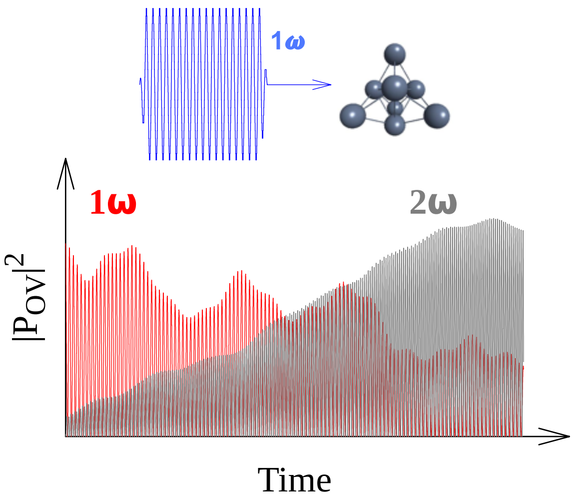
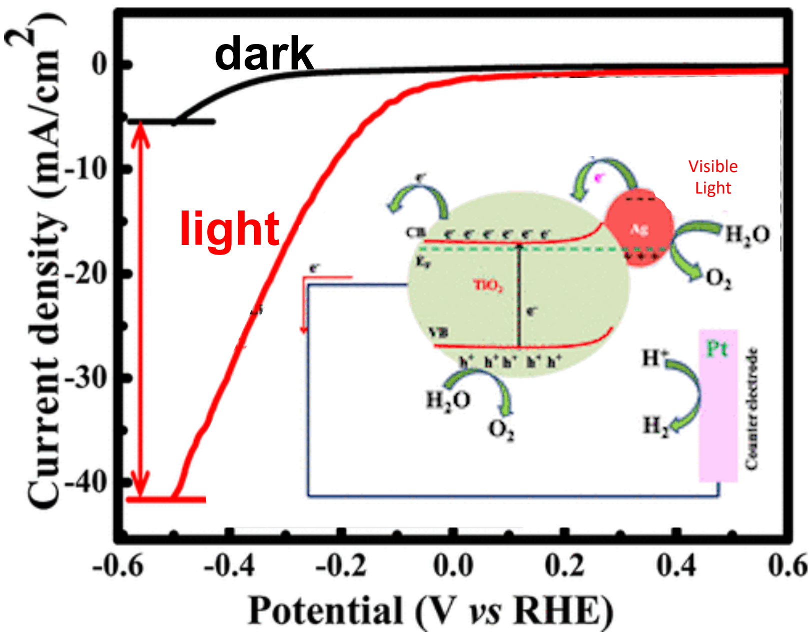
Ultrafast Nonlinear Plasmon Decay Processes in Silver Nanoclusters



Gowri Kuda-Singappulige
Adviser: Christine Aikens

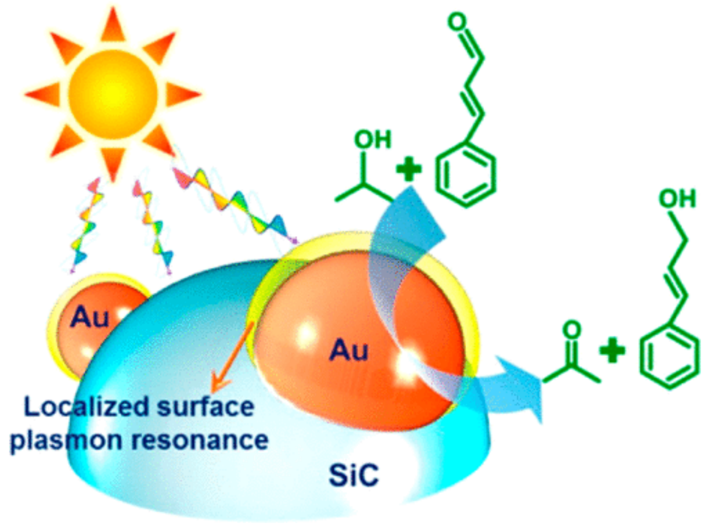
Plasmonic nanostructures for light-induced processes

Enhanced Solar Energy Conversion



ACS Appl. Energy Mater. **2020**, 3, 2, 1821-1830

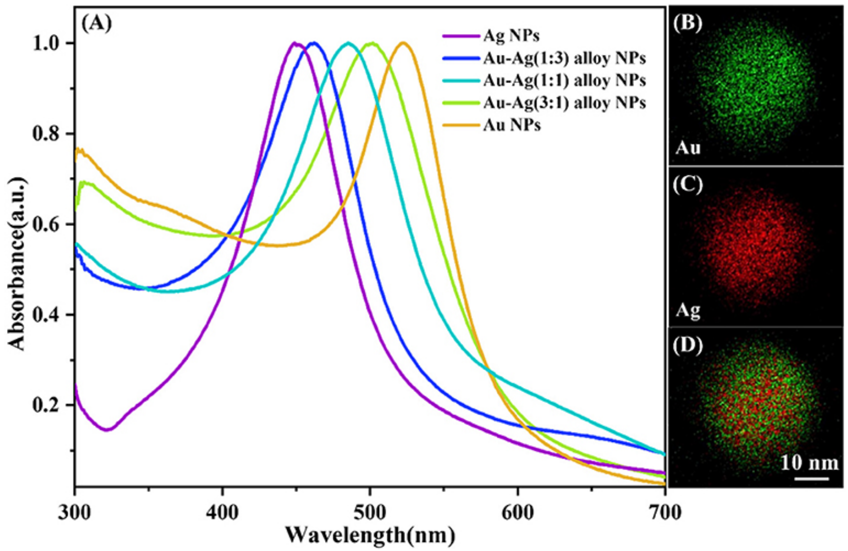
Plasmon-Induced Selective Catalysis



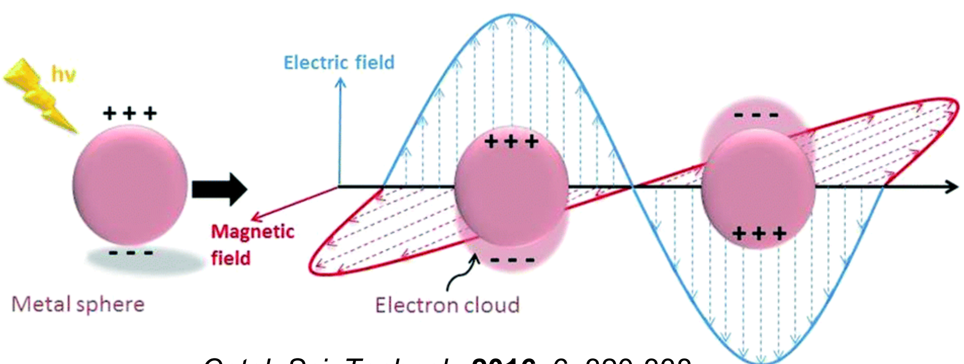
J. Am. Chem. Soc. **2016**, 138, 30, 9361–9364

INTRODUCTION

Plasmon Resonance



Front. Chem. ***2019****, 7, 647-647*

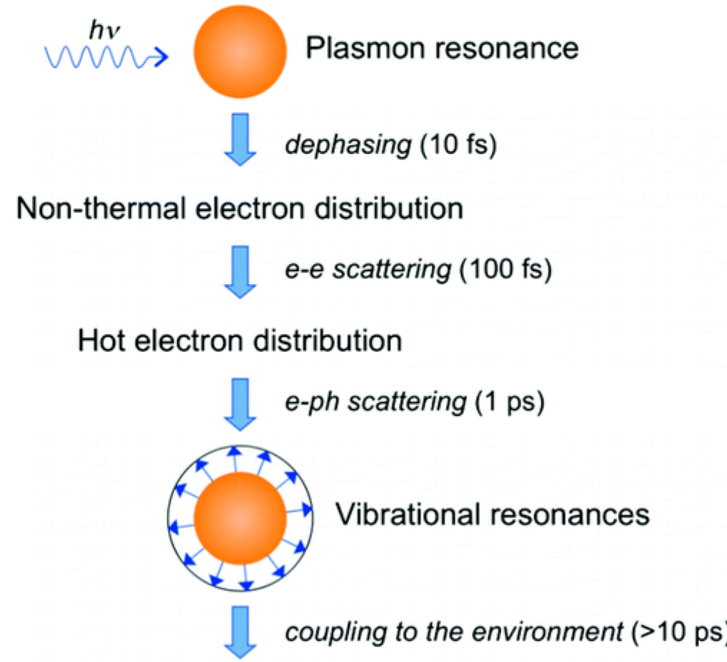


Catal. Sci. Technol., **2016**, 6, 320-338

Rapid plasmon decay:

A challenge for practical applications

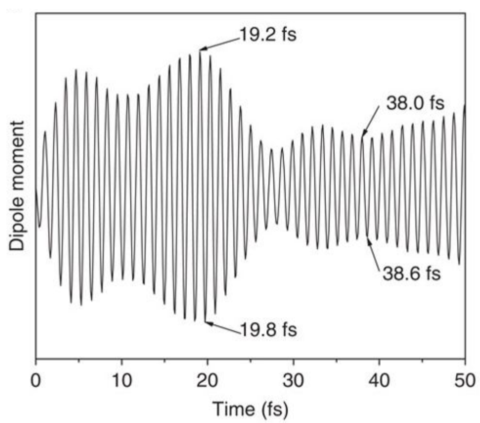
Plasmon decay processes



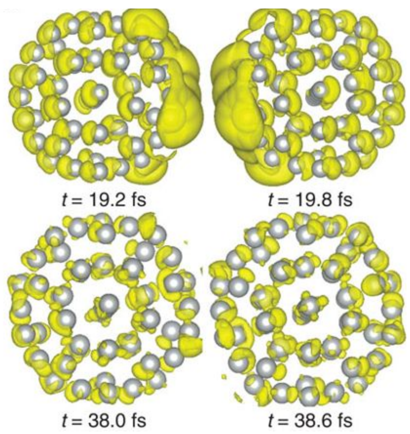
Chem. Rev. **2011**, 111, 6, 3858–3887

Plasmon decay in silver nanoparticles

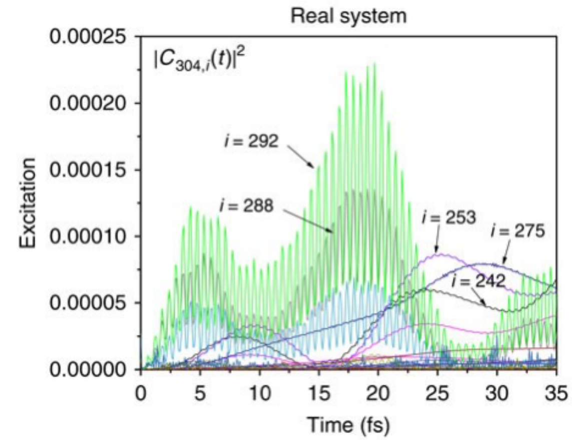
Dipole moment



Charge density

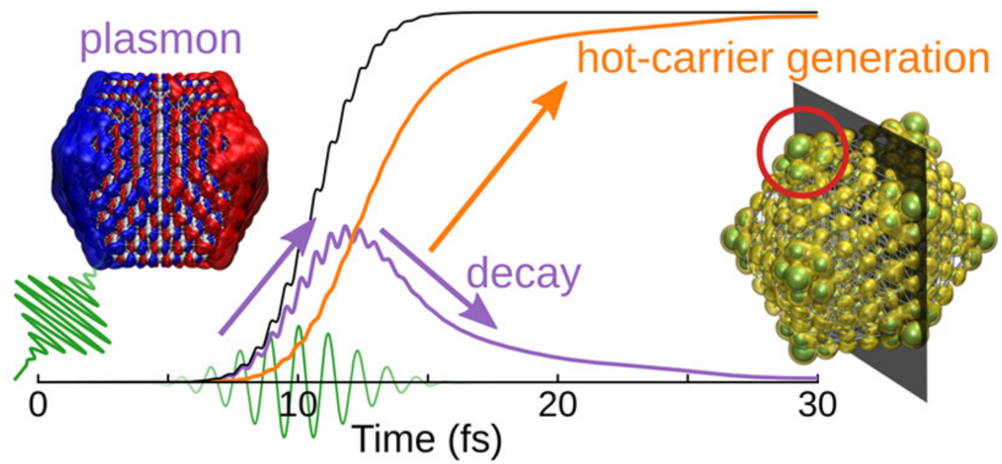


Transition coefficients



Nat. Commun., **2015**, 6, 10107

Plasmonic energy transferred into single-particle (hot-carrier) excitation



ACS Nano ***2020****, 14, 9963−9971*

KANSAS STATE UNIVERSITY

Density matrix (P)

Molecular orbitals as LCAOs

$$\Psi_a = \sum_{\mu}^{N/2} C_{a\mu}\,\phi_\mu$$

Ψ_a = Molecular orbital

ϕ_μ = Atomic orbital

$C_{a\mu}$ = Expansion coefficient

Density matrix elements

$$P_{ab} = 2\sum_{\mu}^{N/2} C_{a\mu}C_{b\mu}^{*}$$

P_{ab} = Density matrix element of molecular orbital pair a and b

N = Number of electrons

Molecular orbital Ψ_i (→)

Molecular orbital Ψ_i (↓)

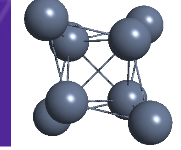
$$\begin{bmatrix} P_{11} & \cdots & P_{1N} \\ \vdots & \ddots & \vdots \\ P_{N1} & \cdots & P_{NN} \end{bmatrix}$$

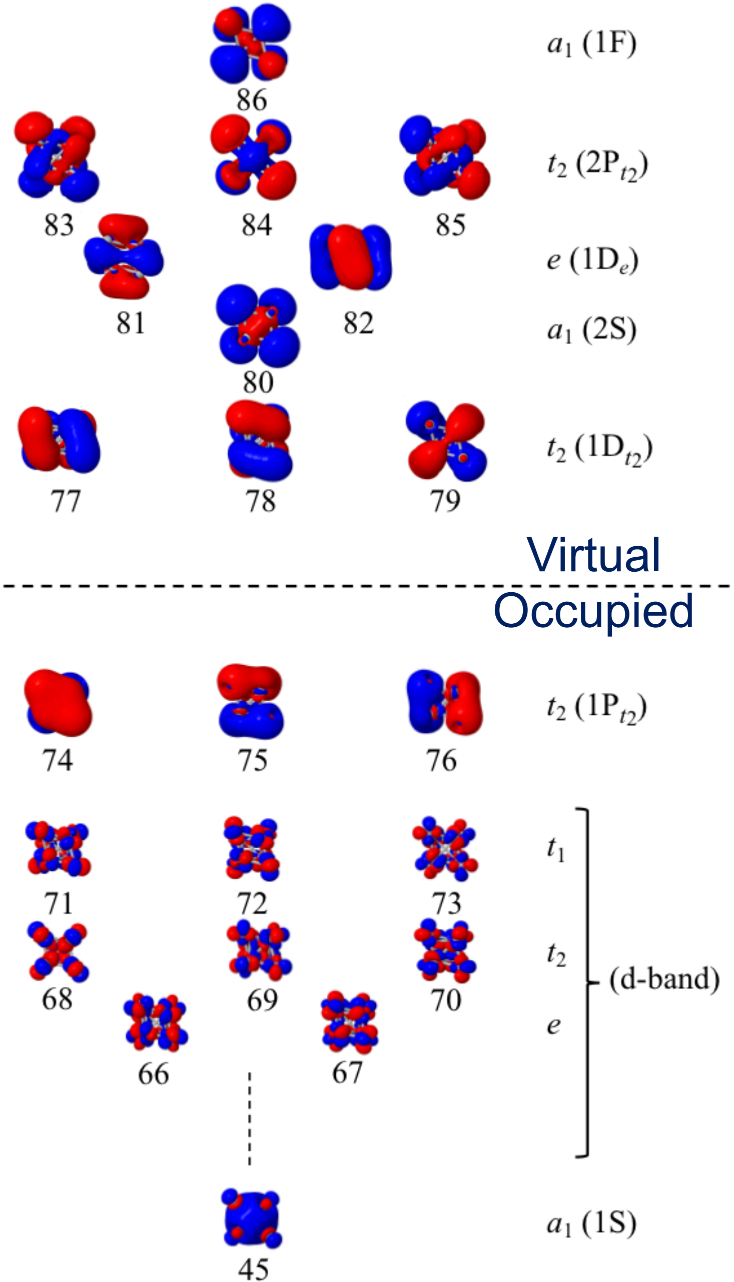
- Diagonal elements $\boldsymbol{P_{aa}}$ → **electron population in molecular orbital $\boldsymbol{a}$**
- Off-diagonal elements $\boldsymbol{P_{ab}}$ → **electron transition between orbitals a and b**

  a = occupied, b = virtual

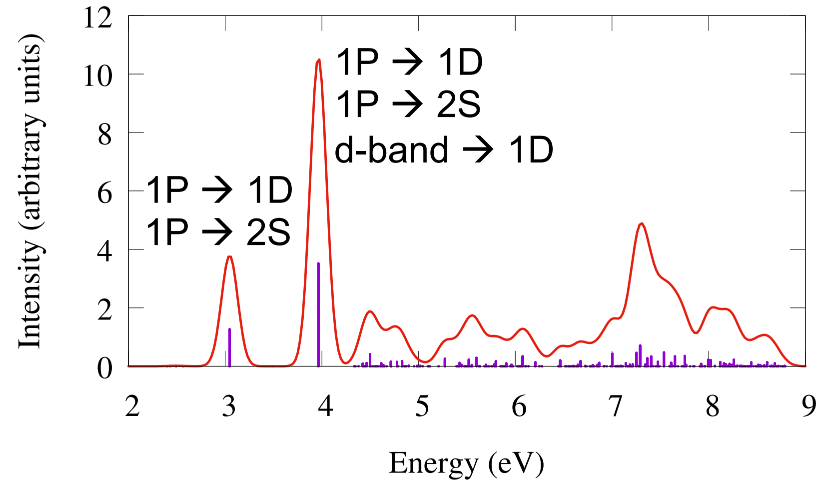
Magnitude of $\mathbf{P_{OV}}$(*t*): Amount of electronic transition occurring between the occupied (O) and the virtual (V) orbital at time *t*.

Ag_8 (T_d) - Electronic structure and optical properties





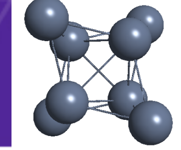
Absorption spectrum from LR-TDDFT



- Two sharp peaks at 3.05 eV and 3.96 eV
- Constructive contribution of multiple electronic transitions: molecular analog of a plasmon resonance in Ag_8 nanocluster

G. U. Kuda-Singappulige, D. B. Lingerfelt, X. Li, and C. M. Aikens, *J. Phys. Chem. C,* **2020**, 124, 37, 20477–20487

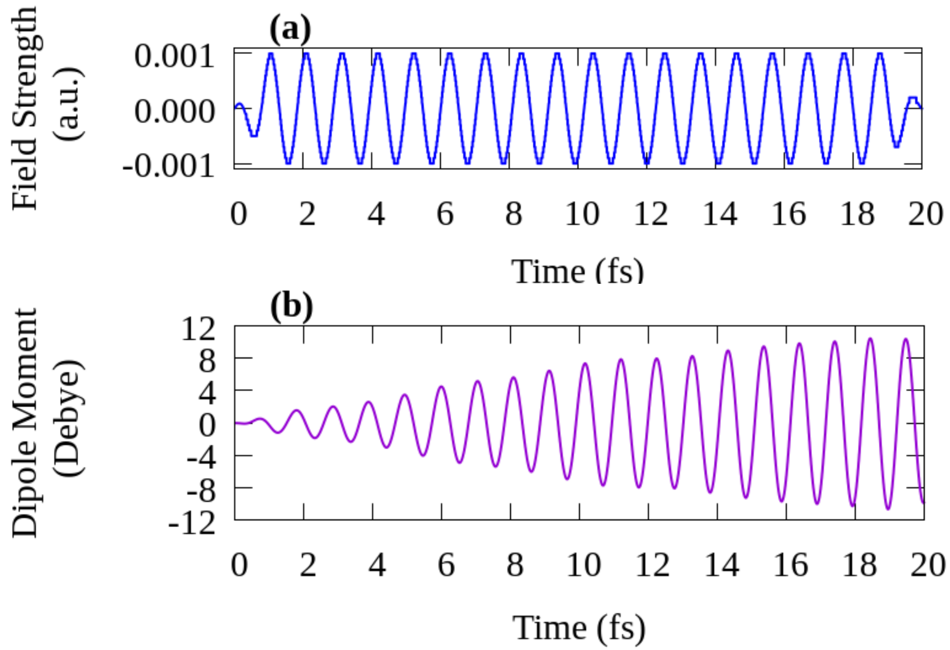
Ag_8 (T_d) - Real-time electron dynamics

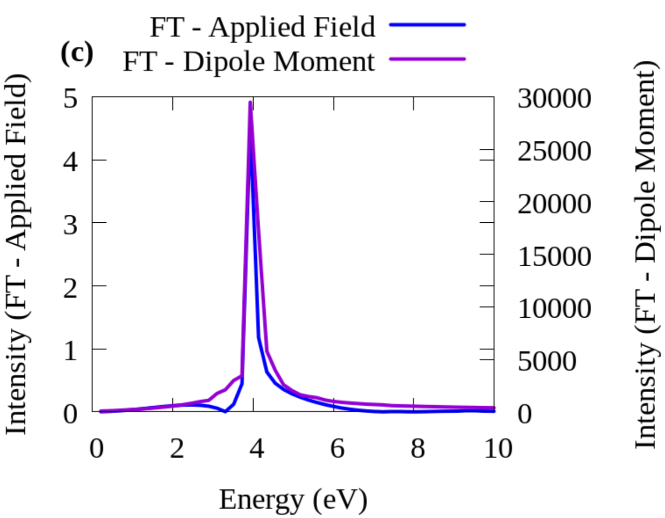


Excite 3.96 eV state

Observe the dipole response

Trapezoidal-shaped electric field



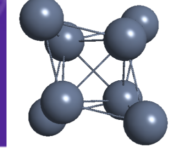


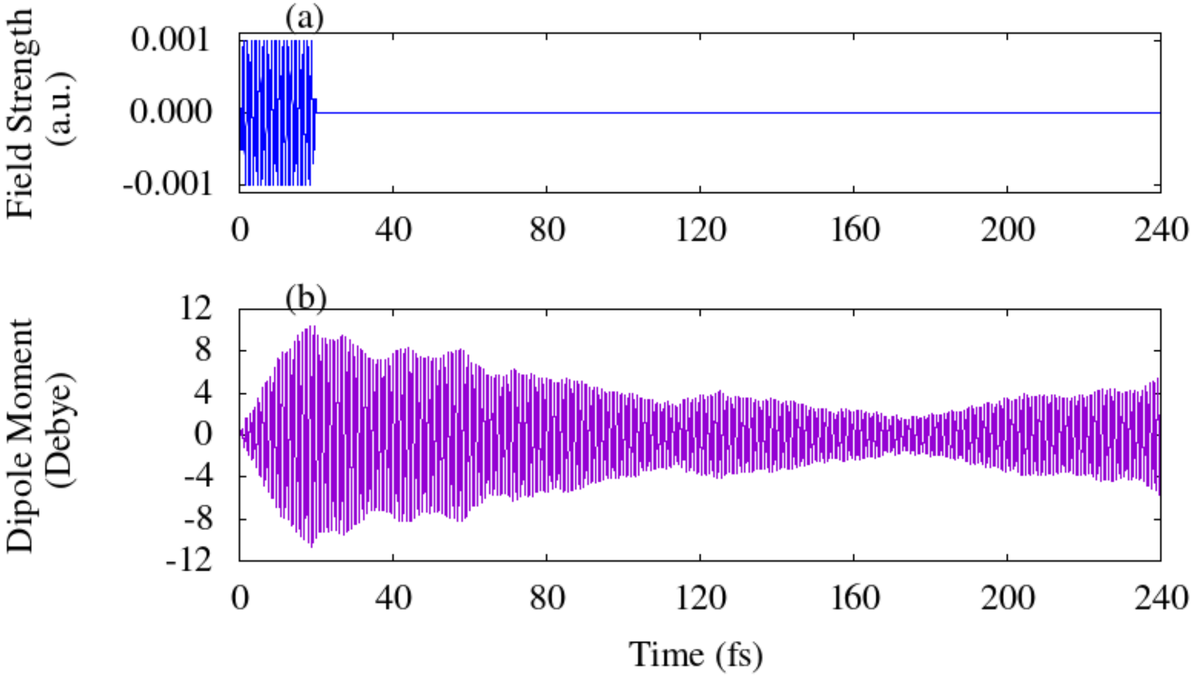
- Maximum strength = 0.001 au (~3.57×10^{13} W/cm^2) with a given frequency
    - Time step = 0.002 fs; Total time = 240 fs
- BP86/LanL2DZ level of theory
- Development version of Gaussian

KANSAS STATE UNIVERSITY

G. U. Kuda-Singappulige, D. B. Lingerfelt, X. Li, and C. M. Aikens, *J. Phys. Chem. C,* **2020**, 124, 37, 20477–20487

Ag_8 (T_d) - Real-time electron dynamics





0-20 fs: Increase

20-175 fs: Decrease

After 175 fs: Increases Again

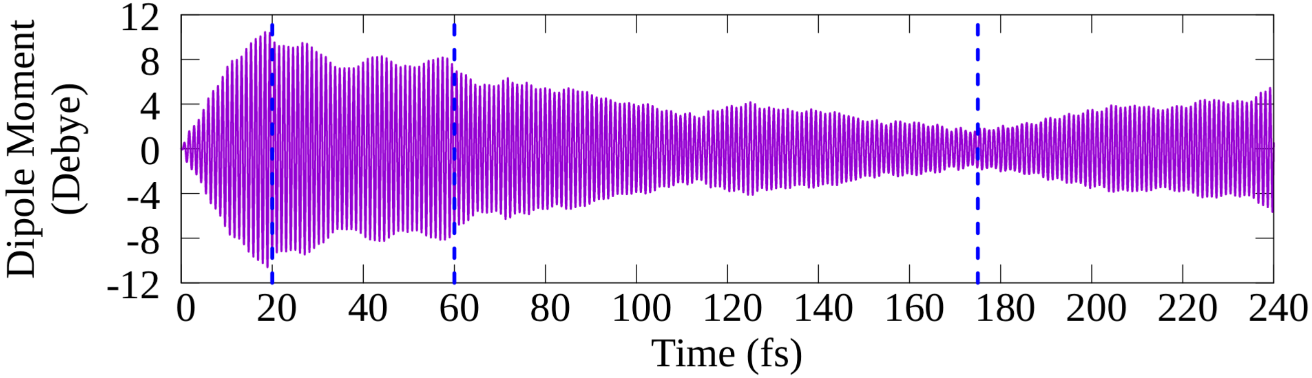
Can we identify the decay mechanism?

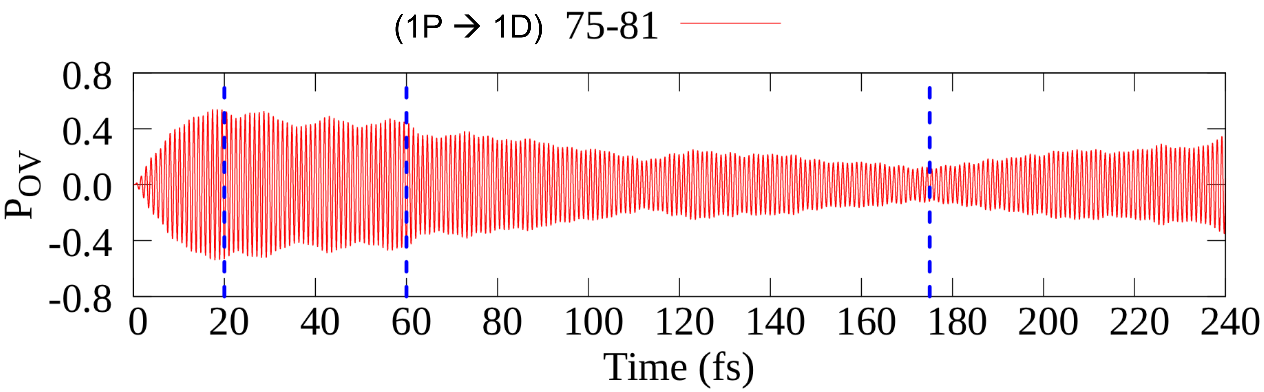
Hypothesis: Electronic Transitions

G. U. Kuda-Singappulige, D. B. Lingerfelt, X. Li, and C. M. Aikens,
J. Phys. Chem. C, **2020**, 124, 37, 20477–20487

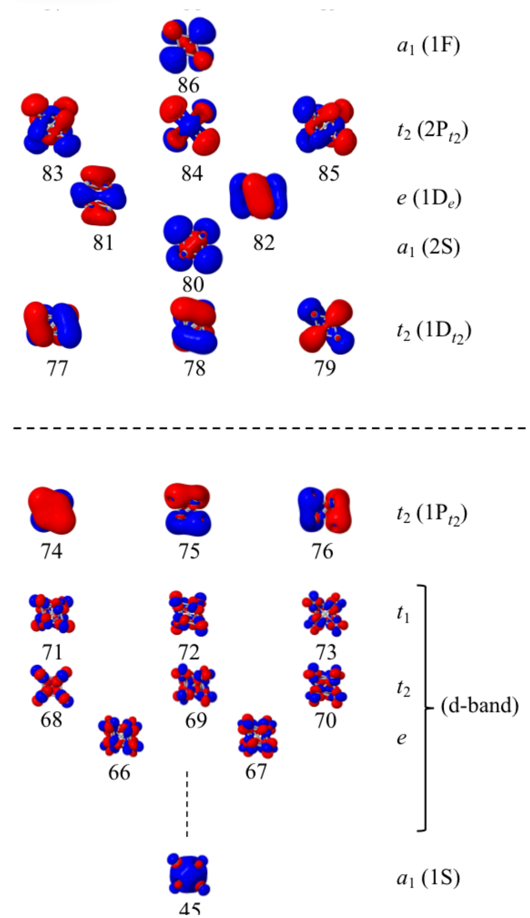
Variation of density matrix elements (P_{ov})

Dipole moment





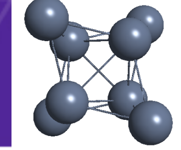
Off-diagonal elements



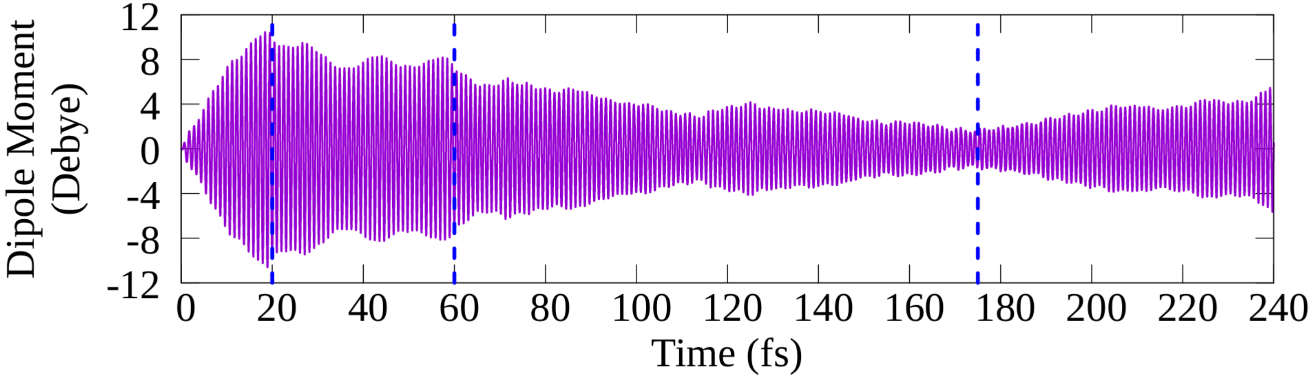
Variation of dipole moment dominated by responsible transitions for a given excitation

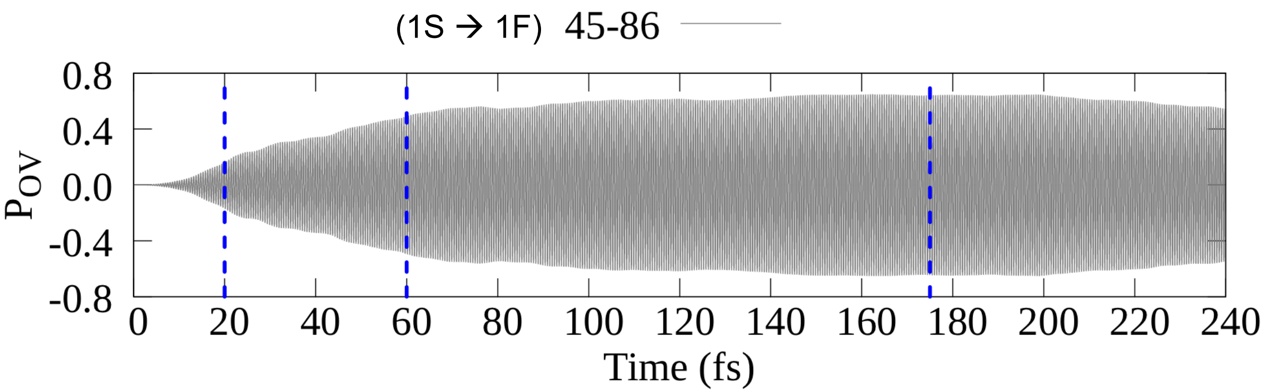
G. U. Kuda-Singappulige, D. B. Lingerfelt, X. Li, and C. M. Aikens, *J. Phys. Chem. C*, **2020**, 124, 37, 20477–20487

Variation of density matrix elements (P_{ov})

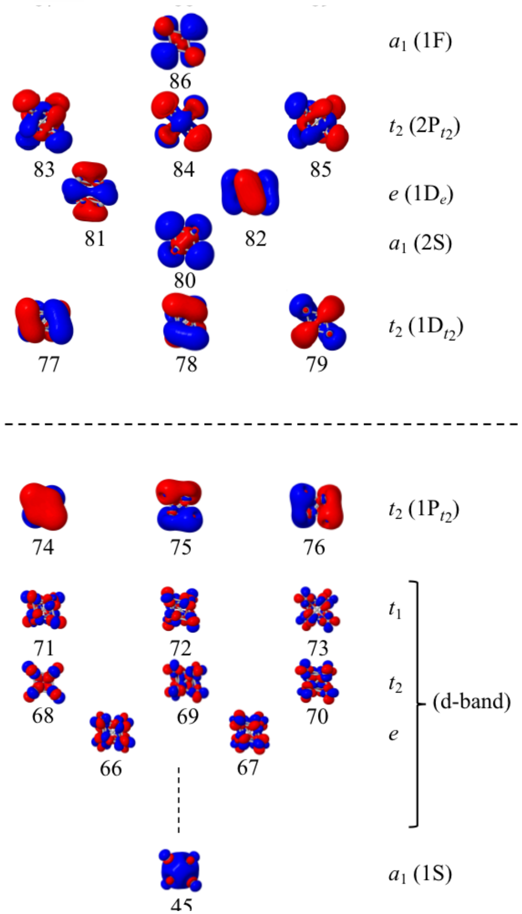


Dipole moment



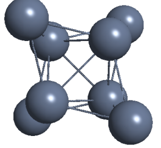


Off-diagonal elements

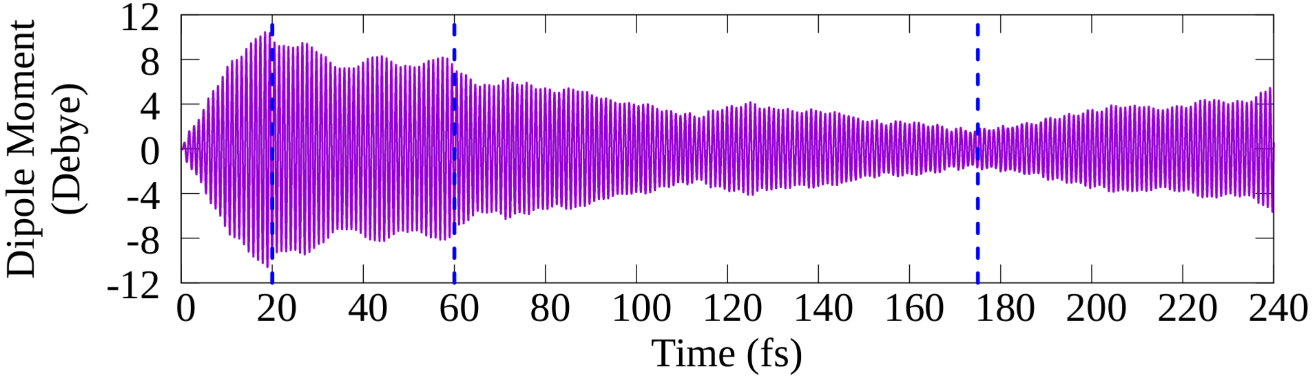


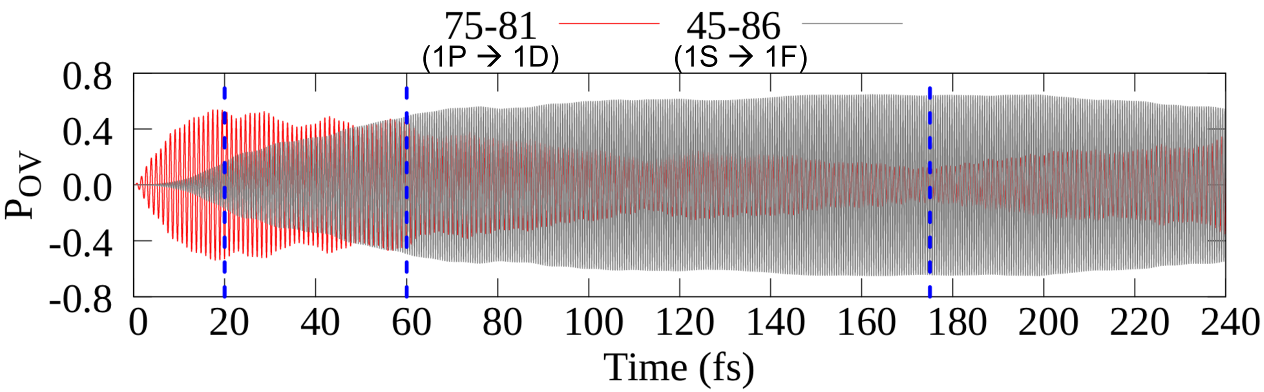
Emergence of other transitions that grow even after the field is turned off

Variation of density matrix elements (P_{ov})



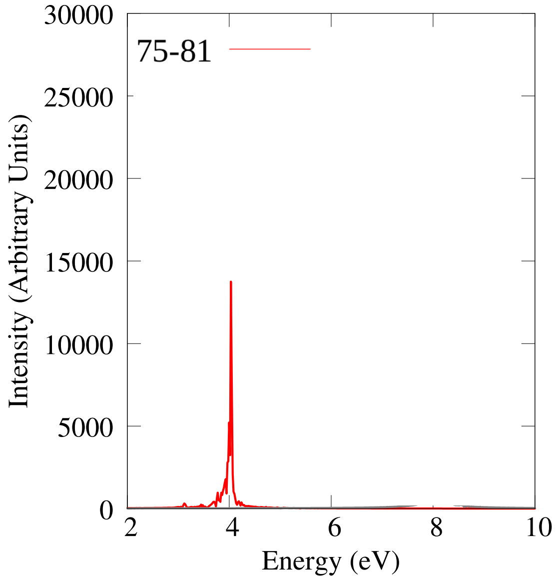
Dipole moment





Off-diagonal elements

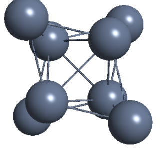
Fourier transform of P_{ov}



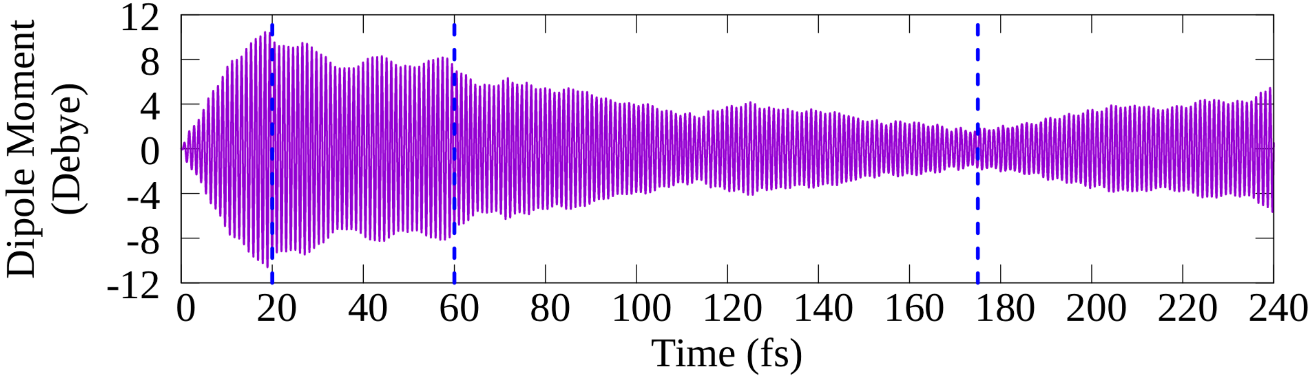
$P_{75\text{-}81}$: One Photon Absorption ($\boldsymbol{\omega}$)

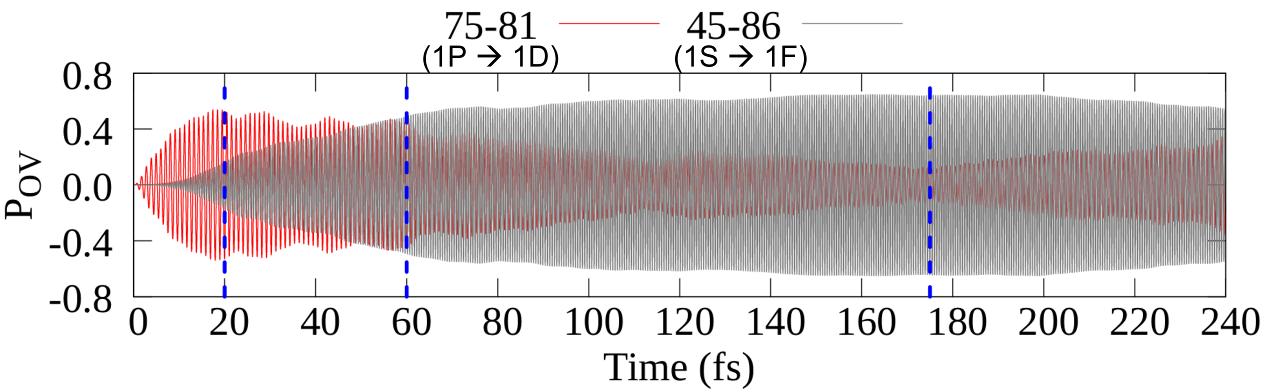
G. U. Kuda-Singappulige, D. B. Lingerfelt, X. Li, and C. M. Aikens, *J. Phys. Chem. C,* **2020**, 124, 37, 20477–20487

Variation of density matrix elements (P_{ov})



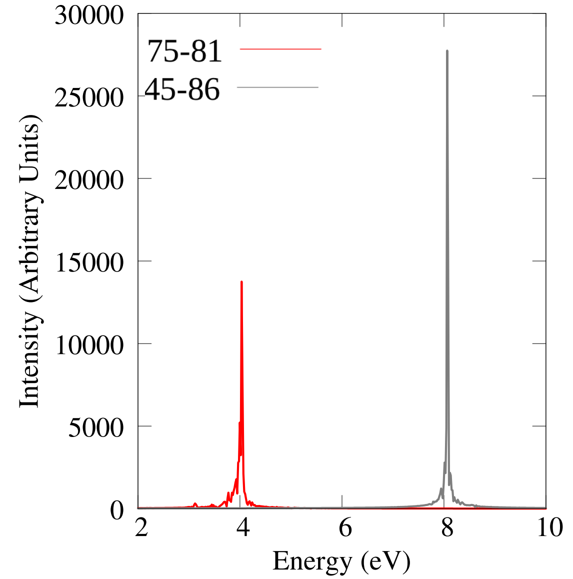
Dipole moment





Off-diagonal elements

Fourier transform of P_{ov}



$P_{75\text{-}81}$: One Photon Absorption (ω)

$P_{45\text{-}86}$: Two Photon Absorption (2ω)

Transitions responsible for the resonant excitation decay into excitations with twice the incident frequency

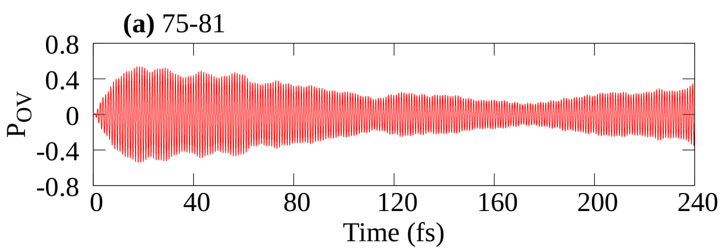
Kansas State University

G. U. Kuda-Singappulige, D. B. Lingerfelt, X. Li, and C. M. Aikens, *J. Phys. Chem. C,* **2020**, 124, 37, 20477–20487

Selection rules - Dipole allowed transitions in T_D

If **direct product** of symmetries of the two orbitals involved in a transition **reduced to T_2**, the transition is allowed for

One-Photon Absorption



Transitions contribute to the resonant excited state follow the OPA selection rules

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	linear functions, rotations	quadratic functions
A_1	1	1	1	1	1		$x^2+y^2+z^2$
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)	
T_2	3	0	-1	-1	1	(x, y, z)	(xy, xz, yz)

Excitation energy (eV)	**Transitions**	**Spherical assignments**	**Symmetry**	**Direct product decomposition into irreducible representation**
4.03	75 → 81 74 → 81	1P → 1D	T_2 → E	T_1 + $\mathbf{T_2}$
	76 → 77	1P → 1D	T_2 → T_2	A_1 + E + T_1 + $\mathbf{T_2}$
	75 → 80	1P → 2S	T_2 → A_1	$\mathbf{T_2}$
	66 → 78 66 → 79	d-band → 1D	E → T_2	T_1 + $\mathbf{T_2}$

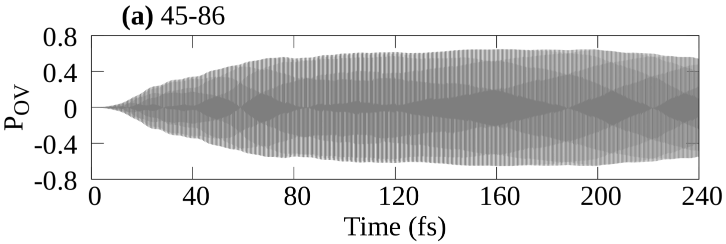
G. U. Kuda-Singappulige, D. B. Lingerfelt, X. Li, and C. M. Aikens, *J. Phys. Chem. C,* **2020**, 124, 37, 20477–20487

Selection rules - Quadrupole allowed transitions in T_D

If direct product of symmetries of the two orbitals involved in a transition can be reduced to **A_1, E or T_2**, then that transition can be allowed for

Two-Photon Absorption

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	linear functions, rotations	quadratic functions
A_1	1	1	1	1	1		$x^2+y^2+z^2$
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)	
T_2	3	0	-1	-1	1	(x, y, z)	(xy, xz, yz)



Excitation energy (eV)	Transitions	Spherical assignments	Symmetry	Direct product decomposition into irreducible representation
8.07	45 → 86	1S → 1F	$A_1 \rightarrow A_1$	**A_1**
	72 → 92 71 → 90 73 → 90	d-band → 1F	$T_1 \rightarrow T_2$	A_2 + **E** + T_1 + **T_2**
	68 → 90 69 → 91 69 → 92 70 → 91 70 → 92	d-band → 1F	$T_2 \rightarrow T_2$	**A_1** + **E** + T_1 + **T_2**

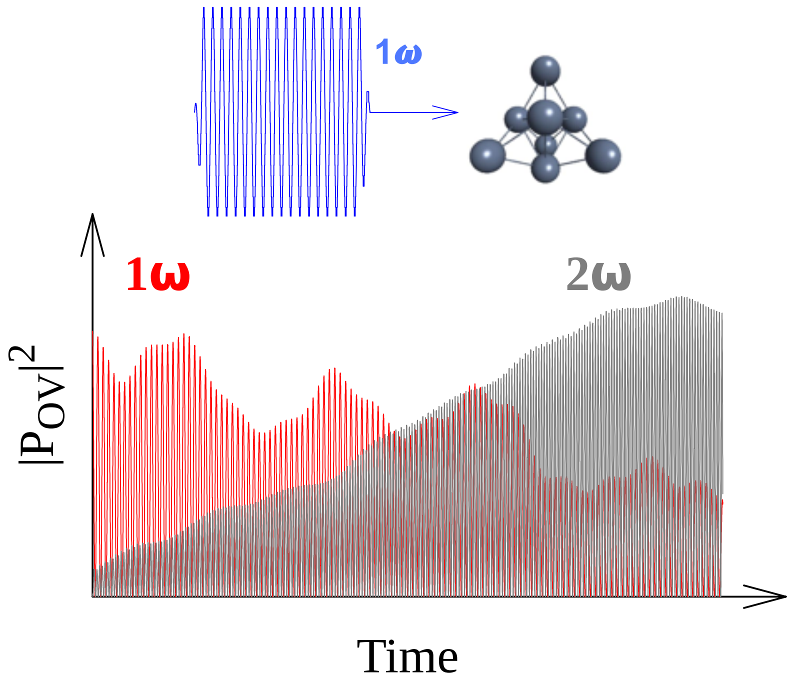
Transitions oscillating with 2ω frequency follow the TPA selection rules

G. U. Kuda-Singappulige, D. B. Lingerfelt, X. Li, and C. M. Aikens, *J. Phys. Chem. C,* **2020**, 124, 37, 20477–20487

CONCLUSIONS

Plasmon decay in silver nanoparticles

- Energy transferred to excite the transitions with twice the resonant energy
- Point group symmetry and frequency analysis of the transitions confirms high energy transitions are due to the two-photon absorption
- **Energy transfer to activate non-linear properties → A plasmon decay mechanism**
- **Plasmon resonance plays a significant role in enhancing non-linear effects**



G. U. Kuda-Singappulige, D. B. Lingerfelt, X. Li, and C. M. Aikens, *J. Phys. Chem. C,* **2020**, 124, 37, 20477–20487

Acknowledgements

Prof. Aikens
Aikens and Liu group members

Prof. Xiaosong Li

Dr. David Lingerfelt

Andrew Wildman

at University of Washington

Department of Chemistry
Kansas State University

Thank you !