

**Figure 1.** An example of adp qualitative comparison between computed, on the left (single cell, yellowish and supercell, coloured), and between computed and experimental, on the right (experimental, yellowish and supercell, coloured).

**Keywords:** adp, Molecular Dynamics, polymorphism, symmetry, pseudosymmetry, Shannon entropy

## MS38-P16 Combining X-ray crystallography and ultrafast infrared spectroscopy – monitoring photo-induced guanine oxidation by $[\text{Ru}(\text{TAP})_2(\text{dppz})]^{2+}$

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Time resolved spectroscopy can be used to study reaction processes on a short timescale (as low as fs). Time-Resolved Infra-Red (TRIR) is a particularly powerful technique as it can be used to monitor the formation and breakage of individual chemical bonds, and therefore can be used to study fundamental chemical processes in biological<sup>1</sup> and chemical systems. However, whilst this technique is very powerful, interpretation of the results can be hampered by a lack of information about the local chemical environment of the group of interest as the sample is usually in solution. This means that, when studying biomolecules and in particular nucleic acids, there may be multiple conformations or binding sites present<sup>2</sup> which can be very difficult to assign.

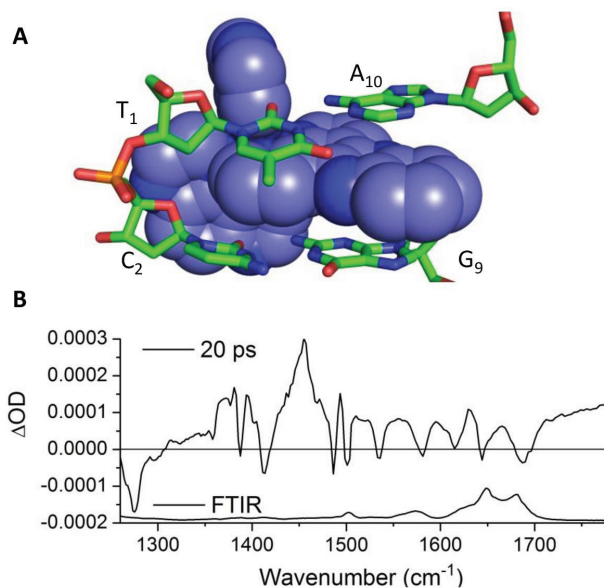
In contrast, X-ray crystallography allows us to determine the position of every ordered atom or group within a crystal, providing unparalleled structural information about the environment within the sample. However, whilst facilities are available for time resolved experiments, it is difficult to reach into the sub-ns time domain without the use of specialised Laue or FEL sources.

Here we present the adaptation of pump-probe TRIR to measure data, in the ns and ps time domain, from samples consisting of 5µm crystal fragments. This technique was used to monitor the one electron photooxidation of guanine by a Ruthenium polypyridyl bound to a DNA duplex, the crystal structure of which we have previously reported<sup>3</sup> (Figure 1). By assigning the spectroscopic result to a known structure, we are able to propose an individual base as the site of oxidation. Additionally, the spectroscopic fingerprint (reaction rate, relative yield, peak position) obtained from a crystal sample allows us to compare with that found in solution.

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**Figure 1.**  $\Lambda$ -[Ru(TAP)<sub>2</sub>(dppz)]<sup>2+</sup> (purple) intercalates into d(TCGGCGCCGA) at the terminal GA step in the duplex. (B) TRIR spectra were at multiple time delays, including 20ps. By fitting the data at multiple time delays, the lifetimes of different excited states can be determined.

**Keywords:** Photochemistry, ultrafast spectroscopy, DNA

**MS38-P17** Theoretical analysis (NBO, NPA, Mulliken Population Method) and molecular orbital studies (hardness, chemical potential, electrophilicity and Fukui Function Analysis) of (E)-2-((4-hydroxy-2-methylphenylimino)methyl)-3-methoxyphenol

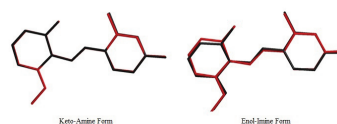
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The molecular structure and spectroscopic properties of (E)-2-((4-hydroxy-2-methylphenylimino)methyl)-3-methoxyphenol, were characterized by X-ray diffraction, FT-IR and UV-Vis spectroscopy. All of theoretical calculations and optimized geometric parameters have been calculated by using density functional theory (DFT) with hybrid method B3LYP by 6-31G(d,p) basis set. The title compound of C<sub>15</sub>H<sub>15</sub>N<sub>1</sub>O<sub>3</sub> have been analyzed according to electronic and energetic behaviors for enol-imine and keto-amine tautomers. Both these tautomers engender six-membered ring due to intramolecular hydrogen bonded interactions. The theoretical vibrational frequencies have been found in good agreement with the corresponding experimental data. A study on the electronic and optical properties, absorption wavelengths, excitation energy, dipole moment, molecular electrostatic potential (MEP) and frontier molecular orbital energies are performed using DFT method. Additionally, geometry optimizations in solvent media were performed with the same level of theory by the polarizable continuum model (PCM). The effect of solvents on the tautomeric stability has been investigated. Mulliken population method and natural population analysis (NPA) have been studied. NBO analysis is carried out to picture the charge transfer between the localized bonds and lone pairs. The local reactivity of the molecule has been studied using the Fukui function. NLO properties related to polarizability and hyperpolarizability are also discussed.



**Figure 1.** Superimposition of the X-ray structure (red) and calculated structure (black) of the enol-imine and keto amine forms of the title molecule.

**Keywords:** Natural Population Analysis (NPA), Fukui Function Analysis, Natural Bond Orbital Analysis (NBO)