

# Chemistry Seminar

Monday, 13 February 2023 at 16:00 in 303 Schrenk Hall

## Vibronic coupling in *N*-methylpyrrole

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**ABSTRACT:** The  $\tilde{A}^1A_2 \leftarrow \tilde{X}^1A_1$  ( $S_1 \leftarrow S_0$ ) electronic transition of *N*-methylpyrrole (NMP) is electric dipole forbidden. Therefore, one would not expect to observe any structure arising from this electronic transition; however, this is not the case and there is extensive structure, even at low internal energies ( $> 1100 \text{ cm}^{-1}$  above the  $S_1$  origin). Herzberg-Teller coupling (more generally, vibronic coupling) is a complicated, although well-established phenomenon whereby intensity is ‘stolen’ from a nearby electronic state, to which a transition from the  $\tilde{X}^1A_1$  electronic state is allowed — this is the key to explaining the observed structure. Assignments of the observed bands are made through a combination of resonance-enhanced multiphoton ionisation (REMPI) and zero-electron-kinetic-energy (ZEKE) spectroscopies, briefly mentioning the two-dimensional laser-induced fluorescence (2D-LIF) technique.

Many of the ZEKE spectra are consistent with the 3s Rydberg nature of the  $\tilde{A}^1A_2$  electronic state (in the Franck Condon region) and the Herzberg-Teller coupling schemes required to prepare the intermediate; however, there is also some activity which is a little more difficult to explain. Comparisons will be drawn to *meta*-fluorotoluene (*m*FT), whose  $S_1 \leftarrow S_0$  electronic transition is electric dipole allowed, as well as a brief discussion on how vibrational couplings *within* the  $S_1$  state, arising from anharmonicity, further add to the complexity of an already intriguing molecule.

**About the speaker:** Alex joined the Grubbs group at the department of chemistry at Missouri S&T in August 2022, as a post-doctoral research fellow, to construct and test a novel, state-of-the-art chirped-pulse Fourier transform microwave spectrometer.

He completed his PhD in physical and theoretical chemistry at the University of Nottingham in the United Kingdom focusing largely on the vibrational and electronic spectroscopy of small, aromatic molecules, notably *meta*-fluorotoluene and *N*-methylpyrrole, as well as van der Waals complexes of the latter with the rare gases. Theoretical projects have included predicting the spectroscopy of small vdW complexes using both high-level single- and multi-reference *ab initio* methods.

He completed his master's degree in 2019 at the same institution, with time spent at the University of Canterbury in New Zealand, working on understanding the fluxional Cope rearrangement in bullvalene and how various substituents can affect the energy barrier and the timescale of this fluxionality.