# Laboratory and Field Studies in Rotational Spectroscopy at the Jet Propulsion Laboratory

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**Abstract**

Rotational spectroscopy of atmospheric molecules has long been a hallmark of laboratory and field studies at the Jet Propulsion Laboratory. In addition to maintenance of the millimeter and submillimeter spectral line catalog, the laboratory has actively pursued the challenging laboratory tasks of quantitative linewidth measurements and transient species identification. Further support of NASA missions has led to a fruitful remote sensing operation which includes the Balloon OH instrument that recently had successful engineering and science flights.

The current projects at the millimeter and submillimeter spectroscopy laboratory strongly reflect the needs and desires of the Earth Observing System - Microwave Limb Sounder mission. EOS-MLS is to be launched in March 2004 aboard the NASA spacecraft Aura. The supporting measurements discussed here include 'calibration' and 'validation' of the instrumentation. These two objectives are better described in working context as 'quantitative laboratory spectroscopy' and 'field measurements', respectively. The quantitative laboratory spectroscopy, i.e. transition frequency, dipole and linewidth measurements, will be described first; followed by an overview of the remote sensing apparatus known as Balloon OH, a Terahertz (THz) limb sounder.

The millimeter and submillimeter spectrometer currently in use at JPL is generally the standard design with a frequency/phase stabilized source, temperature and pressure controlled absorption cell, an appropriate detector and the supporting modulation/demodulation electronics all coupled to computer control (Fig. 1a). Frequency sources include a multiplier chain for direct synthesis of radiation from 70-700 GHz as well as a variety of Klystron and/or BWO oscillators that can be phase-locked to a multiplier chain when greater sensitivity is required. For quantitative measurements the frequency source(s)

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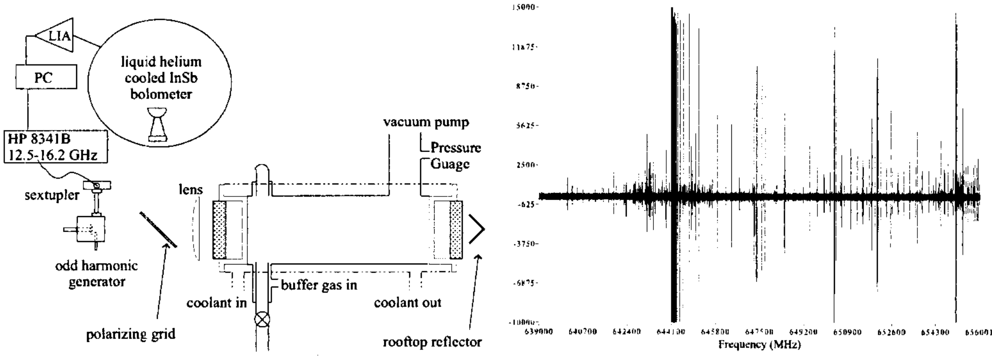


Fig. 1. a) General experimental design. b) 629 - 656 GHz scan of $H^{15}NO_3$.

are locked to a 10 MHz standard and important temperature, pressure measurements are made with primary or secondary standards. Temperature measurements are made with 'T'-type thermocouples imbedded in the jacket of the cell in which cooled (or heated) liquid is circulating. Indented, or 'top-hat' windows are used at the ends of the jacketed cell to insure that all of the absorbing medium is maintained within the temperature-controlled region of the cell. Pressure measurements are made with capacitance manometers calibrated at MKS Inc. When flow systems are required, pressure measurements are made at both ends of the absorption cell to check for pressure gradients.

Both frequency and pressure/temperature dependent linewidth measurements have been the recent focus of the laboratory research. New frequency measurements have been made for the species, $HClO_4$, $H^{15}NO_3$, $CH_3CN$, $(CH_3)_2CO$, $(CH_3)CO(CH_2OH)$, $HO_2NO_2$ and $HO_2NO$. The last species, peroxynitrous acid, has not previously been confirmed to exist in the gas-phase. Use of the multiplier chains often leads to dramatic improvements in ease and range of scanning. Often, entire groups of R-branches can be covered in a single scan, with no source tuning necessary (see Fig. 1b). New pressure/temperature dependent linewidth measurements have been made for $O_3$, $O_2$, HCl, BrO, $CH_3CN$, $SO_2$, HOCl, $HO_2$ and OH. The latter of these species, the hydroxyl radical, done in an experiment that utilizes the Balloon OH apparatus.

Field measurements are generally directed toward new instrumentation or validation of orbital platforms. Currently, two remote sensing rotational transition instruments are in operation at JPL. The Submillimeter Limb Sounder (SLS) and Balloon OH (BOH). Balloon OH (a THz limb sounder built and operated by Dr. Pickett at JPL) has recently had successful engineering and science flights out of Ft. Sumner, New Mexico. This instrument will be deployed for Aura validation studies during the EOS-MLS mission.

BOH is similar to other emissive limb sounding instrumentation in configuration, see Fig 2a. Passive emission from the sky is collimated inside the telescope and passed through polarization-specific optics in combination with

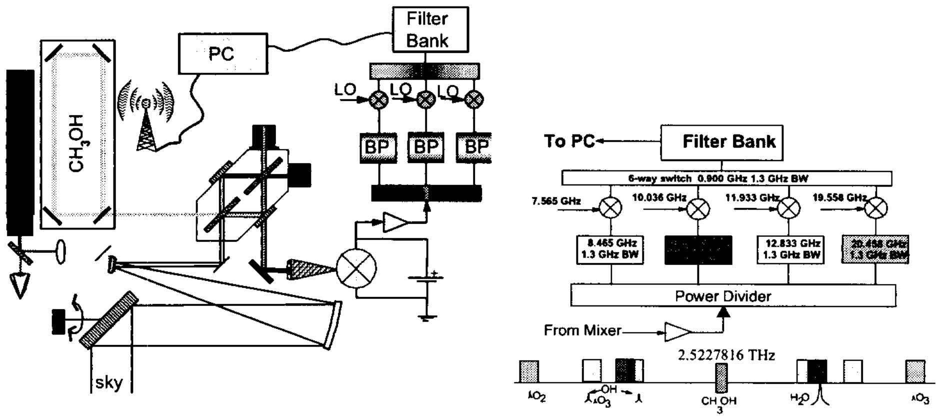


Fig. 2. a) BOH schematic. b) Filter banks and atmospheric signals.

a LASER local oscillator. The two beams are co-aligned into a special 2.5 THz mixer that allows difference frequencies of $\pm$ 22 GHz to be passed towards electronic filters and switches, culminating in heterodyne storage at a 1.3 GHz bandwidth 25-channel filter bank. The LASER local oscillator is a methanol gas LASER operating at 2.5227816 THz ($\sim$ 150 $\mu$ m) pumped with the output of a $CO_2$ LASER at 10 $\mu$ m. The resulting THz frequency is kept stable to less than 2 MHz with piezo-electric tuning of the LASER cavities via onboard computer algorithms. The system operates in dual-sideband mode with some sideband tuning available through translation of one reflector in the Martin-Puplett style diplexer. In flight the diplexer is configured for maximum throughput at the 12.833 GHz OH transition.

During the flight of September $19^{th}$, 2003 data was collected regularly from prior to local noon until well after local midnight. The diurnal cycle of OH shows two sharp transitions at sunset and sunrise, the first of which was dramatically captured in the data set shown in Figure 3. The graph shows the channel two filter bank signals at roughly one hour intervals from just prior to sunset through the end of flight. Each of the time averaged signals are from identical limb viewing angles. In the center of channel two is a pair of lines representing hyperfine components of the lower half of the fine structure doublet for OH at 2.50995 THz. To slightly lower frequency (higher channel no.) is an ozone transition. In this uncalibrated data set, a noticeable decrease in the observed signals circa 6:00 ZULU is noticeable, this is believed to be due to drop in balloon altitude during sunset, altitude was recovered shortly afterwards through a ballast drop. The OH signature, though small, persists through the mid-latitude night.

Data from the laboratory measurements is crucial to determination of concentration profiles in the limb sounding data. Temperature and pressure dependencies of the linewidth are convoluted with the actual temperature and pressure variations within the stratosphere and upper troposphere. In order to

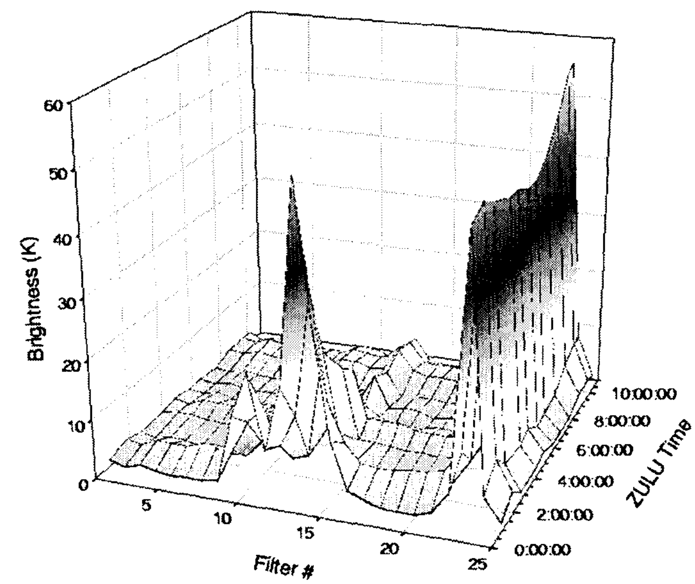


Fig. 3. Raw BOH data from sunset to early morning over New Mexico and Arizona.

minimize errors associated with the deconvolution of atmospheric limb measurements laboratory measurements of pressure broadening are done throughout the temperature range of atmospheric conditions, typically 190 - 300 K. At JPL the close interaction between the remote sensing and laboratory measurements provides a solid foundation for further study of atmospheric chemistry.

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