The Role of Nonadiabatic Couplings in Spectroscopic Calculations of Aromatic Molecules

Soumya Mukherjee[1], Saikat Hazra[1], Satyam Ravi[1,2], Subhankar Sardar[1,3] and Satrajit Adhikari[1,*]

[1]School of Chemical Sciences, Indian Association for the Cultivation of Science, Jadavpur, Kolkata - 700 032, West Bengal, India;
[2]School of Advance Science and Languages, VIT Bhopal University, Bhopal – 466114, India
[3]Department of Chemistry, Bhatter College, Paschim Midnapore, West Bengal, India

*Email: pcsa@iacs.res.in

Poster Presenter's Email: pcsm5@iacs.res.in, soumyamukherjee093@gmail.com

Objective and key features of my work

➢ Born-Oppenheimer (BO) approximation[1,2] : No coupling between fast-moving electrons and slow-moving nuclei (huge differences in masses).

➢ At degenerate points, nonadiabatic coupling terms (NACTs) (electron-nuclei coupling) become infinite (Hellmann-Feynman theorem)[3,4]. At other points also, NACT may have non-negligible value due to substantial coupling between electronic and nuclear motion.

➢ A paradigm shift from adiabatic to diabatic framework is needed.

➢ In diabatic representation, electron-nuclear couplings appear in form of diabatic couplings which are smooth, continuous as well as single-valued.

➢ Diabatic wavefunctions are formed by orthogonal rotation of the adiabatic wavefunction. The elements of such rotation matrix are obtained by employing the Adiabatic-to-Diabatic Transformation (ADT) condition[5,6].

➢ Finally, diabatic potential energy is calculated using the similarity transformation of adiabatic potential energy matrix by the rotation (ADT) matrix.

➢ We have developed a generalized code, 'ADT' to formulate analytic expressions of ADT quantities and compute their numerical values.[7]

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2. Born M. and Huang K., Dynamical Theory of Crystal Lattices, Oxford University Press: Oxford, U.K., (1954)
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Origination of NACT

❖ BO expansion :

$$|\Psi(s_e, s_n)\rangle = \sum_i \psi_i(s_n)|\xi_i(s_e|s_n)\rangle$$

where, $|\Psi(s_e, s_n)\rangle$ ⟶ molecular wavefunction

$|\xi_i(s_e|s_n)\rangle$ ⟶ electronic wavefunctions

$\psi_i(s_n)$ ⟶ nuclear wavefunctions

❖ Total time-independent Schrödinger equation :

$$\hat{H}(s_e, s_n)|\Psi(s_e, s_n)\rangle = E|\Psi(s_e, s_n)\rangle$$

where, $\hat{H}(s_e, s_n) = \hat{T}_n(s_n) + \hat{H}_e(s_e|s_n)$ ⟶ sum of nuclear kinetic energy operator and electronic Hamiltonian

$$\hat{T}_n = -\frac{1}{2}\sum_i \left(\frac{\nabla^2_{s_n,i}}{m_i}\right)$$ ⟶ nuclear kinetic energy operator

❖ Electronic Schrödinger equation :

$$\hat{H}_e(s_e|s_n)|\xi_i(s_e|s_n)\rangle = u_i(s_n)|\xi_i(s_e|s_n)\rangle \qquad [u_i \text{ s are adiabatic potential energy}]$$

❖ Substituting the wavefunction and projecting this equation with $|\xi_j(s_e|s_n)\rangle$,

$$\left[-\frac{1}{2}(\vec{\nabla}_n + \vec{\tau})^2 + \mathbf{U} - \mathbf{E}\right]\psi = 0$$

where **U** ⟶ adiabatic potential energy matrix (diagonal matrix)

$\boldsymbol{\tau}$ ⟶ nonadiabatic coupling matrix (NACM). (skew-symmetric for real wavefunctions)

❖ Here, **NACT** :

$$\vec{\tau}_{ij} = \langle \xi_i(s_e|s_n)|\vec{\nabla}\xi_j(s_e|s_n)\rangle$$

❖ **In BO approximation this is considered as 0 (i.e. no electron-nuclear coupling)** and the above Schrödinger equation becomes,

$$\left[-\frac{1}{2}\nabla_n^2 + \mathbf{U} - \mathbf{E}\right]\psi = 0$$

Diabatic Representation

❖ Adiabatic wavefunctions :

$$\mathbf{\psi} = \mathbf{A}\phi^{\mathbf{d}}$$

where, $\mathbf{A}$ $\longrightarrow$ rotation matrix (orthogonal)

$\phi^{\mathbf{d}}$ $\longrightarrow$ diabatic nuclear wavefunction matrix.

❖ Adiabatic to Diabatic Transformation (ADT) Condition :

$$\vec{\nabla}_n \mathbf{A} + \vec{\mathbf{\tau}}\mathbf{A} = 0$$

❖ Modified Schrödinger equation :

$$-\frac{1}{2}\nabla_n^2\phi^{\mathbf{d}} + (\mathbf{W} - \mathbf{E})\phi^{\mathbf{d}} = 0$$

where,

$$\mathbf{W} = \mathbf{A}^{\dagger}\mathbf{U}\mathbf{A}$$

Here $\mathbf{W}$ is diabatic potential energy matrix (off diagonal terms are diabatic couplings and **they are not singular**)

Example: Diabatization for six state sub-Hilbert space [1]

$$\vec{\tau} = \begin{pmatrix} 0 & \vec{\tau}_{12} & \vec{\tau}_{13} & \vec{\tau}_{14} & \vec{\tau}_{15} & \vec{\tau}_{16} \\ -\vec{\tau}_{12} & 0 & \vec{\tau}_{23} & \vec{\tau}_{24} & \vec{\tau}_{25} & \vec{\tau}_{26} \\ -\vec{\tau}_{13} & -\vec{\tau}_{23} & 0 & \vec{\tau}_{34} & \vec{\tau}_{35} & \vec{\tau}_{36} \\ -\vec{\tau}_{14} & -\vec{\tau}_{24} & -\vec{\tau}_{34} & 0 & \vec{\tau}_{45} & \vec{\tau}_{46} \\ -\vec{\tau}_{15} & -\vec{\tau}_{25} & -\vec{\tau}_{35} & -\vec{\tau}_{45} & 0 & \vec{\tau}_{56} \\ -\vec{\tau}_{16} & -\vec{\tau}_{26} & -\vec{\tau}_{36} & -\vec{\tau}_{46} & -\vec{\tau}_{56} & 0 \end{pmatrix} \qquad U = \begin{pmatrix} u_1 & 0 & 0 & 0 & 0 & 0 \\ 0 & u_2 & 0 & 0 & 0 & 0 \\ 0 & 0 & u_3 & 0 & 0 & 0 \\ 0 & 0 & 0 & u_4 & 0 & 0 \\ 0 & 0 & 0 & 0 & u_5 & 0 \\ 0 & 0 & 0 & 0 & 0 & u_6 \end{pmatrix}$$

$$\mathbf{A} = \mathbf{A}_{12}(\Theta_{12}).\mathbf{A}_{13}(\Theta_{13}).................\mathbf{A}_{45}(\Theta_{45}).\mathbf{A}_{16}(\Theta_{16}).\mathbf{A}_{26}(\Theta_{26}).\mathbf{A}_{36}(\Theta_{36}).\mathbf{A}_{46}(\Theta_{46}).\mathbf{A}_{56}(\Theta_{56})$$

❖ One of the rotation matrix :

$$\mathbf{A}_{12} = \begin{pmatrix} \cos\Theta_{12} & \sin\Theta_{12} & 0 & 0 & 0 & 0 \\ -\sin\Theta_{12} & \cos\Theta_{12} & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}$$

❖ One of the ADT equations :

$$\vec{\nabla}\Theta_{12} = -\vec{\tau}_{12} - \sin\Theta_{12}\{\vec{\tau}_{13}\tan\Theta_{13} + \sec\Theta_{13}$$

$$(\vec{\tau}_{14}\tan\Theta_{14} + \vec{\tau}_{15}\sec\Theta_{14}\tan\Theta_{15} + \vec{\tau}_{16}\sec\Theta_{14}\sec\Theta_{15}\tan\Theta_{16})\}$$

$$-\cos\Theta_{12}\{\vec{\tau}_{23}\tan\Theta_{13} + \sec\Theta_{13}(\vec{\tau}_{24}\tan\Theta_{14}$$

$$+\vec{\tau}_{25}\sec\Theta_{14}\tan\Theta_{15} + \vec{\tau}_{26}\sec\Theta_{14}\sec\Theta_{15}\tan\Theta_{16})\}$$

1. Mukherjee S., Ravi S., Dutta J., Sardar S. and Adhikari S. Phys. Chem. Chem. Phys., 2022, **22**, 2185.

BBO Treatment for $C_6H_6^+$

Ab Initio Calculations :

1. Completely symmetric breathing mode (Q_2).
2. Ring deformation mode (Q_8).
3. Degenerate C–C asymmetric stretching pair (Q_{16x} and Q_{16y} modes).
4. Degenerate in plane bending (Q_{18x} and Q_{18y} modes).
5. One component of degenerate out of plane bending (Q_{19x}).
6. Lowest five doublet states are $\tilde{X}^2 E_{1g}$, $\tilde{B}^2 E_{2g}$ and $\tilde{C}^2 A_{2u}$.
7. At equilibrium, it has D_{6h} symmetry.
8. cc-pVDZ/MRCI level energy calculation.
9. CAS is 9 electrons in 5 orbitals.
10. Nonadiabatic Coupling Terms (NACTs) are calculated by CP-MCSCF method.
11. $Q_i = \rho\cos\phi$ $Q_j = \rho\sin\phi$.
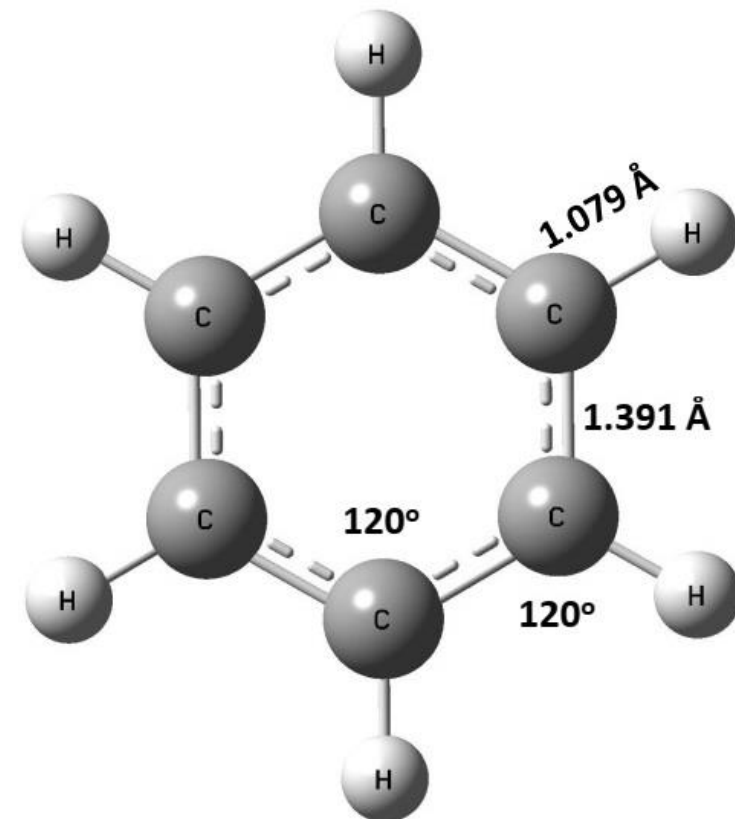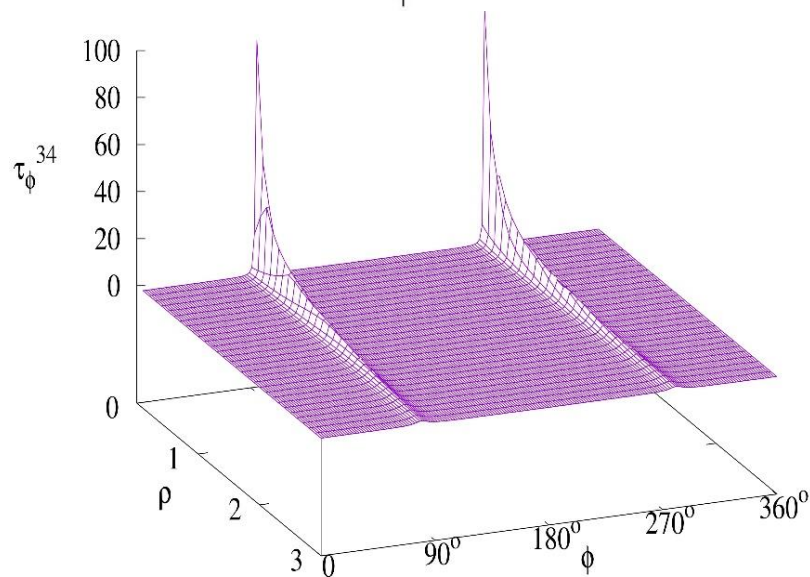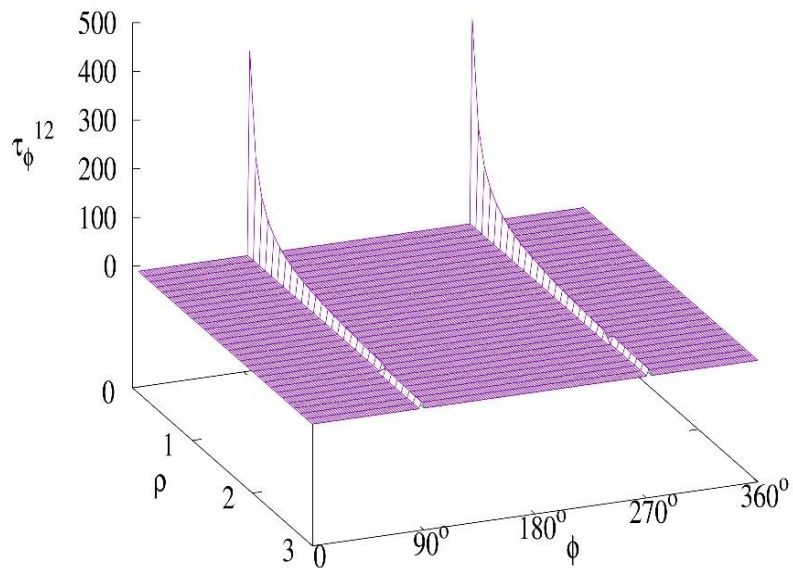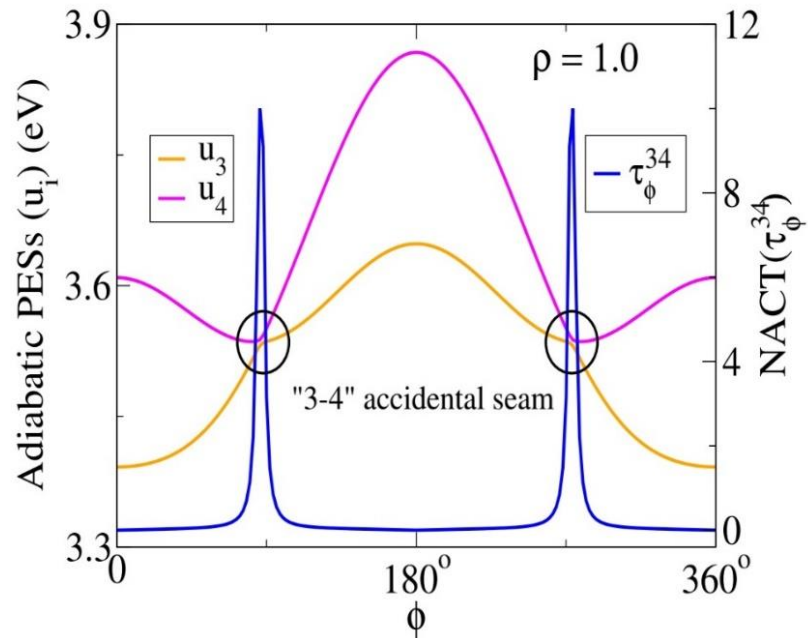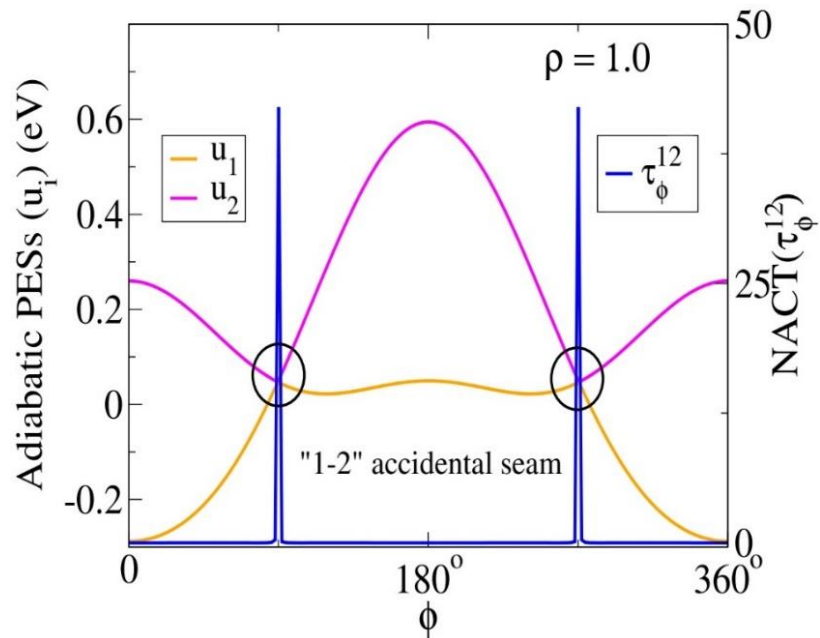
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1.   Mukherjee S., Ravi S., Naskar K., Sardar S. and Adhikari S. J. Chem. Phys., 2021, **154**, 094306.
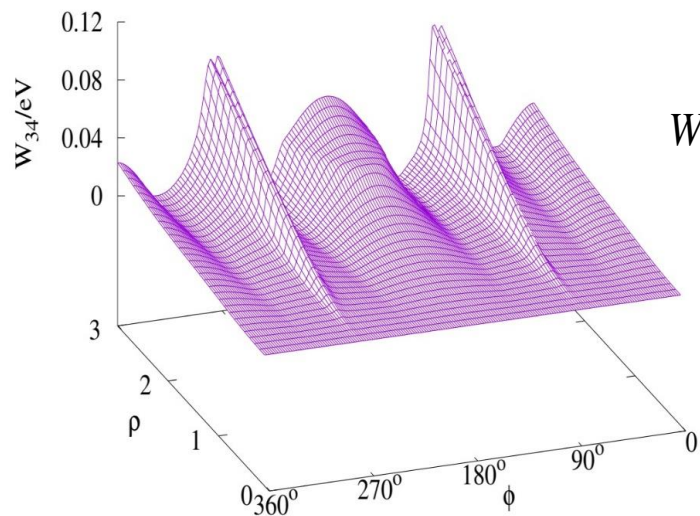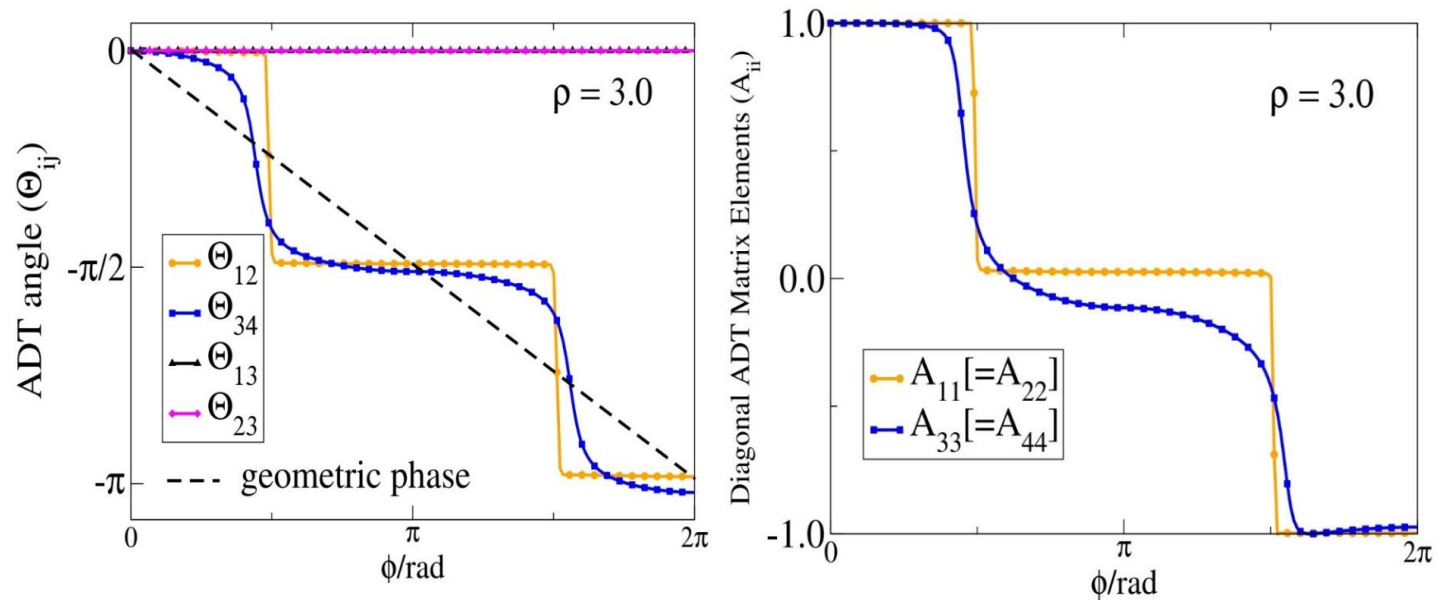
$$W_{ij}(Q_k, Q_l) = \sum_{n=0}^{N} \sum_{m=0}^{M} c_{nm} Q_k^n Q_l^{2m} \quad n, m \equiv \{0, 1, 2, \ldots\}$$
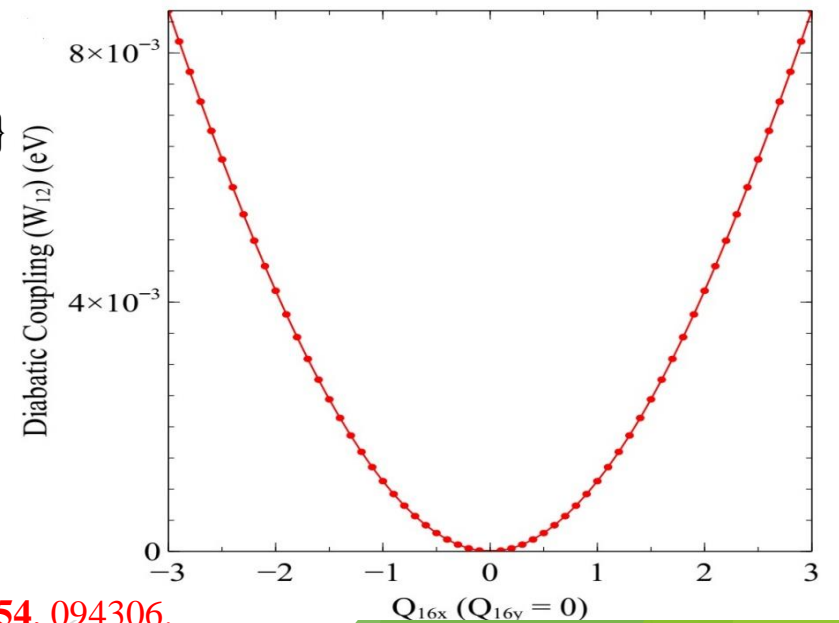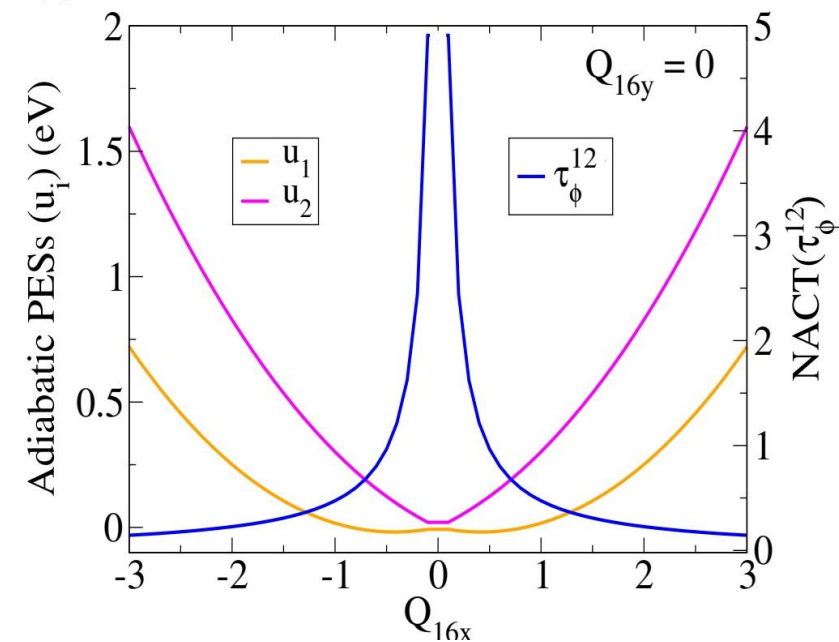
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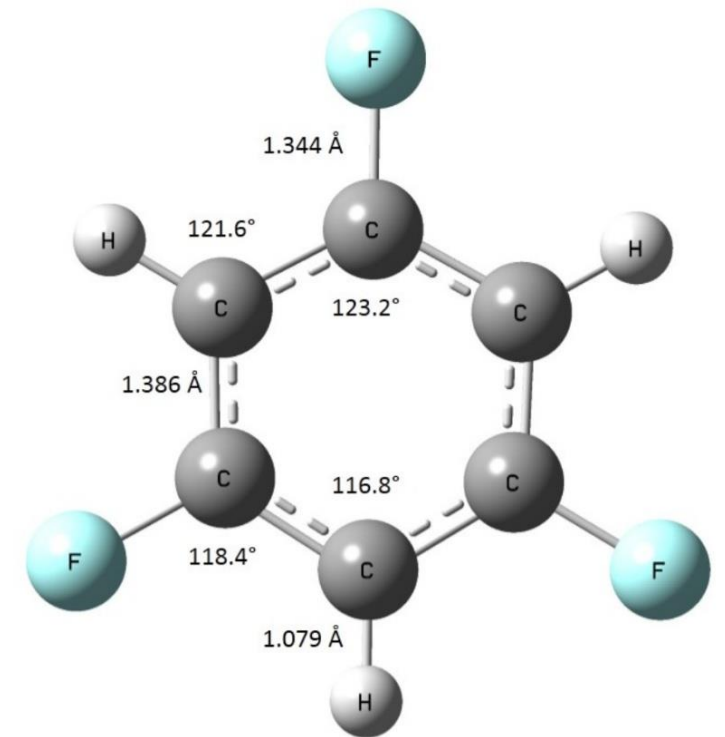
Photoelectron Spectra
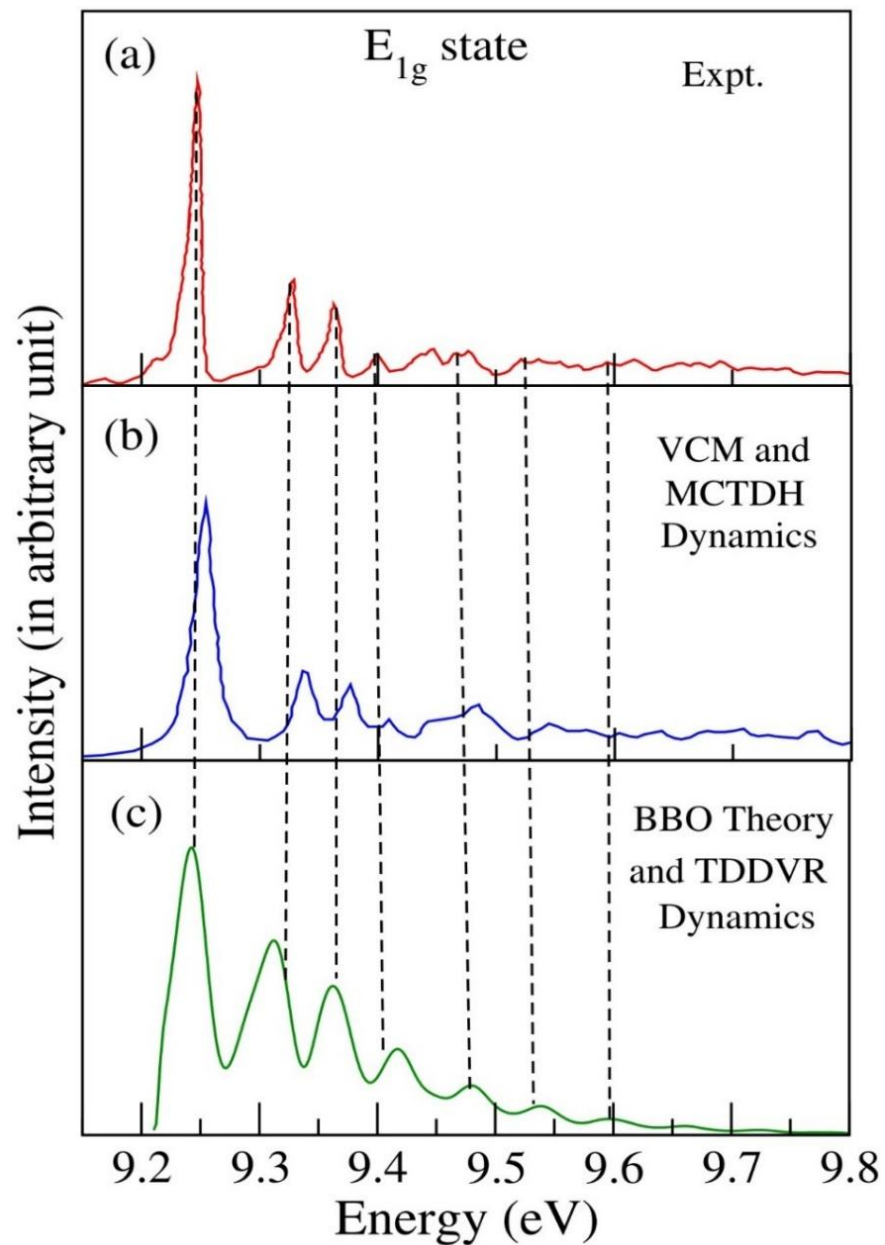
E(eV) (experiment of Baltzer)	E(eV) (MCTDH dynamics)	E(eV) (present work)
9.2431	9.2544	9.2424 *
9.3265	9.3361	9.3120
9.3628	9.3766	9.3620 *
9.4002	9.4092	9.4170
9.477	9.4852	9.4793 *
9.537	9.5443	9.5384 *

1. Baltzer P. et al. Chem. Phys. 1997, **224**, 95.

2. Köppel H., Bâldea I., and Szalay P. G., Adv. Quantum Chem. 2003, **44**, 199.

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BBO Treatment for 1,3,5-$C_6H_3F_3^+$

Ab Initio Calculations :

1. C-F symmetric stretching mode (Q_2).
2. Degenerate C–C asymmetric stretching pair (Q_{9x} and Q_{9y} modes).
3. Degenerate C–C symmetric stretching pair (Q_{10x} and Q_{10y} modes).
4. Degenerate scissoring motion of C-C-C moiety (Q_{12x} and Q_{12y} modes).
5. Degenerate in-plane bending of C-C-C moiety (Q_{13x} and Q_{13y} modes)
6. Degenerate C-C twisting (Q_{18x} and Q_{18y} modes).
7. Lowest six doublet states are $\tilde{X}^2E''$, $\tilde{A}^2A_2''$, $\tilde{B}^2E'$ and $\tilde{C}^2A_2'$.
8. At equilibrium, it has D_{3h} symmetry.
9. cc-pVDZ/MRCI level energy calculation.
10. CAS is 11 electrons in 9 orbitals.
11. Nonadiabatic Coupling Terms (NACTs) are calculated by CP-MCSCF method.
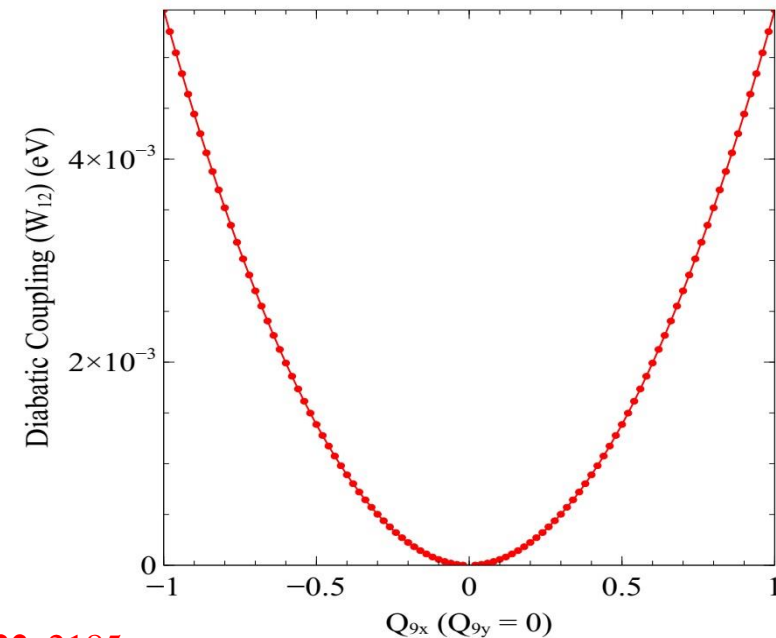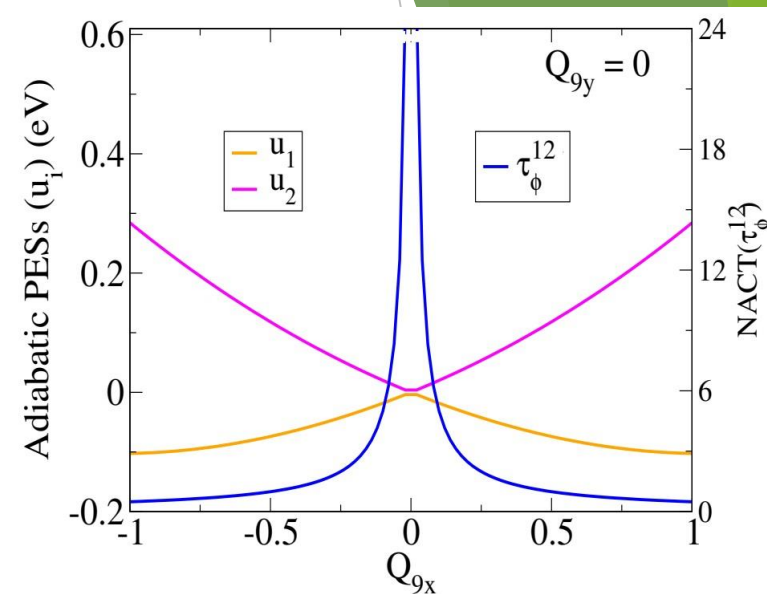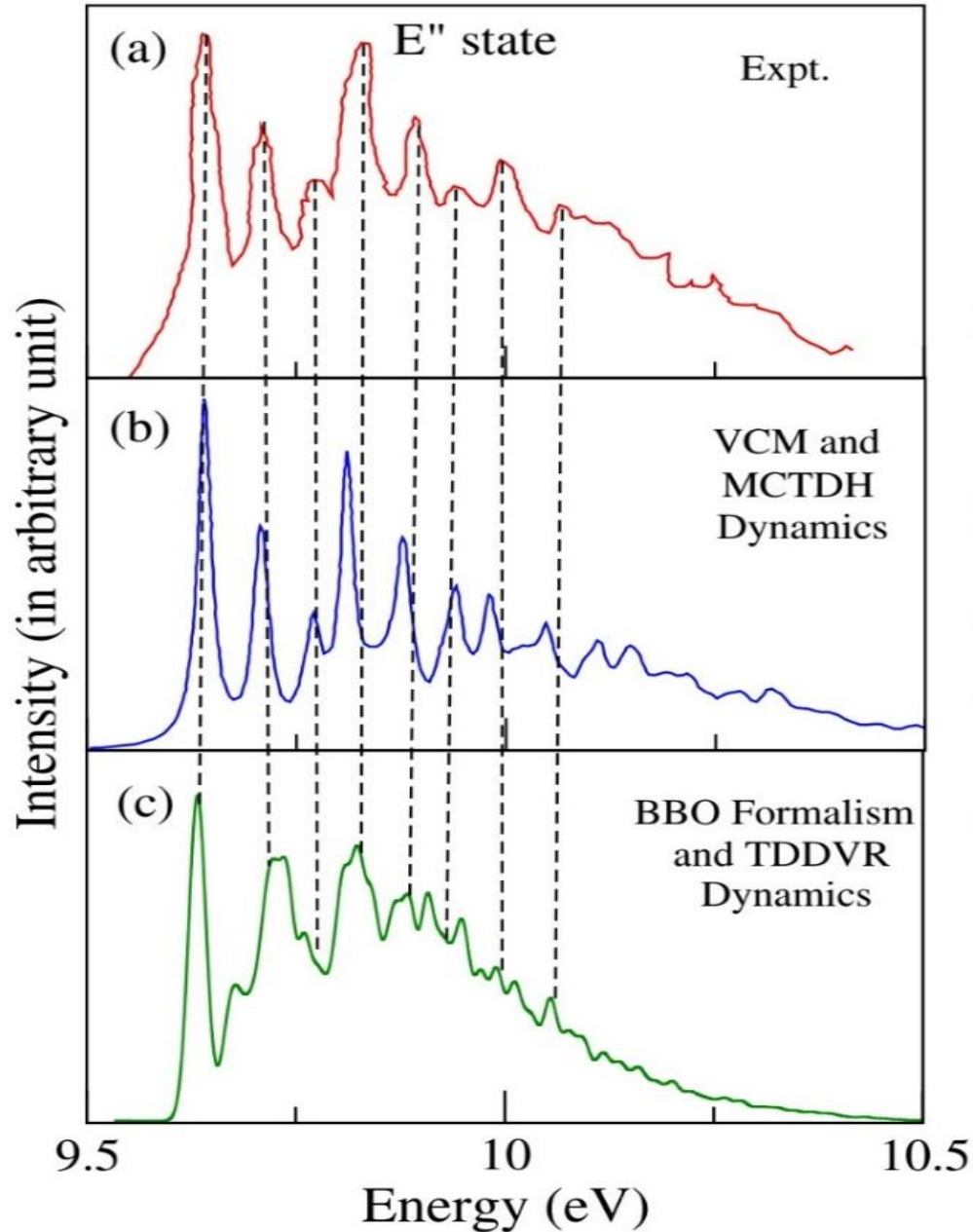12. $Q_i = \rho\cos\phi$ $Q_j = \rho\sin\phi$.

1.344 Å
121.6°
123.2°
1.386 Å
116.8°
118.4°
1.079 Å

1. Mukherjee S., Ravi S., Dutta J., Sardar S. and Adhikari S. Phys. Chem. Chem. Phys., 2022, **22**, 2185.

$$W_{ij}(Q_k,Q_l) = \sum_{n=0}^{N}\sum_{m=0}^{M} c_{nm}Q_k^n Q_l^{2m} \quad n,m \equiv \{0,1,2,...\}$$

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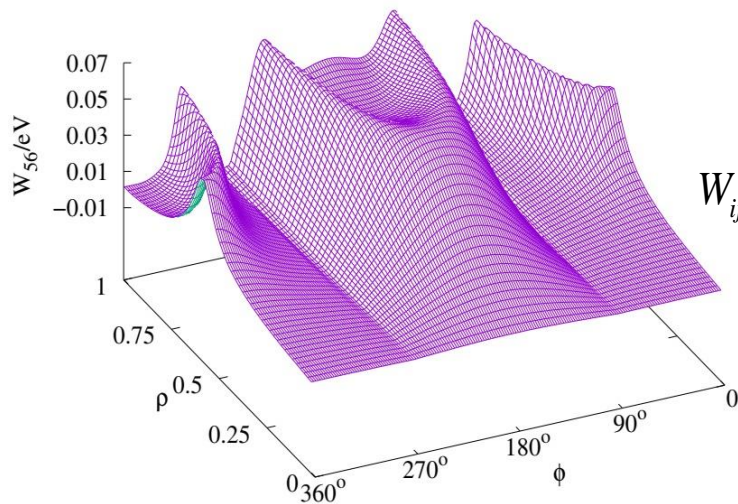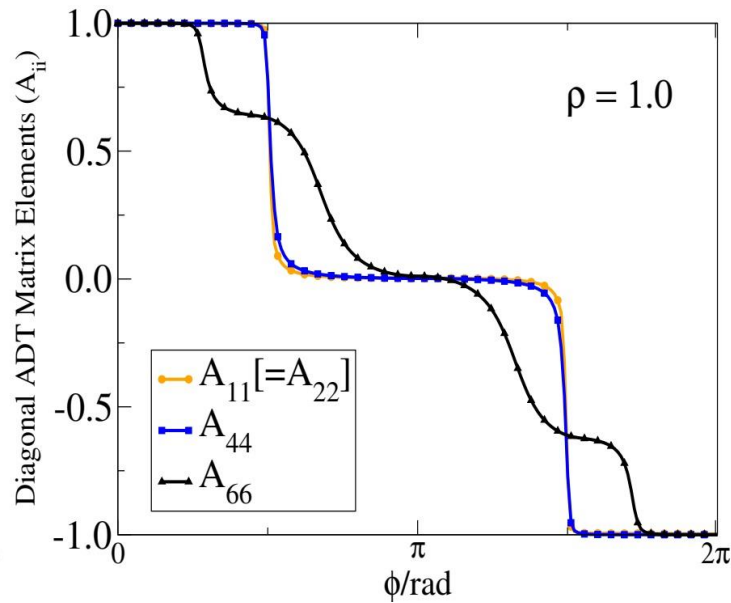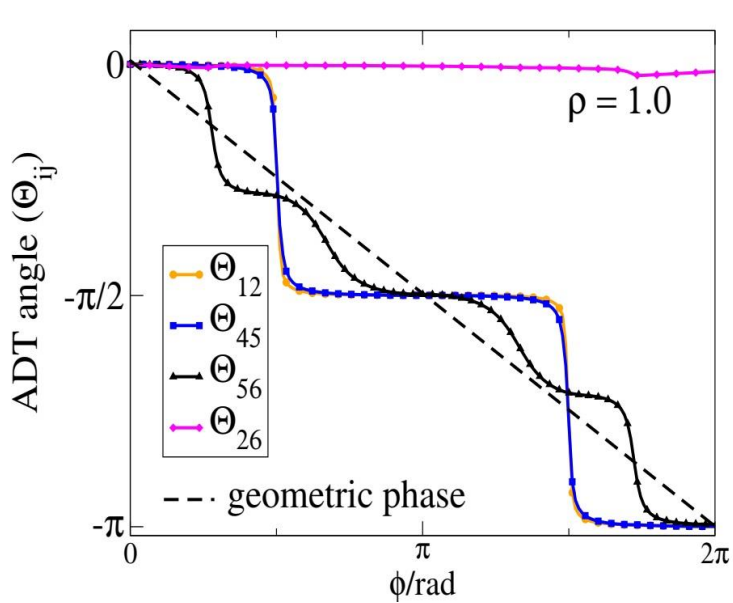
Photoelectron Spectra

$\tilde{X}^2 E''$ state		
E(eV) (experiment of Gilbert *et al.*)	E(eV) (MCTDH)	E(eV) (present work)
9.6383	9.6402	9.6324 *
9.7086	9.7069	9.7238
9.7696	9.7708	9.7600
9.8281	9.8101	9.8233 *
9.8917	9.8768	9.8834 *
9.9382	9.9408	9.9090
9.9939	9.9800	9.9895 *
10.0642	10.0477	10.0545*

Q_{13x}, Q_{13y}, Q_{18x}, Q_{18y}, Q_2, Q_{9x} and Q_{9y}
normal modes are used

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2. Mondal, T.; Mahapatra, S.; Phys. Chem. Chem. Phys. 2009, **11**, 10867-10880.

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Including Q_{10x}, Q_{10y}, Q_{12x}, Q_{12y} normal modes

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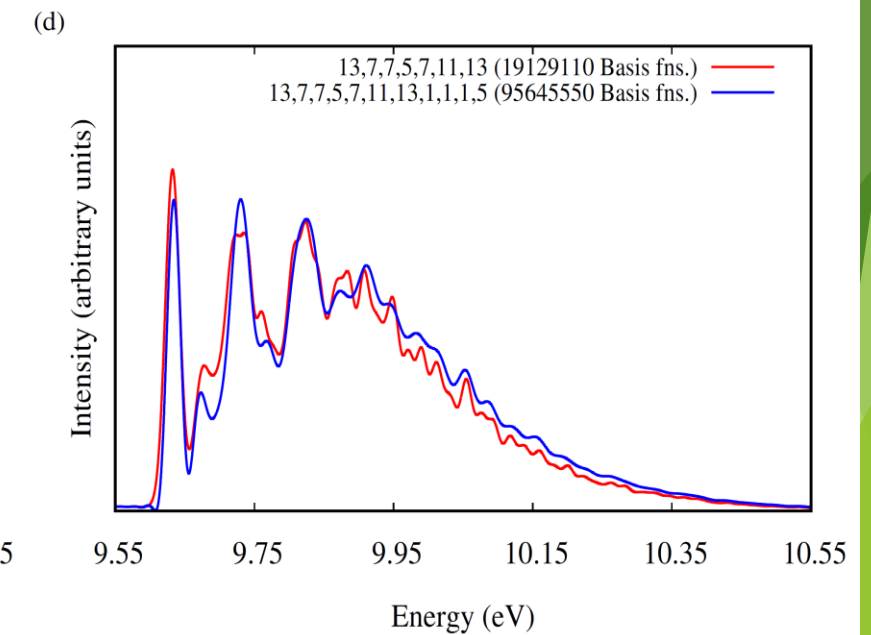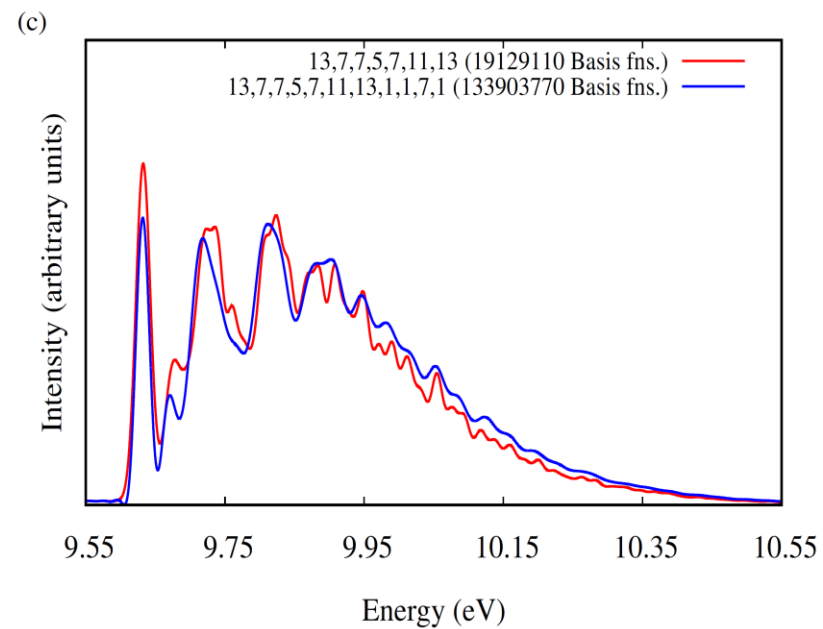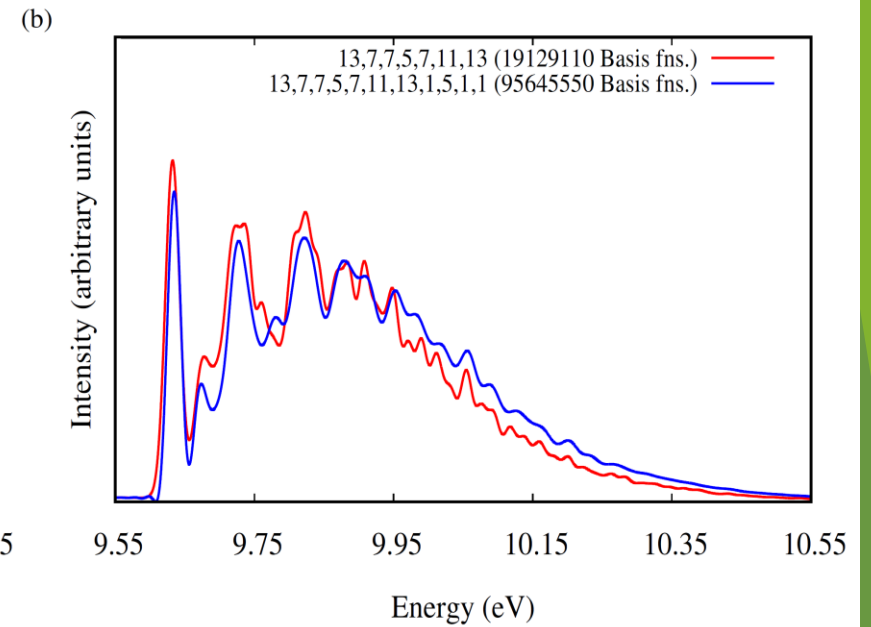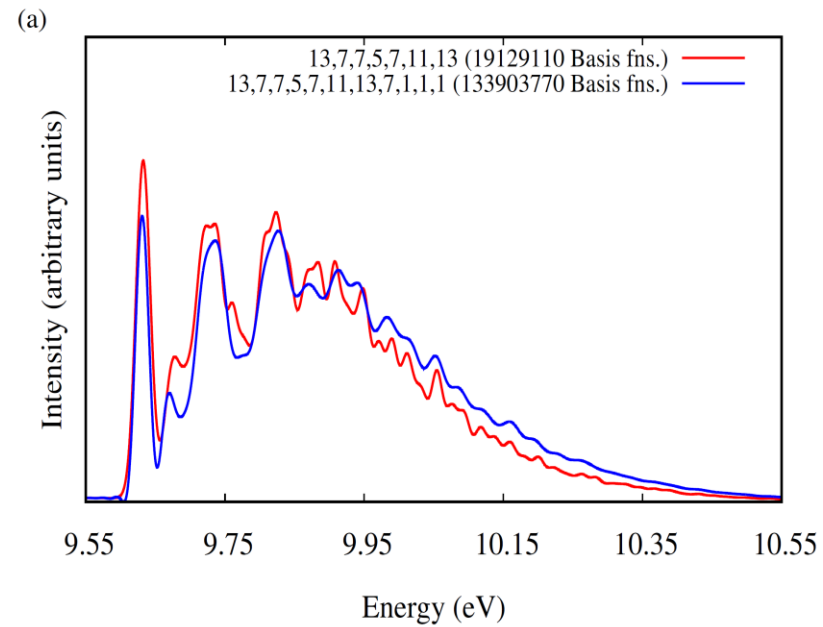
Future Plans

➢ Investigation of non-adiabatic interactions of o-diflurobenzene and pyridine cations by scanning the pairs of normal modes.

➢ Calculation of theoretical photoabsoprtion spectra of the neutral counterparts by TDDVR dynamics.

Acknowledgements

Thank You