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Spectroscopic Investigation of Cyano Functionalized Combustion Intermediates

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The spectroscopy performed on atoms, molecules, and clusters inside helium droplets have addressed a wide range of issues in the physical sciences that have affected areas of study ranging from acid-base chemistry and astrophysics to thermochemistry and plasma physics. The goal of this project is to gain insight into combustion chemistry by isolating the cyano radical (CN) in helium nanodroplets and react it with stable molecules such as oxygen. The first step was to assemble a helium nanodroplet spectrometer (see figure 1), which was completed in the first year of this grant (2016-2017), and it has been upgraded in the last year (2017-2018) to include a Stark cell and pyrolysis source. The Stark cell will allow for us to perform dipole moment measurements on the reactive intermediates we plan to study, and the pyrolysis source will be used to make the CN radical. I have an undergraduate student who has recently completed the design and assembly of the Stark cell (including electronics), and another who is working towards completing the assembly of the pyrolysis source. Getting the pyrolysis source into operation has been challenging, but we are confident about completing it soon. In the meantime we have been studying several different chemical systems in helium nanodroplets.

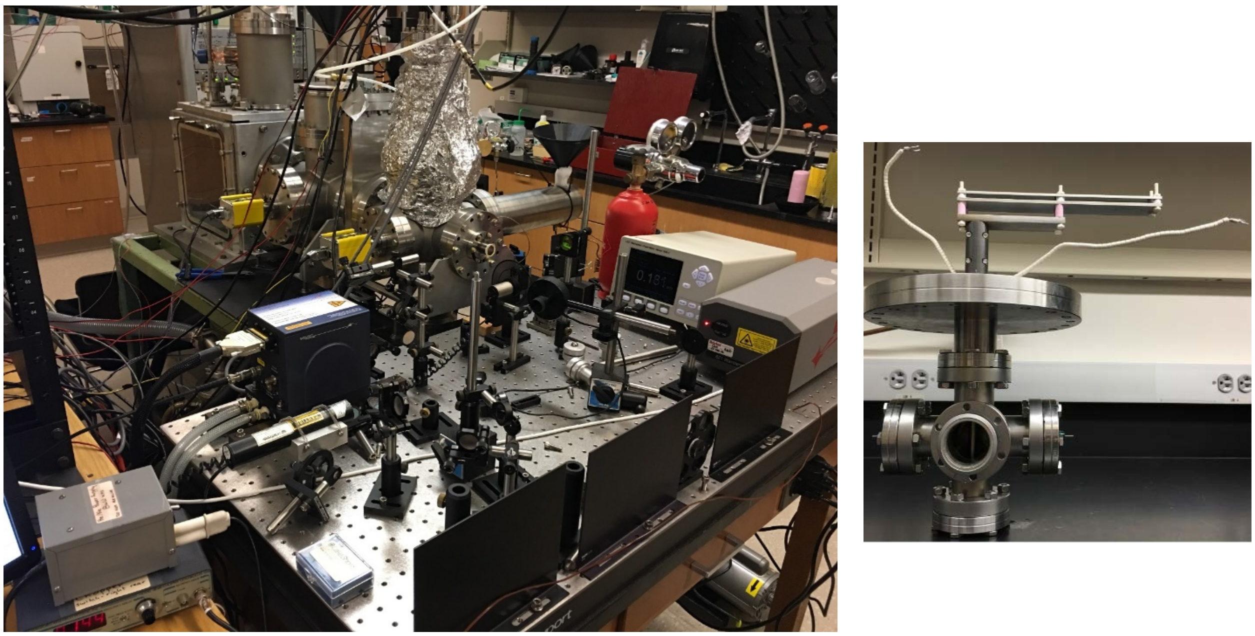

Figure 1: Upgraded JMU Helium Nanodroplet Isolation Spectrometer (left) and Stark cell (right).

The chemical system we spent most of the last year studying is methanol. In particular, we investigated methanol isotopologues around 4.8 to 4.9 µm. This spectral region allowed for coverage of the CO stretching overtone band of CH_3OH/D and the symmetric CD_3 stretching fundamental of CD_3OH/D. Figure 2 shows spectra measured on methanol in the overtone band, which highlights the sensitivity of our spectrometer, and indicates that we are sensitive enough to observe the very weak CN stretch in the cyano radical. We found that lines in the CO stretching overtone band of methanol isotopologues were found to be an order of magnitude sharper than those in the stretching fundamental, and we attribute the line broadening to Fermi coupling, which has been theoretically predicted to be important for the symmetric stretch in methanol. Rovibrational analyses of CH_3OH, CH_3OD, and CD_3OH were possible and allowed for us to fill in an inertial gap that existed in the study of helium solvated isotopologues in the "moderately light rotor" regime. We found that the moment of inertia of helium that couples to rotation increases with that of the methanol isotopologue, according to the relation, $\Delta I_{He} \approx 1.6 \text{ x } I_G$, over the small inertial window investigated (I_G = 21-26 amu*Å^2). This relation puts methanol in the "intermediate region", for which there is a large degree of breakdown of the adiabatic following approximation.

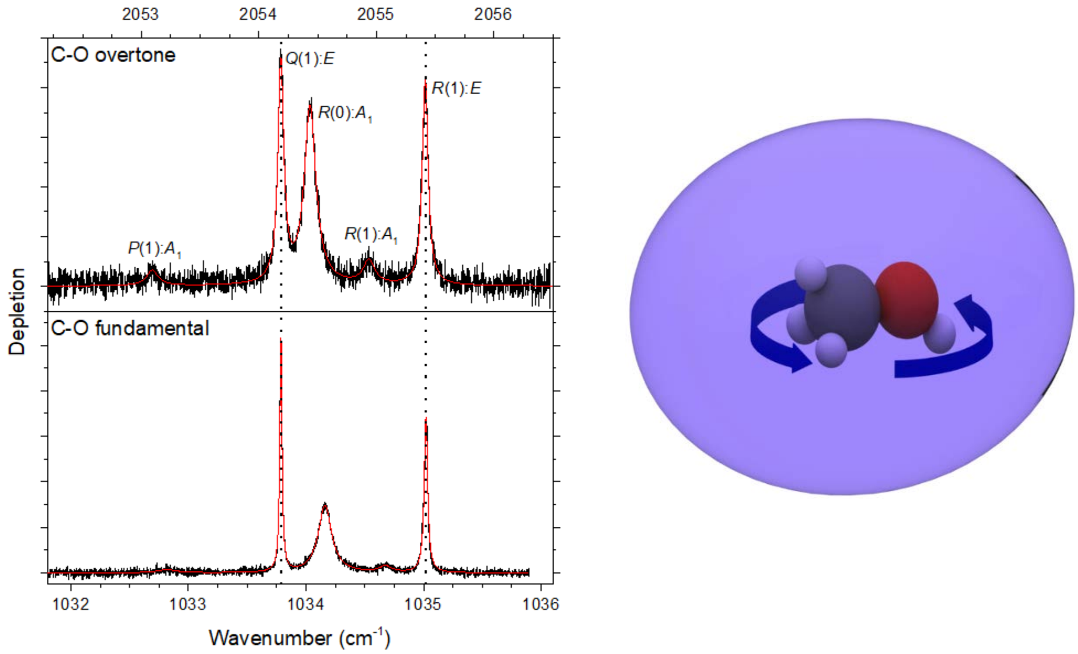

Fig. 1. Left: Comparison of the depletion spectra of normal methanol (CH_3OH) in the CO stretching fundamental and overtone bands (pick-up chamber pressure was ~$5x10^{-6}$ torr). The red curves are simulations using the fitted parameters given in Table 1. Right: Schematic of methanol rotating in helium nanodroplets.

Support from the PRF UNI grant most importantly allowed for completion of the helium nanodroplet spectrometer, from which we recently published our first article (with two undergraduate students as co-authors). I currently have three students working on projects using this machine and another two who are performing calculations to complement the measured spectra. The spectrometer requires continual maintenance and development, which in turn requires drawing from many areas, such as high vacuum technology and laser engineering. This enables students to develop a diverse skill set, often by solving problems. For example, in the last year, students have replaced a turbo pump, wavemeter, ion gauge, chiller, etc., they have been working with our (undergraduate) student supported machine shop in designing the Stark cell and pyrolysis source, and have been routinely reconfiguring the plumbing (for coolant and gas handling). Results using this machine have been presented by students at various conferences including ACS New Orleans. The spectrometer is in use 3-4 days each week, during which time we routinely collect high quality spectra. Support from this grant, has thus had a very large positive impact on my research. In the next year, we will perform Stark spectroscopy, and will focus on completing the pyrolysis source so we can investigate cyano radical intermediates.