Warwick Chemistry Departmental Seminar

The Warwick Chemistry Research Fellows Lecture

Dr Matthew R. Gyton

Rhodium(III) and Iridium(III) Complexes of a NHC-Based Macrocycle: Persistent Weak Agostic Interactions and Reactions with Dihydrogen

Meridional pincer ligand architectures are an exceedingly well utilised ligand family in organometallic chemistry and catalysis. Variants featuring phosphine donors are particularly widespread, while NHC-based systems are attracting growing interest.1 Recent research from the Chaplin group, in particular, has demonstrated the versatile coordination chemistry of a family of macrocyclic NHC-based pincer ligands.2,3 Exploiting copper(I) transmetallation protocols, 4 the synthesis of low-coordinate rhodium(III) and iridium(III) 2,2'-biphenyl complexes of a NHC-based macrocycle is reported.5 These complexes are stabilised by the adoption of C–H agostic interactions and have been comprehensively characterised in solution and the solid state. The application of IR spectroscopy is highlighted and provides unequivocal evidence for the presence of these weak and typically transient M···H–C interactions in solution. Hydrogenolysis of the 2,2'-biphenyl ligand under dihydrogen results in the formation of interesting hydride derivatives, of which the structure and dynamics will be discussed from both experimental and computational perspectives.

Dr Nat das-Neves-Rodrigues-Lopes

Wavepacket insights into the photoprotection mechanism of the UV filter methyl anthranilate

What happens to sunscreen active ingredients when they absorb solar radiation? All molecules, including sunscreen active ingredients, become excited after absorbing radiation, acquiring excess energy that makes them unstable. In a sunscreen context, it is important that the excess energy is dissipated without generating any harmful species and without breaking apart – and this usually required the molecule to dissipate the excess energy as heat within a femto- (10-15) to pico- (10-12) second timescale.

During her PhD studies, Nat found that methyl anthranilate (MA), the precursor to the sunscreen active ingredient Meradimate, does not efficiently dissipate excess energy after irradiation with UVB (330–300 nm). Instead, excited state population seems to become 'trapped' in the first singlet electronic excited state of MA, presumably due to ultrafast phenomena which drive population to the state's energetic well.

In this talk, Nat will explore how the observation quantum beats in the time-resolved photoelectron spectra of MA allowed the team to garner wavepacket insights into its photophysical mechanisms. Specifically, there is evidence for highly efficient intramolecular vibrational energy redistribution which hinders efficient relaxation of the first singlet electronic excited state of MA, making MA a poor choice for an efficient, efficacious sunscreen chemical filter.

Thursday 10 January 2019

4.00 pm, Physics Lecture Theatre, Science Concourse