2) *Rotationally resolved vibrational spectroscopy of atmospheric pollutants containing methyl rotors*

Methyl nitrite is a gas phase molecule formed in the atmosphere by the reaction of methoxy radicals with nitric oxide:

$$CH_3O\bullet + NO\bullet \rightarrow CH_3ONO \quad (1)$$

In equation (1), the dots indicate that those molecules are radicals with unpaired electrons. This makes these radicals particularly reactive. In daylight, methyl nitrite rapidly photolyzes to reform these radicals:

$$CH_3ONO + h\nu\ (\lambda \leq 440\ nm) \rightarrow CH_3O\bullet + NO\bullet \quad (2)$$

Since the methoxy radical ($CH_3O\bullet$) and nitric oxide ($NO\bullet$) are both key intermediates in photochemical air pollution, methyl nitrite serves as a night-time reservoir, or storage molecule, that contributes to the "aged smog" phenomenon. This is where a pollution episode is worse on a second day due to pollutants that have not been removed from the atmosphere overnight.

High resolution Fourier Transform infrared spectrometry has been used on a variety of reactive molecules to measure their abundance in the atmosphere. This measurement technique uses the Beer-Lambert law which says that the absorbance is proportional to the concentration of the absorbing molecule and the path length over which this absorption occurs:

$$A(\lambda) = -\,Ln\left(\, I(\lambda) / I_o(\lambda)\,\right) = (\alpha(\lambda))x(concentration)x(pathlength) \quad (3)$$

Here $I(\lambda)$ and $I_o(\lambda)$ are light (as a function of wavelength) with and without absorber. The absorption coefficient is a characteristic of the particular molecule being studied. In the atmosphere, the concentrations are typically so low that a long pathlength (100's of meters) is typically required. The absorption coefficient is measured in a separate experiment, the pathlength is determined by the geometry of the experiment, and the absorbance is calculated from measurements of $I(\lambda)$ and $I_o(\lambda)$ so that the concentration can then be determined.

The role of laboratory studies such as in this project is to measure the absorption coefficient as a function of wavelength (λ), understand how it changes with pressure and temperature, and, most importantly, to understand why the absorption coefficient (or the "spectrum") of the molecule looks the way it does. This understanding is particularly crucial when the spectrum of the molecule being measured overlaps with the spectrum of other molecules that are present in the atmosphere and therefore might interfere with determining the concentration of methyl nitrite. Figuring out which lines (features in the spectrum) belong to which molecules can be a challenging task.

In a simple linear molecule like CO_2, the spacing between the lines is directly proportional to the moment of inertia. Using the masses of the atoms and the moment of inertia, the bond lengths can be determined. For a large, asymmetric molecule like methyl nitrite, the pattern of lines is more complex and figuring out which lines correspond to which transitions between energy levels ("assigning the spectrum") is an involved process. The amount of information that can be obtained is also larger as well. The methyl group in methyl nitrite can rotate and this internal rotation can be investigated. Methyl nitrite also possesses two isomers. These two isomers only differ by rotation about the O-N bond. Both of these isomers are present in a sample of methyl nitrite and are observed in the spectrum.

The objective of this project is to measure and analyze the vibrational bands of methyl nitrite. The measurements will be made in the William R. Wiley Environmental Molecular Sciences Laboratory (EMSL) which is operated by Pacific Northwest National Lab (PNNL) for the Department of Energy. The High Resolution Infrared Spectroscopy Laboratory within EMSL has a Bruker IFS120 spectrometer that is capable of measuring infrared spectra at 0.0015 cm^{-1} resolution. Once the spectra have been measured at high resolution, they will be assigned and a nonlinear least squares fit will be performed to extract the constants characterizing the structure, cis-trans isomerism, and internal rotation of the molecule. Additional methyl rotor containing molecules to be investigated include methyl glyoxal, CH_3COCHO.