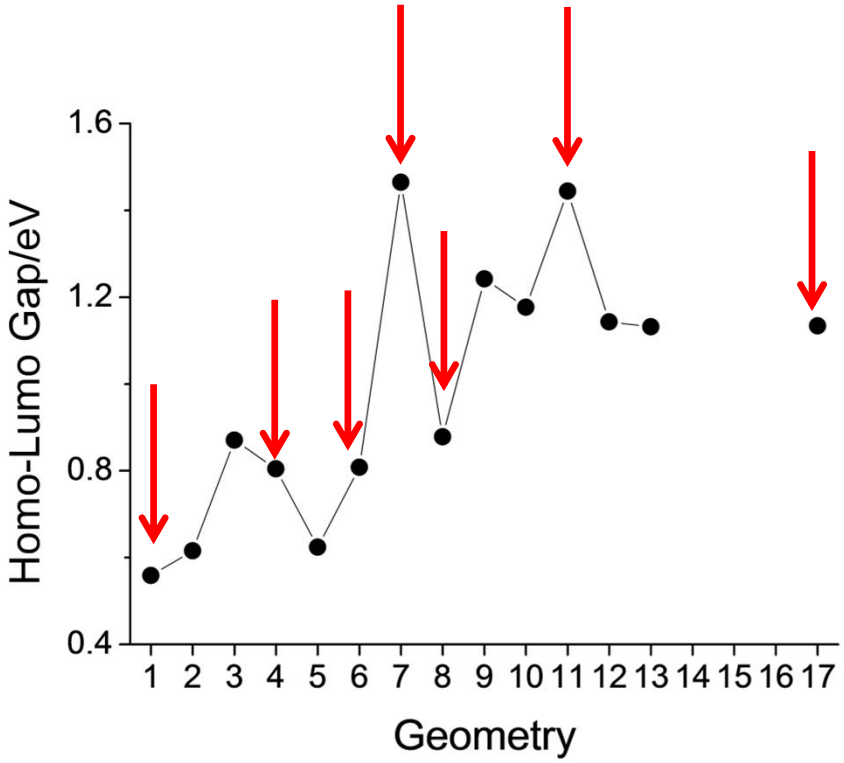
Au_8-ring

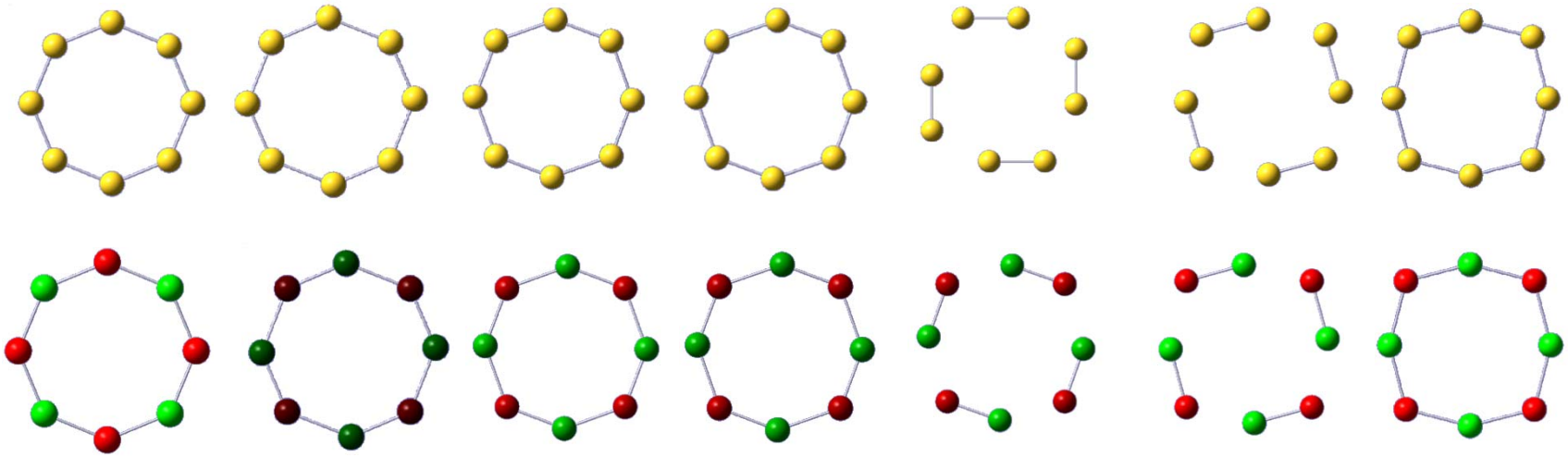


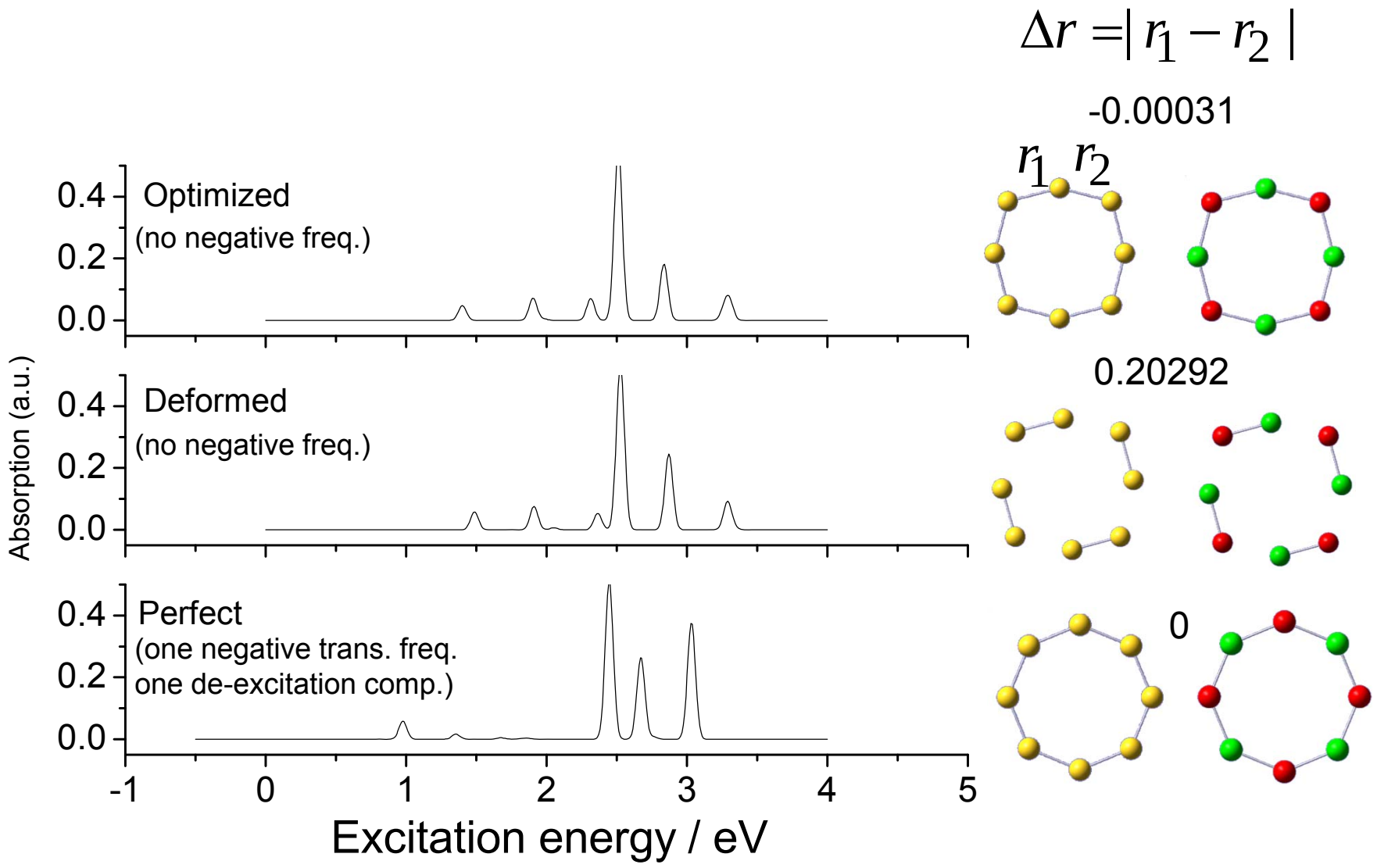
Optimized stable structure



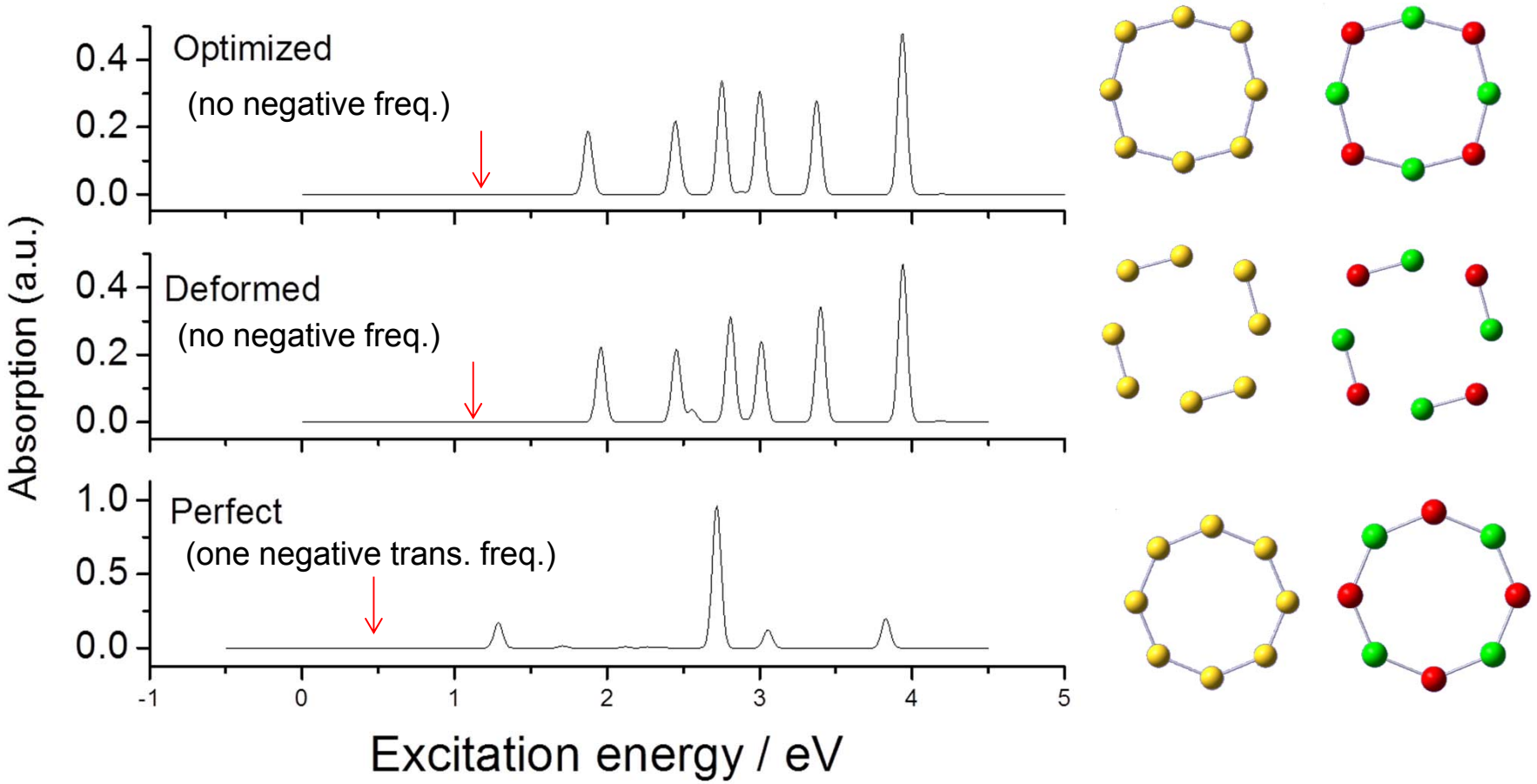
B3LYP


Homo-Lumo Gap/eV
1.6
1.2
0.8
0.4
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
Geometry



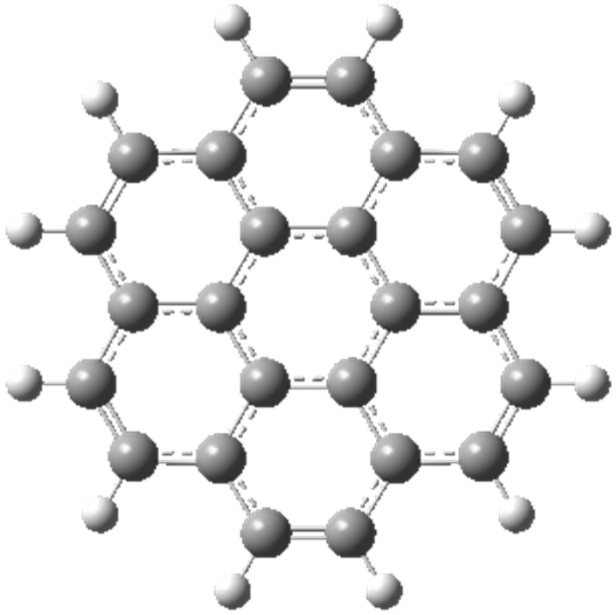


B3LYP Both DFT & LR-TDDFT

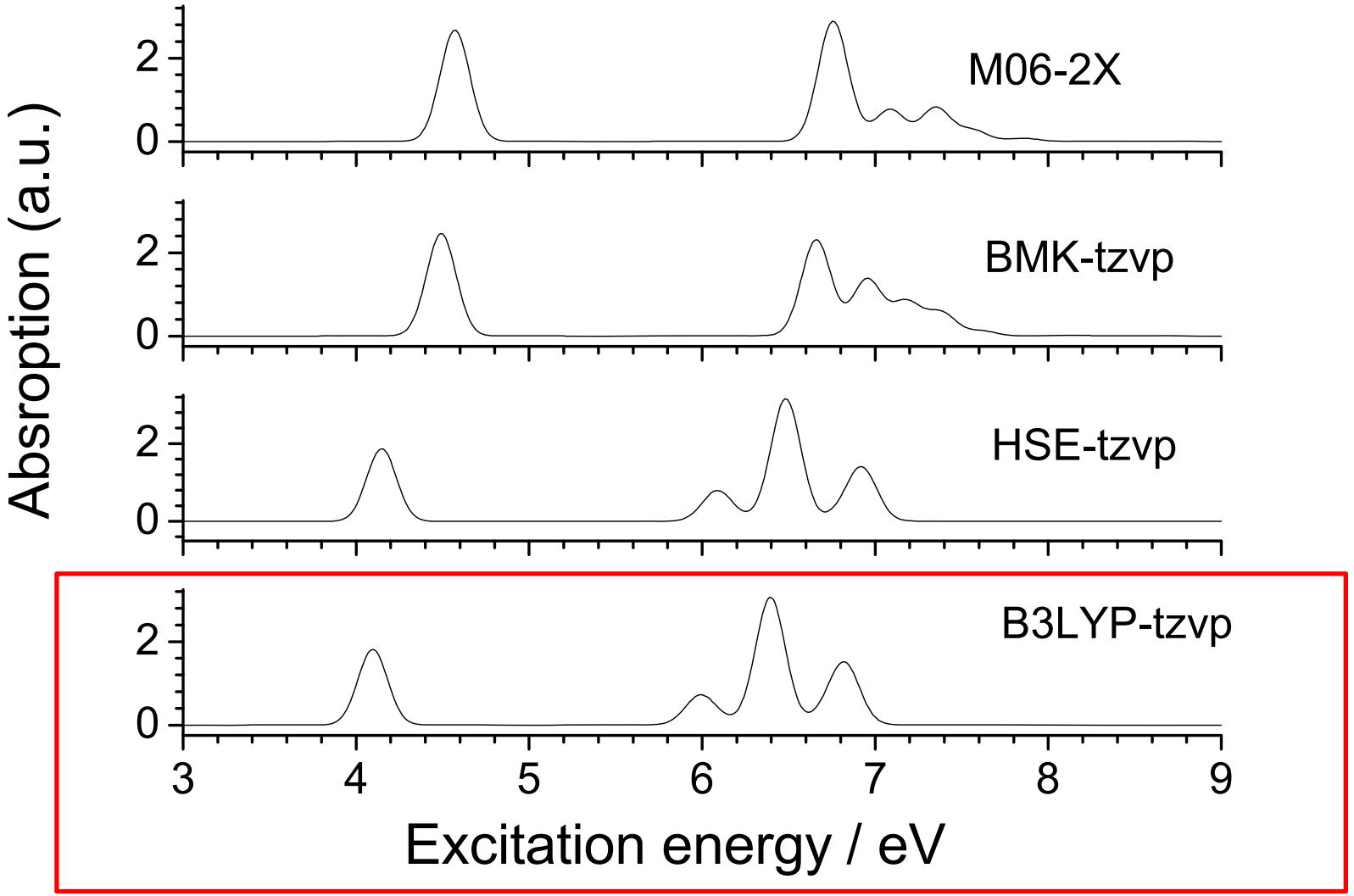


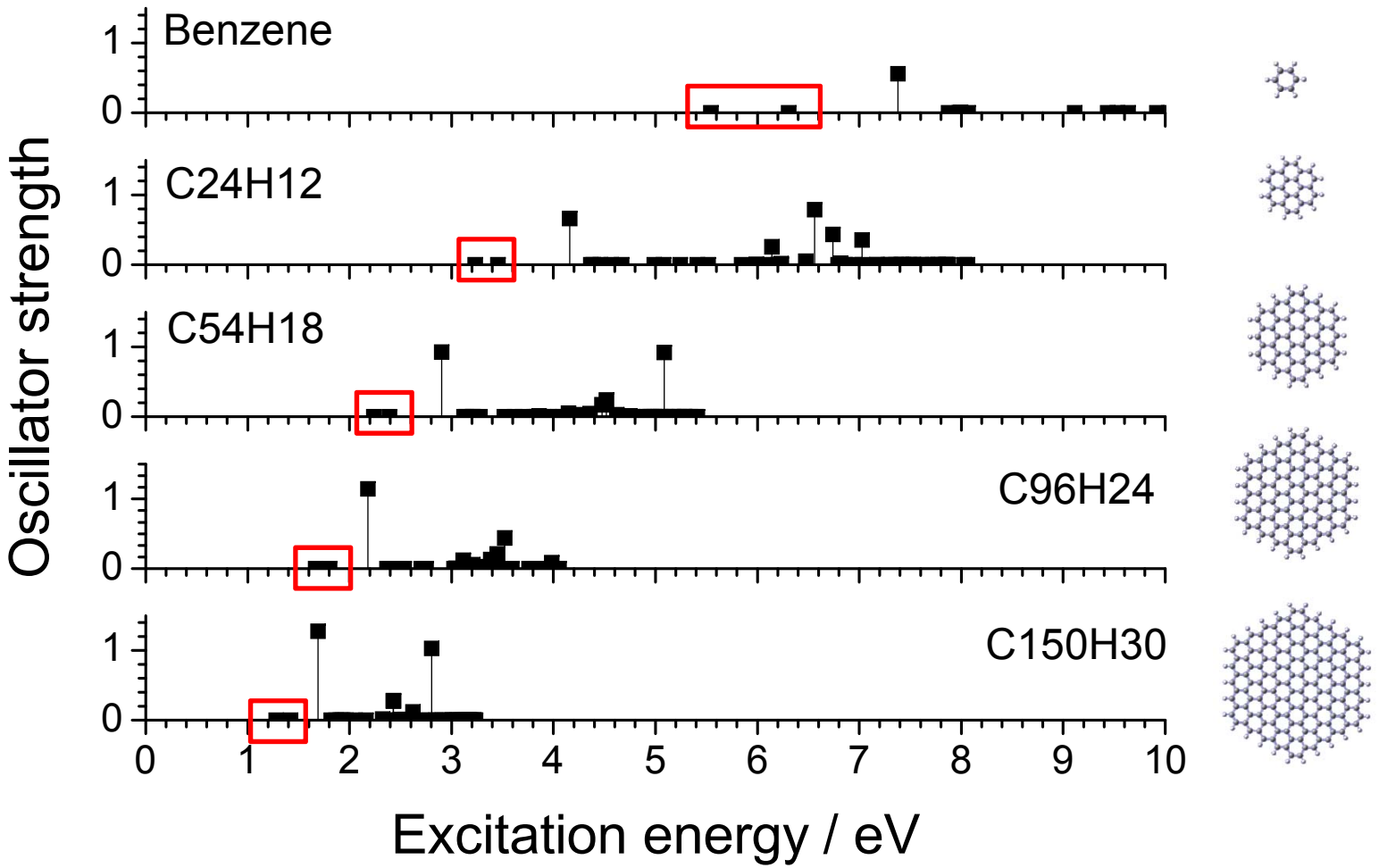
CAM-B3LYP for LR-TDDFT

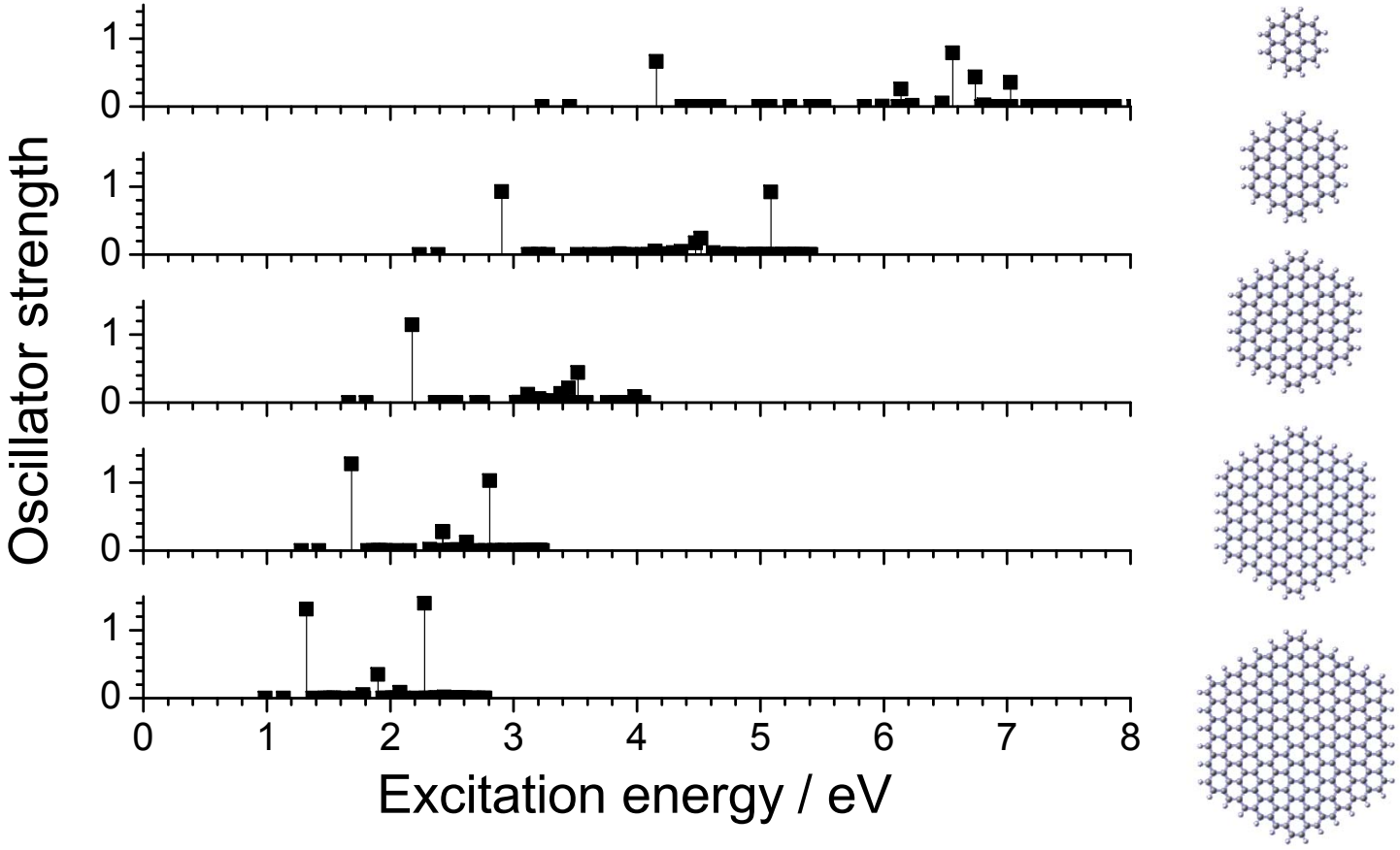
C24H12

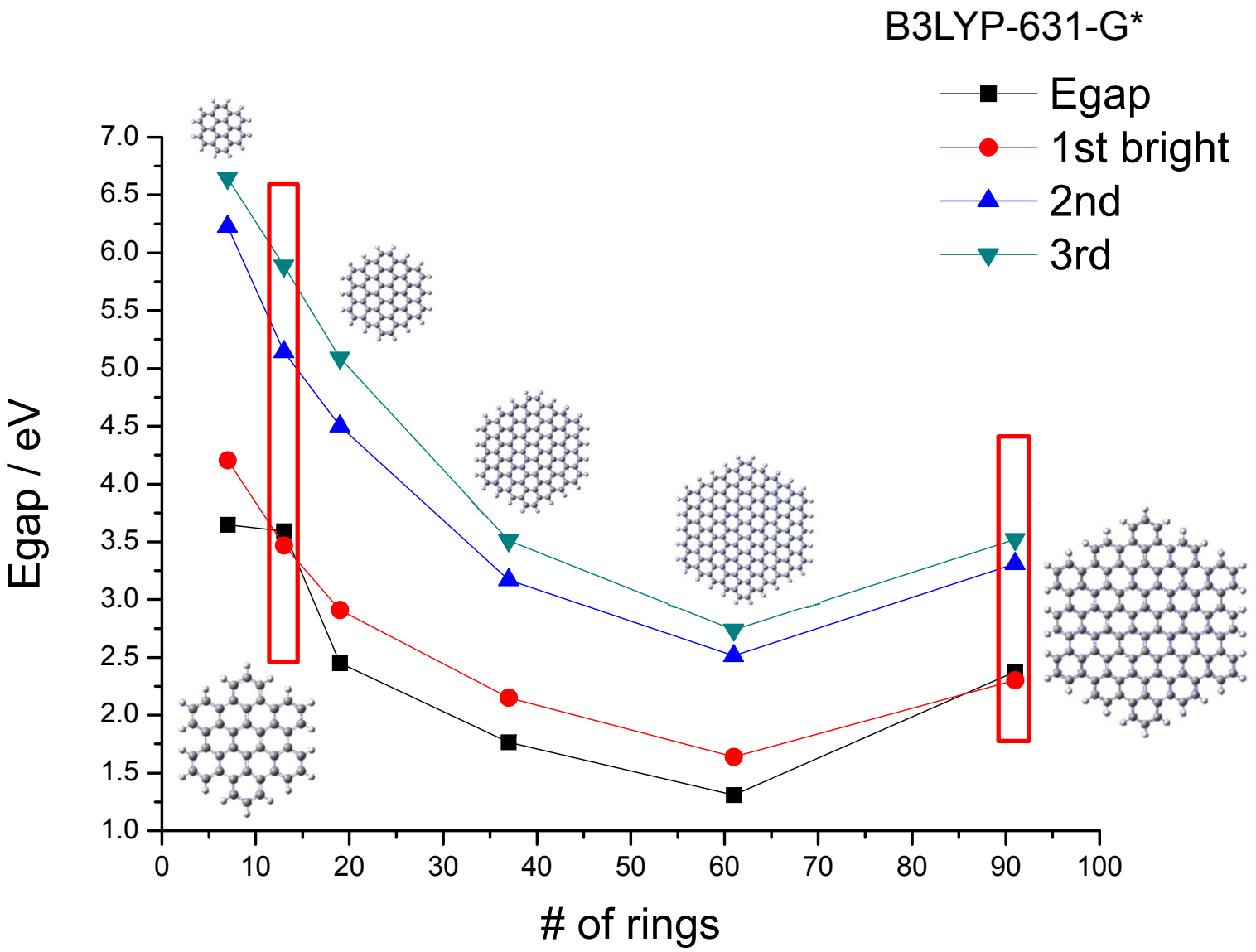


Geometry is fully optimized.

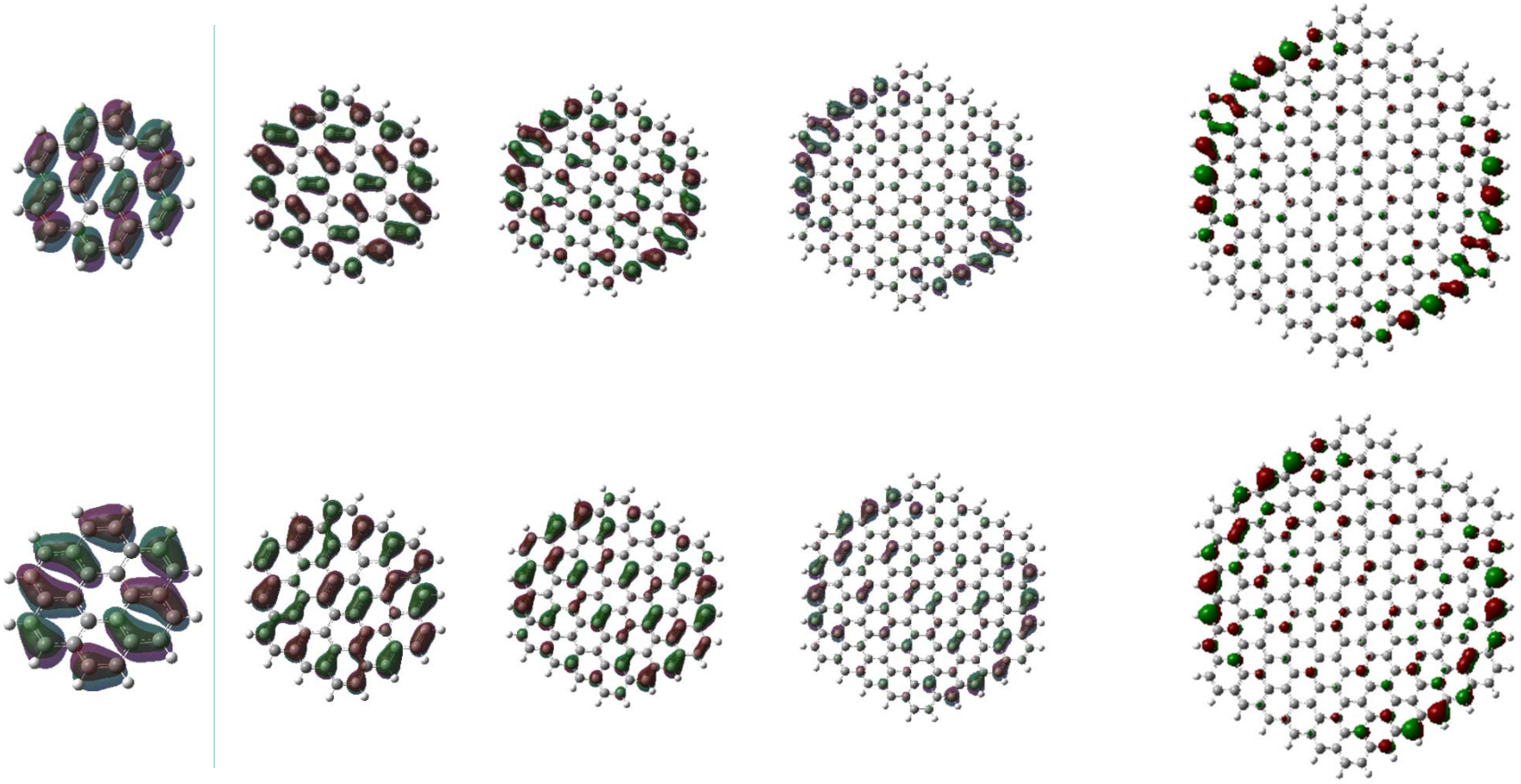



Benzene
C24H12
C54H18
C96H24
C150H30
Oscillator strength
Excitation energy / eV
0
1
2
3
4
5
6
7
8
9
10


Oscillator strength
1
0
Excitation energy / eV
0
1
2
3
4
5
6
7
8


B3LYP-631-G*
Egap
1st bright
2nd
3rd
Egap / eV
# of rings
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0
10
20
30
40
50
60
70
80
90
100

HOMO-LUMO of HGF



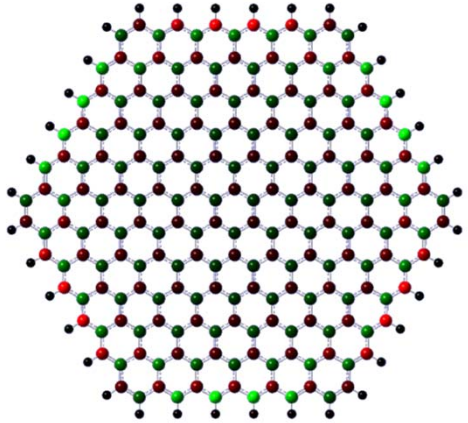
C24 C54 C96 C150 C216

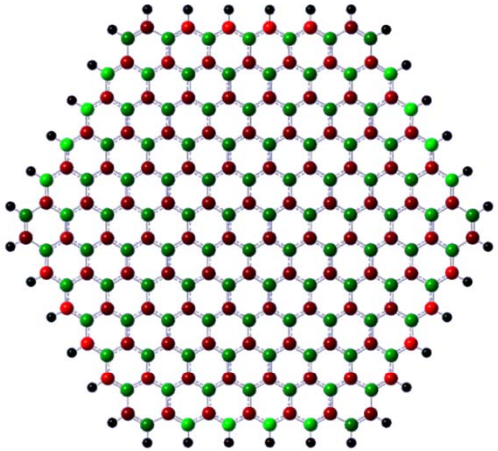
Spin (difference) density

ub3lyp

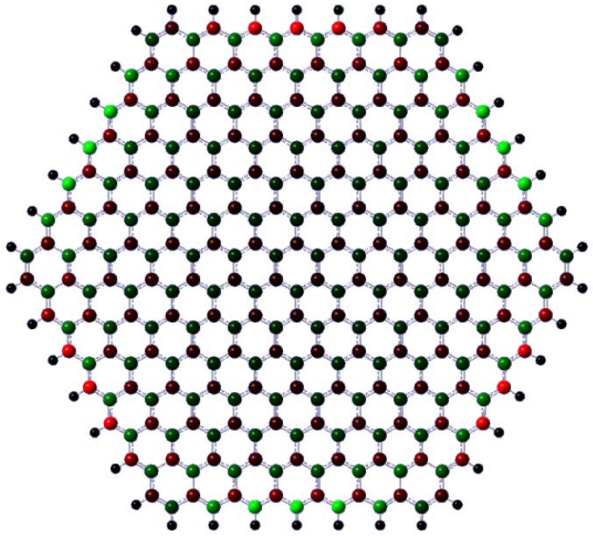
Ucam-b3lyp

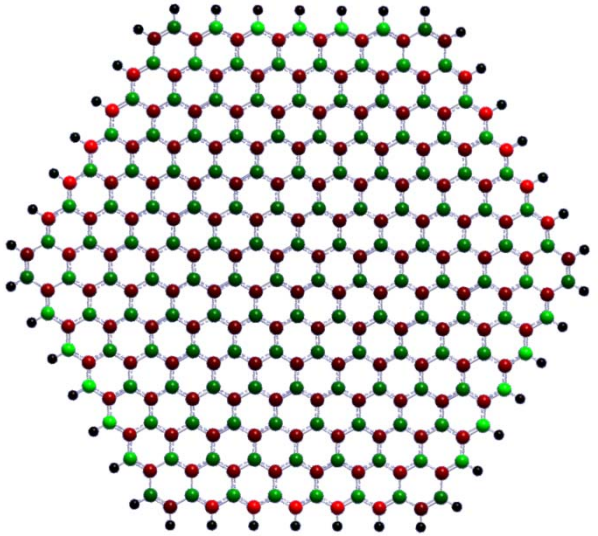
C216





C294

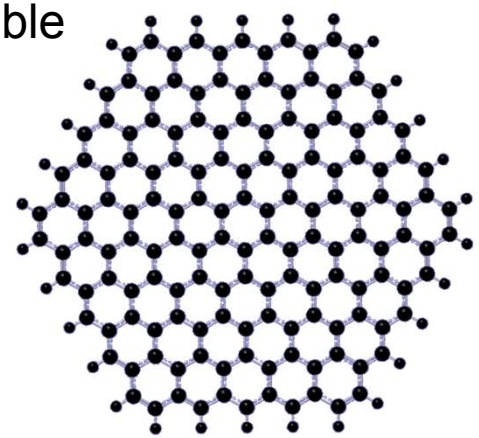




mixed guess for initial functions

Orbital stability

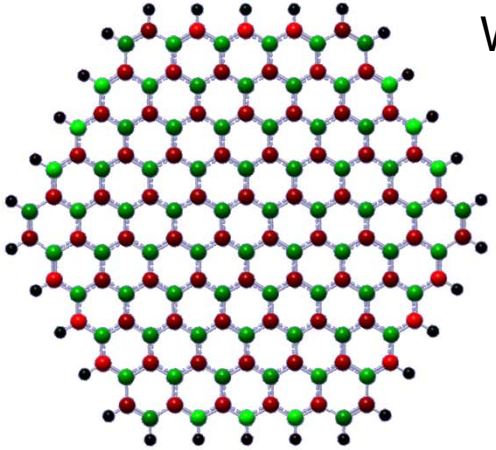
WF not stable



C216

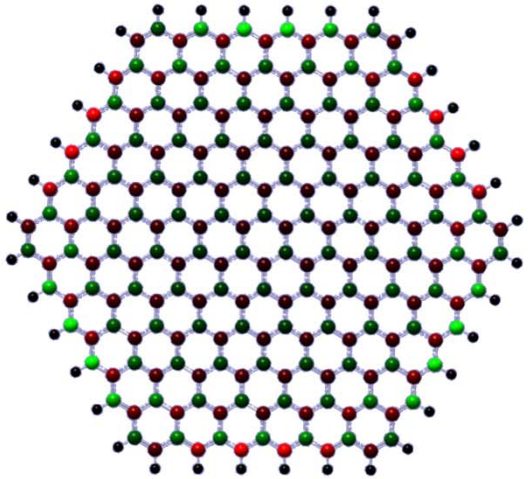
2S+1=1

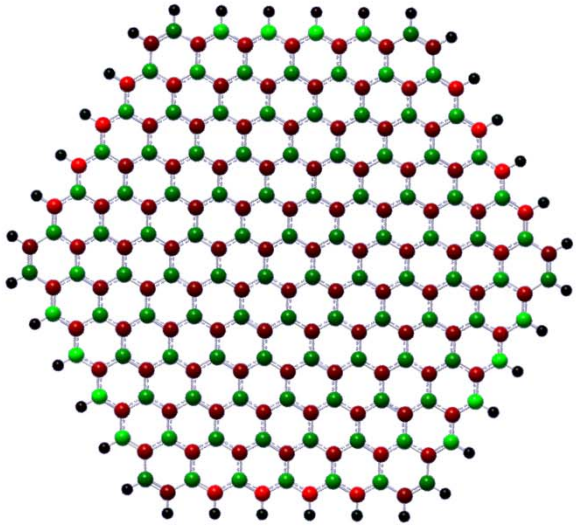
Singlet



WF stable

C294





Summary

Collectivity index provides a more detailed picture of plasmon-like excitations of metal atom chains or rings

The ground state and electronic excitation of Au8-ring are studied by DFT and LR-TD-DFT.

Slightly deformed ring structure is found and charge alternation is also observed.
Excitation spectra are simulated for different ring structures.
Optimized structure and some structure near the optimized one gives positive transition energies and no de-excitation components.