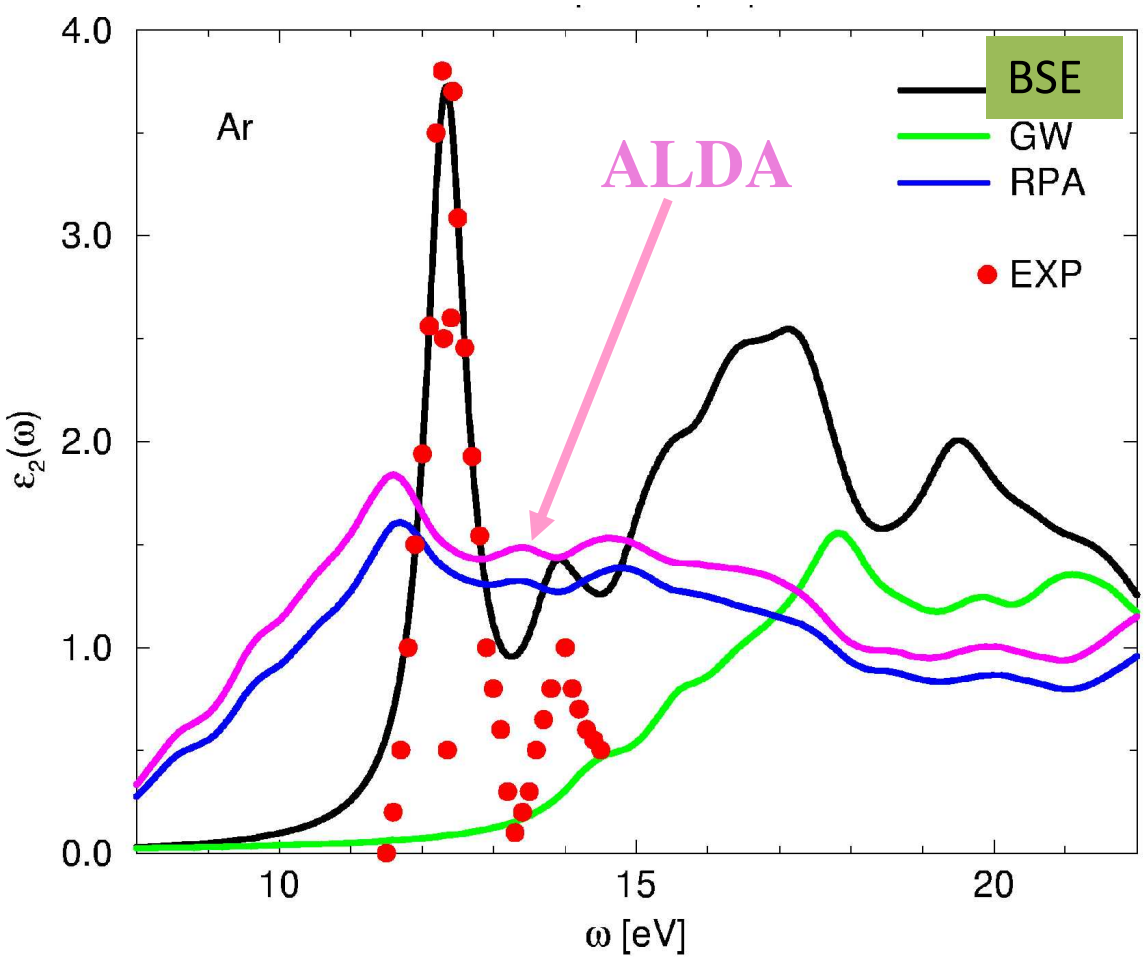
Solid Argon



L. Reining, V. Olevano, A. Rubio, G. Onida, PRL 88, 066404 (2002)

Excitons are completely missing for simple xc functionals like ALDA!

EXPLANATION: Optical absorption in solids probes primarily q=0. In the TDDFT response equation, the Coulomb interaction and the xc kernel only appear as a sum $(v + f_{xc})$.

$v(q)$ diverges like $1/q^2$ for $q \rightarrow 0$
$f_{xc} \rightarrow$ const (in ALDA)

Hence results are close to $f_{xc} = 0$ (RPA) in the $q \rightarrow 0$ limit.

CONCLUSION:
Approximations for f_{xc} are needed which, for $q \rightarrow 0$, correctly diverge like $1/q^2$. Such approximations can be derived from many-body perturbation theory (see, e.g., L. Reining, V. Olevano, A. Rubio, G. Onida, PRL 88, 066404 (2002)).

$$\varepsilon^{-1}(\mathbf{q},\omega) = 1 + \chi_S(\mathbf{q},\omega)\, v(\mathbf{q}) \left[1 - \left(v(\mathbf{q}) + f_{xc}^{approx}(\mathbf{q},\omega) \right) \chi_S(\mathbf{q},\omega) \right]^{-1}$$

Two problems of LDA/ALDA need to be fixed:

- **Onset of absorption is dictated by χ_S , i.e. is identical to the LDA gap for ω-independent kernel (such as ALDA)**

- **Description of excitons requires $1/q^2$ behavior of f_{xc}**

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Use better ground-state functional, such as HSE, which yields a reliable gap (in GKS) and reliable response function $\tilde{\chi}(\mathbf{q},\omega)$

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Bootstrap kernel

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(Sharma, Dewhurst, Sanna, EKUG, PRL **107**, 186401 (2011))

$$f_{\mathrm{xc}}^{\mathrm{boot}}\left(\mathbf{q},\omega\right)=\frac{\varepsilon^{-1}\left(\mathbf{q},\omega=0\right)}{\tilde{\chi}^{00}\left(\mathbf{q},\omega=0\right)}$$

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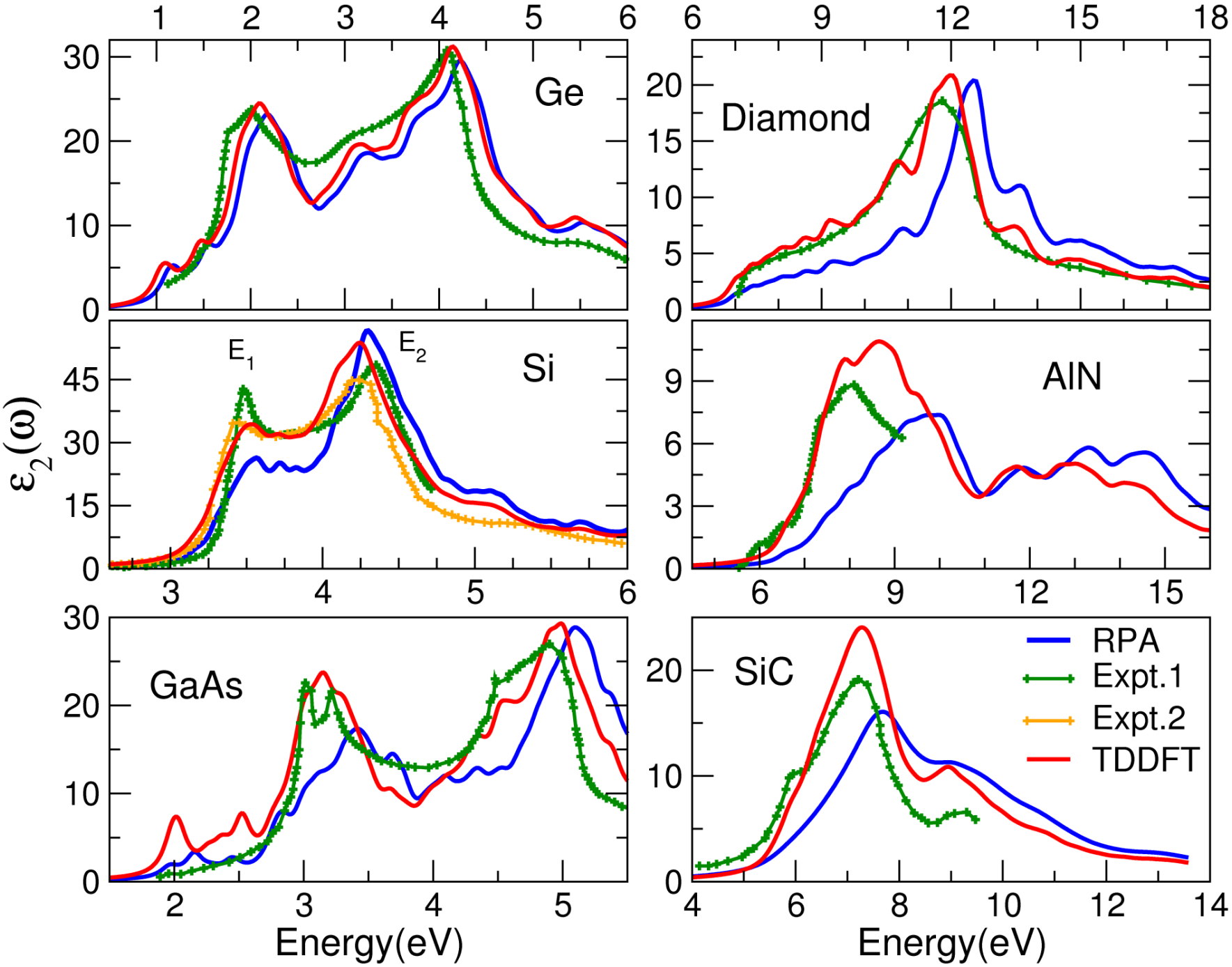
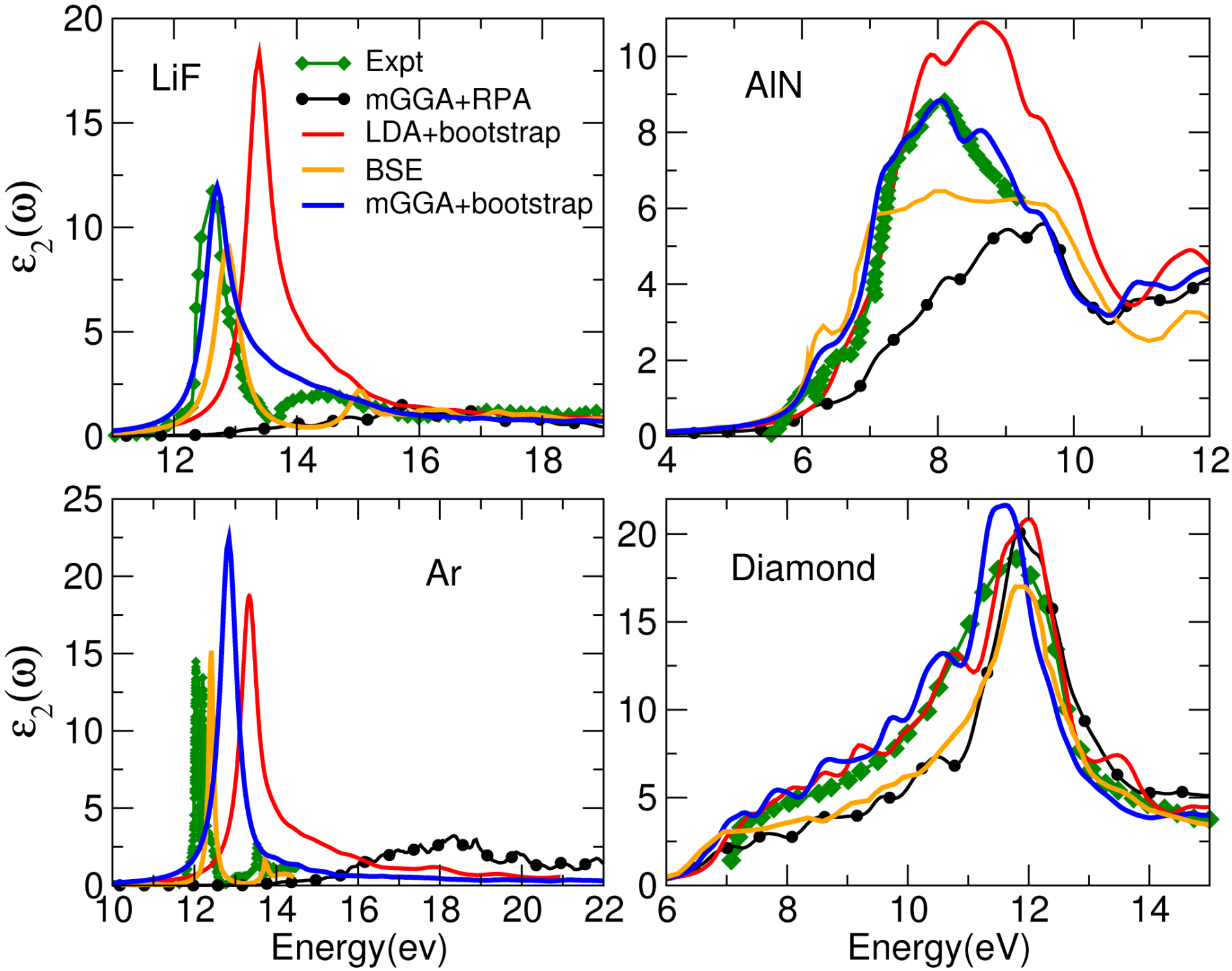
(Sharma, Dewhurst, Sanna, EKUG, PRL **107**, 186401 (2011))

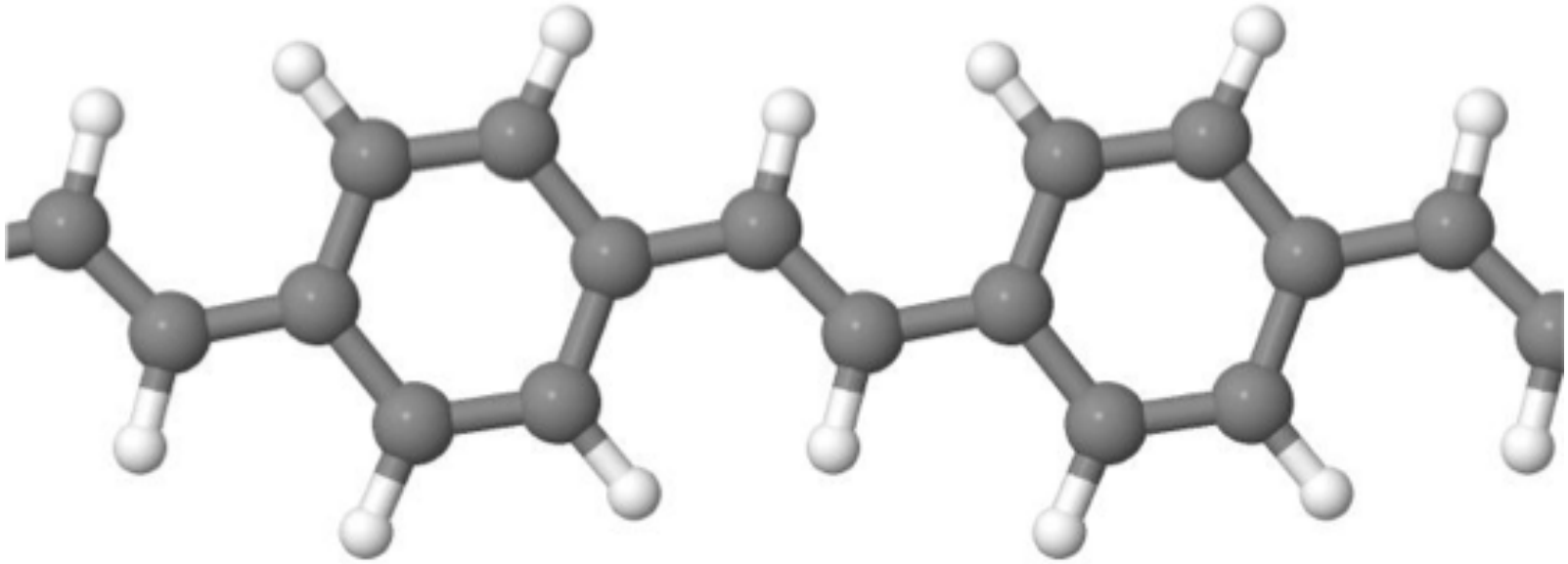
$$f_{xc}^{boot}(\mathbf{q},\omega) = \frac{\varepsilon^{-1}(\mathbf{q},\omega=0)}{\tilde{\chi}^{00}(\mathbf{q},\omega=0)}$$

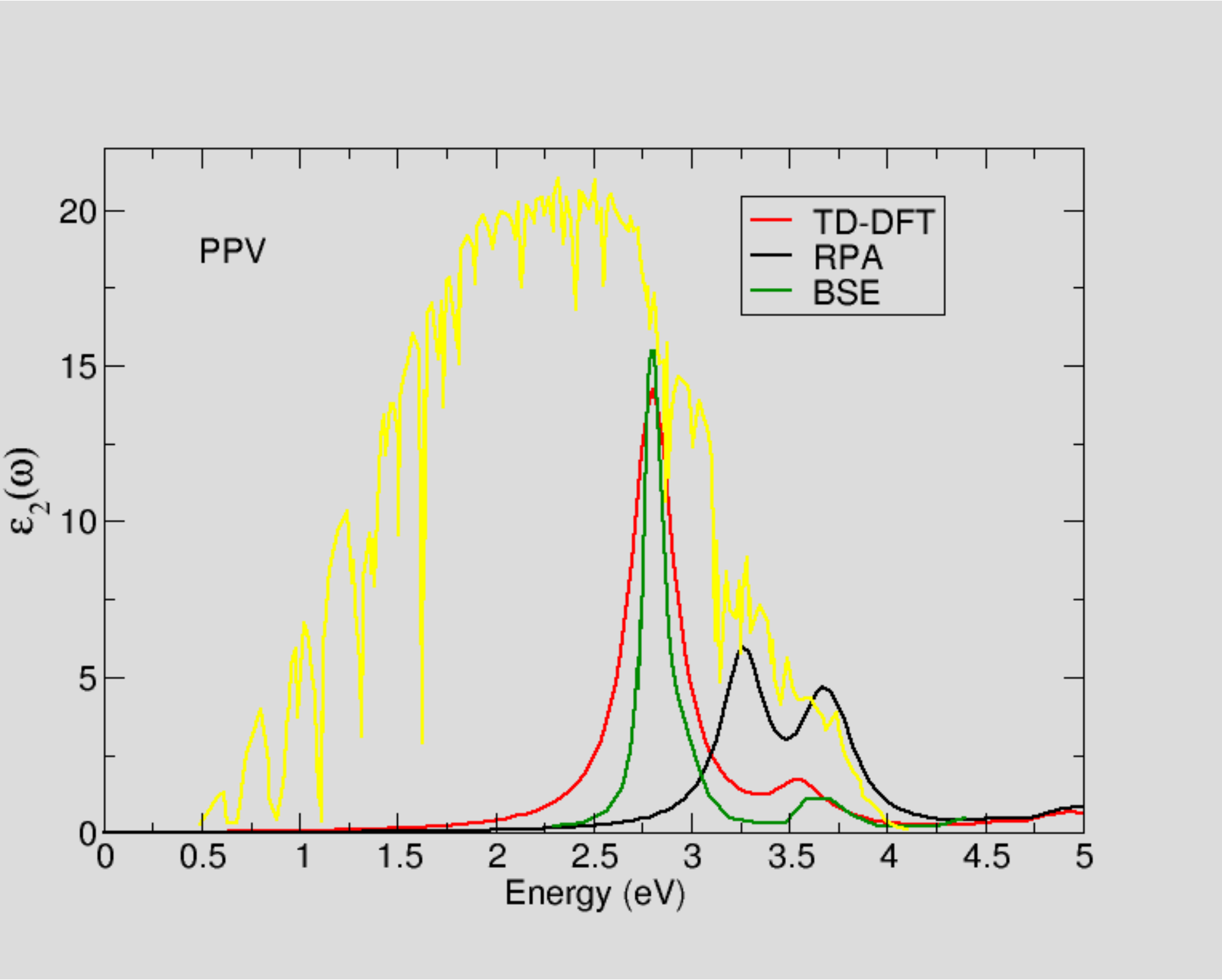
$$\varepsilon^{-1}(\mathbf{q},\omega) = 1 + \tilde{\chi}(\mathbf{q},\omega)v(\mathbf{q})\left[1 - \left(v(\mathbf{q}) + f_{xc}^{boot}(\mathbf{q},\omega)\right)\tilde{\chi}(\mathbf{q},\omega)\right]^{-1}$$


Ge
Diamond
Si
AlN
GaAs
SiC
E1
E2
RPA
Expt.1
Expt.2
TDDFT
ε2(ω)
Energy(eV)
Energy(eV)

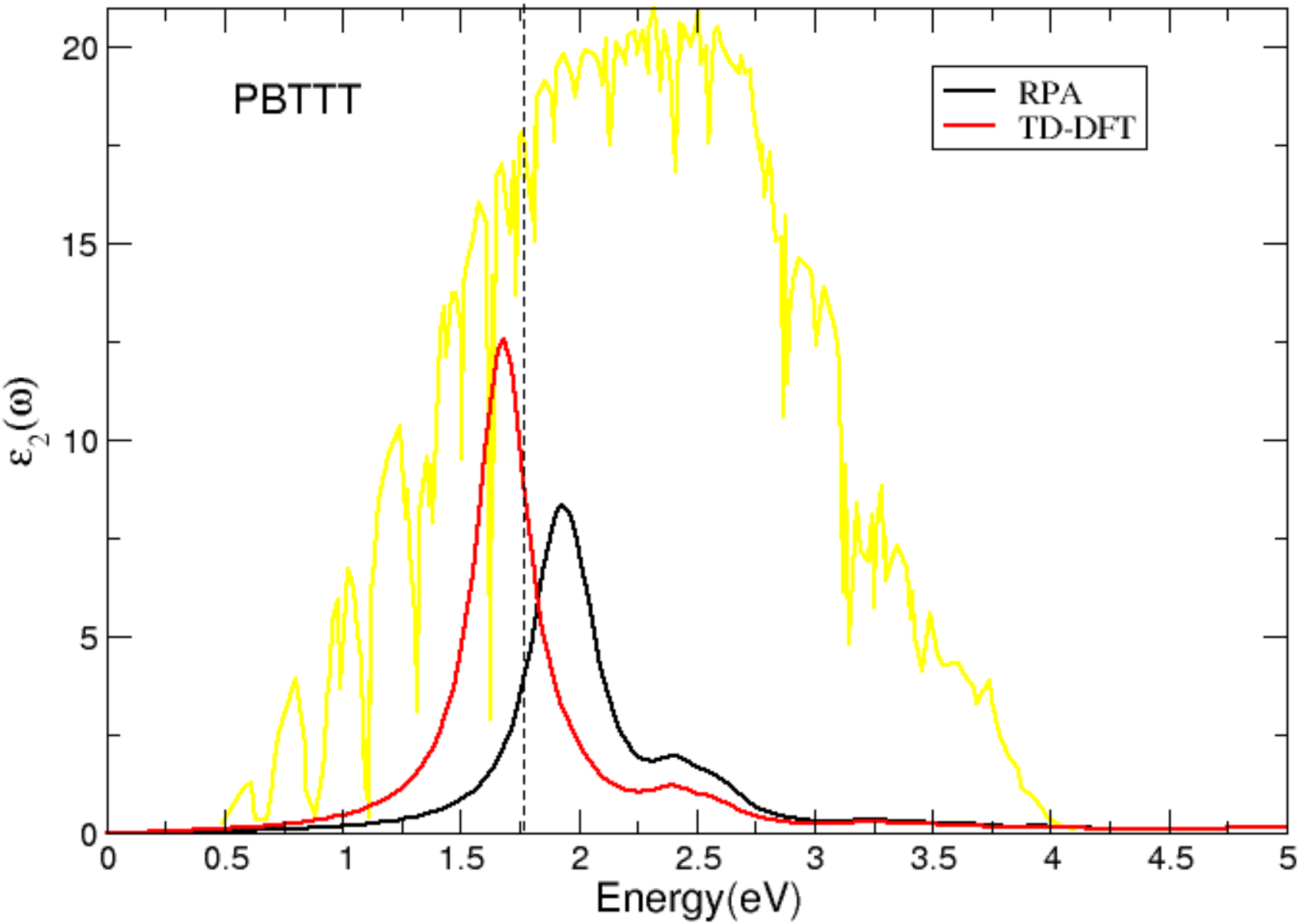

LiF
Expt
mGGA+RPA
LDA+bootstrap
BSE
mGGA+bootstrap
AlN
Ar
Diamond
$\varepsilon_2(\omega)$
Energy(ev)
Energy(eV)

PPV



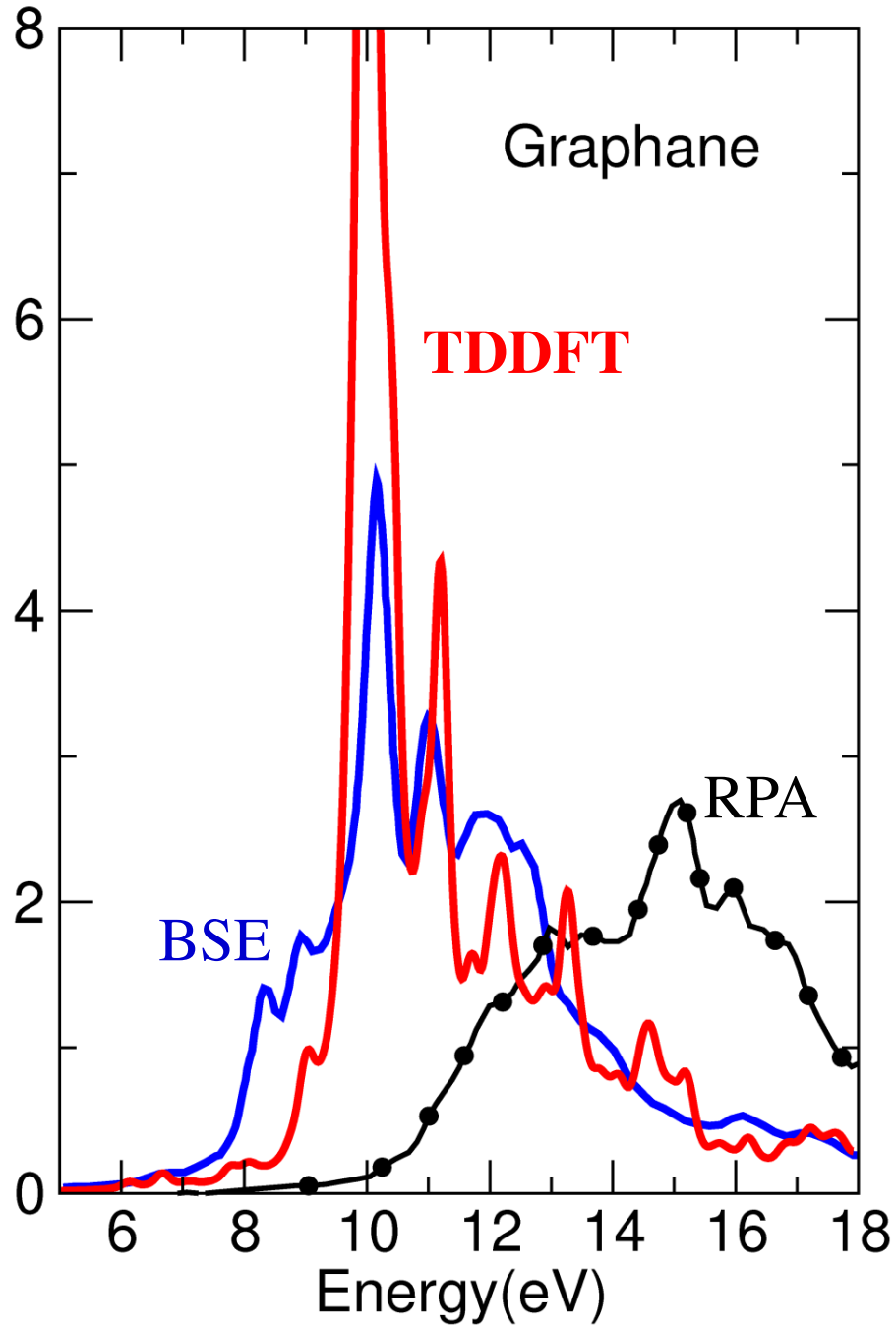

PPV
TD-DFT
RPA
BSE
$\varepsilon_2(\omega)$
Energy (eV)
0
5
10
15
20
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5

PBTTT


PBTTT
RPA
TD-DFT
$\varepsilon_2(\omega)$
Energy(eV)
0
5
10
15
20
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5

Linear-response TDDFT is now being used to predict and to interpret experimental optical spectra in essentially all corners of physics and chemistry.

Some examples:


Graphane
TDDFT
BSE
RPA
0
2
4
6
8
6
8
10
12
14
16
18
Energy(eV)

Inorganic Chemistry

Article

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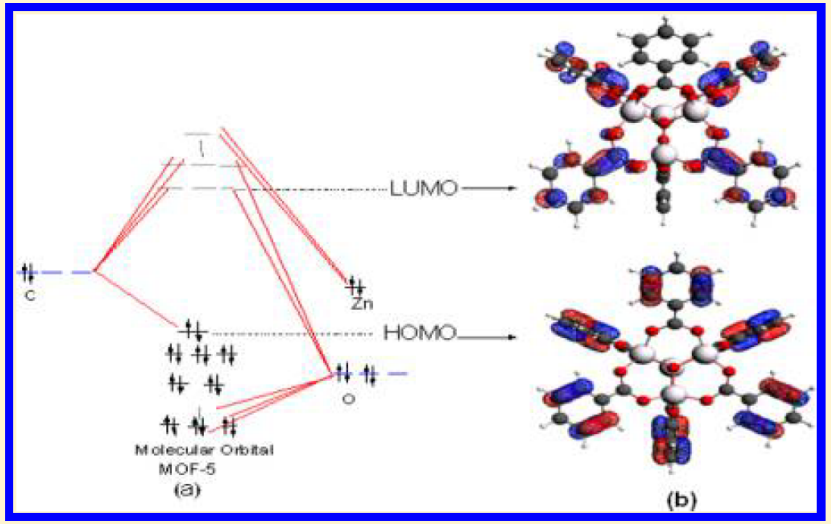
Luminescent Properties of Metal–Organic Framework MOF-5: Relativistic Time-Dependent Density Functional Theory Investigations

Min Ji, Xin Lan, Zhenping Han, Ce Hao,* and Jieshan Qiu

State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, Liaoning, China

ABSTRACT: The electronically excited state and luminescence property of metal–organic framework MOF-5 were investigated using relativistic density functional theory (DFT) and time-dependent DFT (TDDFT). The geometry, IR spectra, and UV–vis spectra of MOF-5 in the ground state were calculated using relativistic DFT, leading to good agreement between the experimental and theoretical results. The frontier molecular orbitals and electronic configuration indicated that the luminescence mechanism in MOF-5 follows ligand-to-ligand charge transfer (LLCT), namely, $\pi^* \rightarrow \pi$, rather than emission with the ZnO quantum dot (QD) proposed by Bordiga et al. The geometry and IR spectra of MOF-5 in the electronically excited state have been calculated using the relativistic TDDFT and compared with those for the ground state. The comparison reveals that the Zn_4O_{13} QD is rigid, whereas the ligands BDC^{2-} are nonrigid. In addition, the calculated emission band of MOF-5 is in good agreement with the experimental result and is similar to that of the ligand H_2BDC. The combined results confirmed that the luminescence mechanism for MOF-5 should be LLCT with little mixing of the ligand-to-metal charge transfer. The reason for the MOF-5 luminescence is explained by the excellent coplanarity between the six-membered ring consisting of zinc, oxygen, carbon, and the benzene ring.



A NANOPLASMONIC SWITCH BASED ON MOLECULAR MACHINES

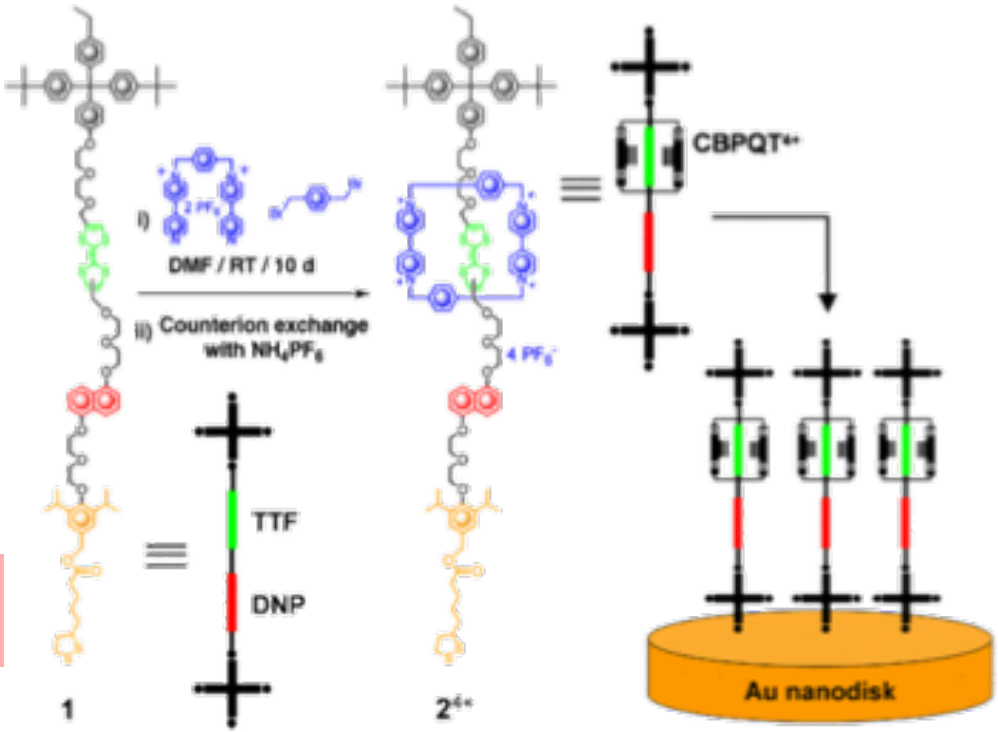
Yue Bing Zheng[1], *Ying-Wei Yang*[2], *Lasse Jensen*[1], *Lei Fang*[2], *Bala Krishna Juluri*[1], *Paul S. Weiss*[1], *J. Fraser Stoddart*[2], *Tony Jun Huang*[1*]

[1]The Pennsylvania State University, University Park, Pennsylvania 16802 USA

[2]Northwestern University, Evanston, Illinois 60208 USA

ABSTRACT

We aim to develop a molecular-machine-driven nanoplasmonic switch for its use in future nanophotonic integrated circuits (ICs) that have applications in optical communication, information processing, biological and chemical sensing. Experimental data show that an Au nanodisk array, coated with rotaxane molecular machines, switches its localized surface plasmon resonances (LSPR) reversibly when it is exposed to chemical oxidants and reductants. Conversely, bare Au nanodisks and disks coated with mechanically inert control compounds, do not display the same switching behavior. Along with calculations based on time-dependent density functional theory (TDDFT), these observations suggest that the nanoscale movements within surface-bound "molecular machines" can be used as the active components in plasmonic devices.



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PAPER

First-principles calculation of electronic spectra of light-harvesting complex II†

Carolin König and Johannes Neugebauer*