

# Invited Lectures E

September 5, Wednesday, 9:00 – 10:30

## Chirped Pulse THz and IR Spectroscopy

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Arbitrary waveform generators operating in the MW region are used for rapid source control of pulse duration and bandwidth at frequencies approaching a THz. By frequency extension of the chirp pulse methods developed in the MW [1] using amplifier/multiplier chains and sub-harmonic heterodyne detectors [2], phase coherent absorption and free induction decay measurements in a 25 m White cell are being used to enhance detection of small molecules, pyrolysis and discharge products in static cells and from pulsed nozzle sources. Extension of arbitrary waveform methods to the visible/IR regions is made possible using waveguide based electro-optic phase modulators. A compact fiber optic system operating near 1.6  $\mu\text{m}$  is demonstrated in applications to cavity ring-down spectroscopy and remote sensing.

### References

- [1] B. C. Dian, G. G. Brown, K. O. Douglass, and B. H. Pate, *Science* **320**, 924, 2008.
- [2] E. Gerecht, K. O. Douglass and D. F. Plusquellic, *Optics Express*, **19**, 8973, 2011.

### Theoretical Insights into the Spectroscopy of $\text{NO}_3$

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Knowledge of the vibronic energy level structure associated with the electronic ground  $X^2A_2'$  state of the nitrate radical ( $\text{NO}_3$ ) is assessed on the basis of existing experimental observations and a high-quality model Hamiltonian that has recently been constructed. It is conclusively demonstrated that the coupling between the  $X^2A_2'$  state and the  $B^2E'$  electronic state (approximately 2 eV above it) has profound implications for the level structure and spectroscopy of the ground state; any sort of reasonable assignment of the levels in terms of vibrational quantum numbers essentially becomes impossible only 1500-2000  $\text{cm}^{-1}$  above the zero-point level. Nevertheless, the energy levels predicted by the vibronic Hamiltonian are in excellent agreement with positions that have been observed spectroscopically, although the interpretation of some of these states is in conflict with existing assignments. Three types of spectroscopy used to interrogate the ground state of  $\text{NO}_3$  – negative ion photodetachment, infrared absorption, and dispersed fluorescence – will be analyzed, the latter from approximately five upper B state levels that have recently been studied in the laboratory by Fukushima and collaborators.