MOLECULAR SPECTROSCOPY AT THE UNIVERSITY OF TORONTO AND FUTURE APPLICATIONS TO MARS

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Introduction:
Molecular spectroscopy measurements in our lab at the Department of Physics are being resumed with the restoration of a small cell and the commissioning of a multi-pass White cell. Both gas cells are coupled to a Fourier-transform infrared spectrometer to acquire spectral data. The small cell is being used to retrieve absorption-cross sections, whereas the multi-pass cell, once commissioned, will allow the measurement of weakly absorbing gases. In particular, the multi-pass cell will enable the measurement of CO_2-broadened spectroscopic line parameters. These CO_2-broadened parameters have applications to Martian trace gas retrievals because the Martian atmosphere primarily consists of CO_2. This presentation will provide an overview of the laboratory spectroscopy facility, absorption cross sections obtained with the small cell, and plans for future measurements.

The Small Cell and the Multi-pass Cell:
The small cell system consists of a high resolution (0.004 cm^{-1}) ABB Bomem DA8 Fourier-transform spectrometer and a 10 cm sample cell inside a vacuum jacket, shown in Figures 1 and 2. The reassembled small cell has been heat-cleaned to reduce outgassing and enable accurate pressure measurements needed to retrieve absorption cross-sections. Spectra of two halogenated compounds were recorded and analyzed to test the spectroscopic accuracy of the system. In both cases, spectral measurements and derived absorption cross-sections agreed with previous measurements (Godin et al., 2017; Godin et al., 2019) within uncertainty. Therefore, the small cell can be used to retrieve absorption cross-sections, but spectral measurements of weakly absorbing gases are not possible because the optical path through the cell is limited to 10 cm.

A multi-pass cell can be used to measure the spectra of weakly absorbing gases by significantly increasing the optical path through the sample. One way to accomplish this is using a cell with spherical mirrors of the same radii of curvature placed on either end, as is shown in Figure 3 (White, 1942). Indicated in red is the optical path of the multi-pass cell currently being commissioned. This path involves a parabolic mirror focusing a parallel beam from the spectrometer into the cell. Given the arrangement of mirrors inside the cell, any light that illuminates mirror 1 is focused to a point on mirror 3 and reflected to a corresponding point on mirror 2, and vice versa, increasing the optical path length. The beam then exits the cell and is focused onto the detector by parabolic mirrors. The mirrors inside the cell have a theoretical reflectance of >98%, allowing up to 25 reflections and providing a path length of 50 meters.

Applications to Mars:
Martian trace gas retrievals require CO_2-broadened spectroscopic line parameters. For example, efforts to retrieve atmospheric profiles of CH_4 from spectra recorded by the ExoMars Atmospheric Chemistry Suite (ACS) and the Nadir and Occultation for Mars Discovery (NOMAD) instruments (Korablev et al., 2019) use line parameters from the high-resolution transmission molecular absorption database (HITRAN) (Gordon et al., 2017). Presently, the database is missing some CO_2-broadened spectroscopic line parameters for Martian trace gases such as CH_4, C_2H_6, and C_2H_4. Furthermore, some line parameters are missing for HCl (Korablev et al., 2021). The multi-pass system will enable the measurement of such parameters to fill the gaps in the HITRAN database, and this effort may help with future retrievals of trace gases in the atmosphere of Mars.

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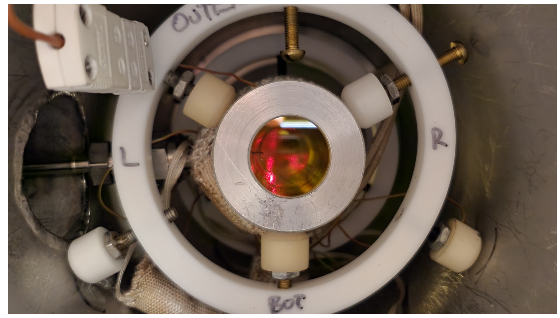

Figure 1: The 10 cm cell inside the vacuum jacket.

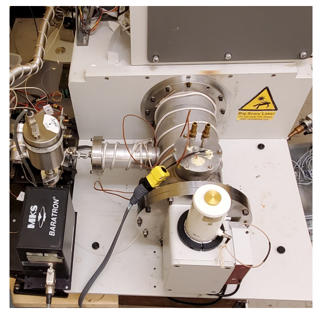

Figure 2: A top-down view of the small cell setup including the Bomem DA8 and the sample insertion system. The cell is inside the large cylindrical vacuum jacket.

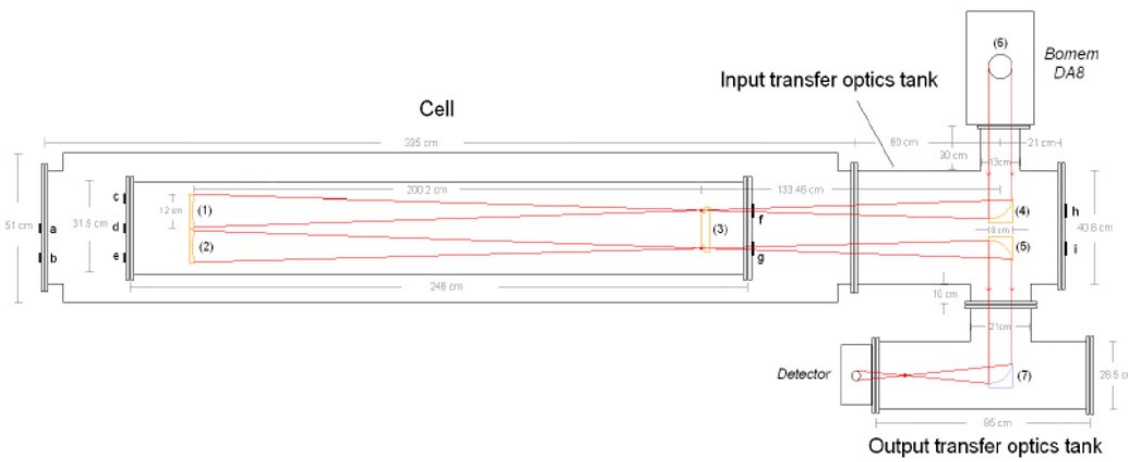

Figure 3: Path of the Bomem DA8 beam through the long-path system into the multi-pass cell and to the detector (Yan, 2008). Mirrors 1,2,3 are gold plated spherical mirrors of the same radii of curvature. Mirrors 1 and 2 are D-shaped whereas mirror 3 is T-shaped. Mirrors 4,5,7 are parabolic mirrors used to direct the beam. Mirror 6 is a flat collimating mirror.