

ROTATIONAL SPECTROSCOPY AT THE JET PROPULSION LABORATORY

SHORT TITLE: ROTATIONAL SPECTROSCOPY AT JPL

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Abstract- Environmental monitoring, atmospheric remote sensing and astrophysical studies promoted by NASA require a strong basis of spectroscopic information. The rotational spectroscopy capabilities at NASA's Jet Propulsion Laboratory (JPL) are currently maintained for the measurement of key mission priorities that enable modeling and retrieval of geophysical data from the atmosphere as well as validation of the space-borne instruments in the Earth Observing System, particularly the Microwave Limb Sounder. Rotational spectra are measured using a variety of spectroscopic techniques including pulsed-beam Fourier transform microwave spectroscopy (at CalTech); millimeter wavelength Stark spectroscopy; millimeter, submillimeter and THz FM spectroscopy; laser sideband spectroscopy and Fourier Transform far-infrared spectroscopy. Remote measurements of atmospheric rotational spectra are made using two limb-sounder instruments in the submillimeter and THz. Recent advances in the direct synthesis of THz radiation that enable more efficient laboratory science will be presented. Software for comprehensive and systematic study of different molecular systems is maintained at JPL, the software is freely available via <http://spec.jpl.nasa.gov> and is used by our group to create and sustain the JPL spectral line catalog also available online.

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1. Introduction

Environmental security is a fundamental driving force of the earth sciences. Thorough understanding of physics, chemistry, biology and mathematics are all required to secure the complex earth system. Spectroscopy has long served as a tool for probing the environment as well as controlled experiments. A focussed combination of these processes at the Jet Propulsion Laboratory (JPL) has led to significant advances in remote and in-situ earth science. The myriad of available spectroscopic techniques each has unique capabilities for environmental remote sensing; this work will focus on the efforts in rotational spectroscopy.

Rotational spectroscopy has several advantageous aspects for probing the earth system. These include; sensitivity to terrestrial emission that enables equivalent diurnal measurements, high sensitivity to radical species such as OH and ClO, line-of-sight through cloud particles, and due to the common origin (at zero frequency) of all rotational spectra, nearly all polar stratospheric species are observable. The Earth-Observing-System, Microwave Limb Sounder (EMLS, Waters *et al.* 1999) has been taking advantage of these probes with continuous global monitoring since its launch onboard the Aura satellite in July 2004. Supporting balloon-borne instruments are also in use at JPL including the BOH (Pickett *et al.* 2005) and SLS (Stachnik *et al.* 1999) instruments.

Much of the required knowledge for remote sensing utilizing rotational spectra was either unknown, or scattered throughout the chemistry and physics literature. In the late 1970s Robert Poynter set out to fix this issue and created the Millimeter and Sub-millimeter Spectral Line Catalog (Pickett *et al.* 1998), which is now available online at <http://spec.jpl.nasa.gov>. A complimentary laboratory program, championed initially by Herbert Pickett and Edward Cohen and now continued by Brian Drouin, fills in the gaps of necessary quantitative spectroscopy as the field instruments progress. In addition to new spectral characterization of many species, this group has also led many new laboratory spectroscopy developments (Matsuura *et al.* 2000, Farhoomand 1985, Drouin 2005a).

1.1. EMLS

Products of EMLS include daily global maps of Temperature, geopotential height, ozone column, cloud ice, and the following chemical species; O₃, H₂O, OH, HO₂, CO, HCN, N₂O, HNO₃, HCl, HOCl, ClO, BrO, and SO₂. Sensitivity is best in the stratosphere, where simultaneous measurements of chemically active and reservoir species enables tight constraints on global climate modeling. Near and below the tropopause, space-borne rotational spectroscopic

remote sensing instruments are hindered by continuum blindness and increased cloud sensitivity. Much of the current research for EMLS is concentrated on analysis of this important region where pollution, weather and climate interact in critically important fashion. Further discussion of EMLS is given by Georges Wlodarczak in his contribution to this document.

1.2. LABORATORY STUDIES

Remote sensing of rotational transitions requires quantitative spectroscopic information including; 1) transition frequency, 2) lower state energy, 3) line intensity, and 4) air-broadened linewidth. The first two of these quantities are typically determined with high precision through measurements of a subset of spectral features that are analyzed quantum-mechanically and then predicted for the entire spectrum. Line intensities are best determined through measurements of the dipole moment using the Stark effect; inclusion of the measured dipole moment in the quantum-mechanical spectral prediction then transfers this measurement onto the entire rotational band (if centrifugal distortion of the dipole moment can be neglected). Finally, air-broadened linewidths present a continuing challenge to both laboratory and theoretical spectroscopists. State-of-the-art laboratory measurements are often limited in accuracy that can be the limiting accuracy in a remote sensing measurement. This manuscript will describe recent advances in frequency-multiplication as a source for quantitative spectroscopy as well as recent measurements in the laboratory.

1.3. THEORETICAL STUDIES AND CATALOGING

The compilation of predicted and measured rotational spectra in the JPL Spectral Line Catalog created a single source for the first 3 pieces of quantitative information mentioned in section 1.2. It also created a need for a standard tool that would predict all of the different types of rotational spectra in a consistent manner. Generally, measured spectra are fit utilizing a model specific to a class of species, e.g. linear molecule, symmetric top, asymmetric top, open-shell linear molecule, open-shell symmetric top... Quantitative cataloging requires comprehensive inclusion of the massive number of possible combinations within one framework. For this purpose Herb Pickett produced SPFIT/SPCAT, a multi-purpose spectral fitting program. The complexities of molecular spectra manifest in a challenging user interface that allows nearly all spectra to be modeled within a cohesive framework. The fitting program SPFIT is utilized to analyze literature data or new lab measurements and the prediction program SPCAT are used to generate catalog format files. The program is continuously upgraded (Pickett 1997, Pickett 2004) to include more features

important to compelling research problems. Recent progress in the efficient modeling of centrifugal distortion of the dipole moment will be outlined in this manuscript.

2. Quantitative Laboratory Spectroscopy

The atmospheric laboratory spectroscopy program at JPL has been engaged in mission critical air-broadened linewidth measurements (Drouin 2004c, Drouin et al. 2004b, Yamada 2003, Drouin 2005e); as well as exploratory searches for new species (Drouin 2004d, Oh 2005, Miller and Cohen 2003); and extensions of existing models (Chen et al. 2005, Drouin et al. 2005c, Drouin and Maiwald 2005d, Fry et al. 2005, Groner et al. 2002, Pickett et al. 2005a).

The spectrometer and flow cell system is shown schematically in Figures 1 and 2. Figure 1 shows the static/flow cell system. For temperature control, methanol or isopropanol is passively cooled with liquid nitrogen and flowed continuously through an exterior jacket that is in direct contact with the white cell. A solenoid switch controls liquid nitrogen flowed through the alcohol reservoir. Inset polypropylene windows ensure that the gas under study is completely enclosed in the temperature-controlled region.

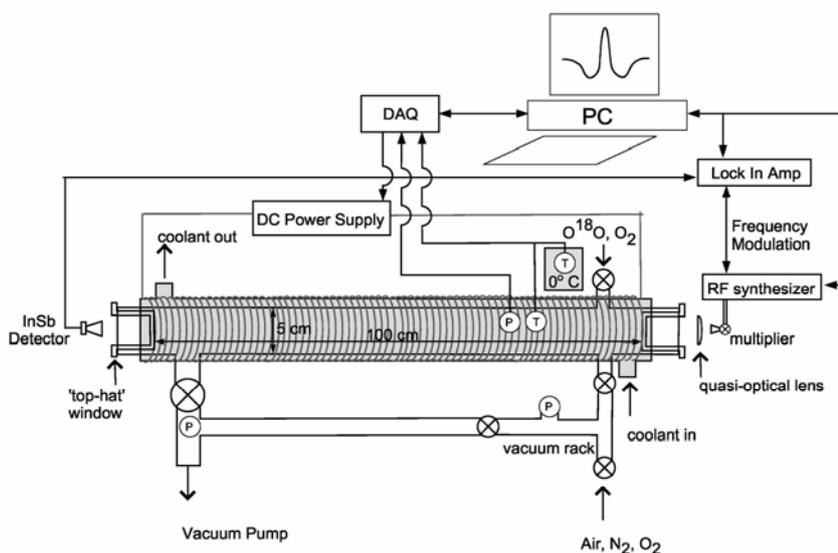


Figure 1. Spectrometer schematic

Secondary windows are added when the cell is below 0°C to prevent condensation on the cold inset windows. Pressure is monitored using calibrated capacitance manometers directly in contact with the sample. A data-acquisition

interface card (DAQ) in the computer (PC) allows continuous recording of the pressure and temperature (thermocouple voltages) during spectral sweeping. The frequency source is a computer controlled sweep synthesizer multiplied up to the desired frequency. Either room temperature diode detectors or liquid helium cooled bolometers (InSb or Si) are utilized for phase-sensitive detection at the lock-in-amplifier.

Figure 2 illustrates the components used in a wide-band frequency multiplication source. The sweep synthesizer is continuously tunable in 1 Hz increments from 10 MHz – 26.5 GHz, it is utilized between 12 and 20 GHz for the frequency multiplication scheme. A tunable YIG filter is voltage tuned to track the sweep synthesizer to eliminate harmonics of the fundamental YIG oscillator in the sweep synthesizer. The mm-wave module is a sextupler, producing frequencies in the 72-120 GHz range, which can be immediately used for spectroscopy using free-space coupling to the gas-cell. Four submillimeter wavelength generation the output of the mm-wave module is amplified using monolithic-membrane integrated circuit (Wang 2001) technology prior to injection into a cascaded set of harmonic multipliers (Bruston 2000). Modulation applied at the sweep synthesizer is transferred directly to the higher frequency radiation.

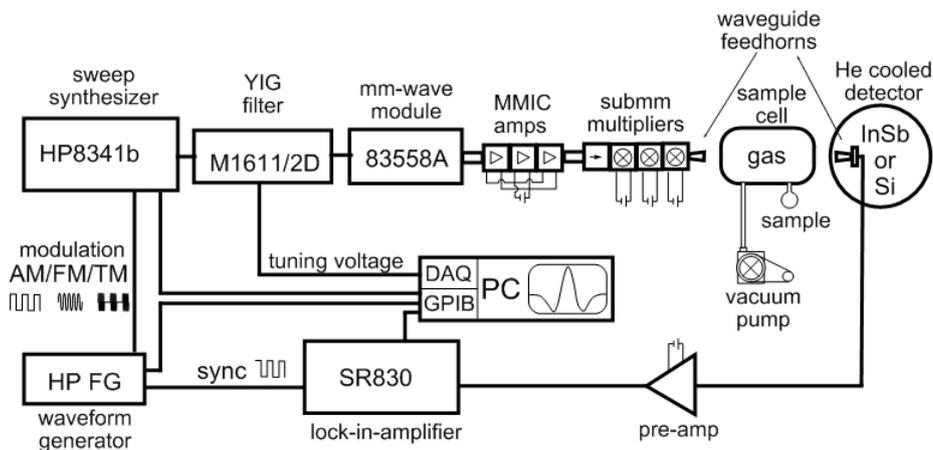


Figure 2. Cascaded frequency multiplier system.

Table 1 shows the frequency range, maximum power, typical power and harmonic content of each source available for the system. Sources can be interchanged with all other system components constant.

Table 1. Harmonic multipliers in use at JPL. AMC & MUT are Millitech devices, VDI is Virginia Diodes, JPL devices were developed for Hershel/HIFI.

| Device | Multi-plier | Range (THz) | Max Power (μ W) | Typ. Power (μ W) | Harmonic Content |
|----------------|-------------|-------------|----------------------|-----------------------|------------------|
| AMC-15 | 4 | 0.05-0.07 | 4000 | 2000 | < -30 dB |
| AMC-10 | 6 | 0.07-0.11 | 3000 | 1000 | < -30 dB |
| Agilent 83558A | 6 | 0.07-0.12 | 2000 | 1000 | < -30 dB |
| MUT-05 | 3 | 0.14-0.22 | 400 | 50 | < -30 dB |
| MUT-04 | 3 | 0.18-0.27 | 120 | 40 | < -30 dB |
| VDI 1.9x5 | 5 | 0.40-0.60 | 40 | 10 | -20 dB x6,x7 |
| VDI 1.5x6 | 6 | 0.60-0.75 | 100 | 30 | -20 dB x4 |
| VDI 1.2x5 | 10 | 0.77-0.85 | 50 | 10 | < -30 dB |
| JPL x2x2x2 | 8 | 0.70-0.83 | 800 | 50 | - |
| JPL x2x2x3 | 12 | 0.84-0.95 | 400 | 50 | -23 dB x8 |
| JPL x2x2x3 | 12 | 1.05-1.28 | 100 | 30 | -26 dB x16 |
| JPL x2x3x3 | 18 | 1.55-1.65 | 12 | 4 | - |
| JPL x2 | 2 | 1.65-1.75 | < 0.1 | << 0.1 | -10 dB x3 |
| JPL x3 | 3 | 2.57-2.65 | <0.01 | <<0.01 | 10 dB x2 |

2.1. LINEWIDTH MEASUREMENTS

The most uncertain lineshape component with direct impact on atmospheric composition retrievals is the pressure-broadened linewidth. Direct spectral analyses of absorption lineshapes requires attention to linewidth, lineshift, line-narrowing effects and instrumental effects. For practical purposes the convolution method (Pickett 1980) has allowed reliable determination of the Lorentzian (pressure broadened) linewidth and lineshift through comparisons of spectra without rigorous extraction of line-narrowing and instrumental parameters. The method requires a reproducible instrument function and strict attention to systematic errors such as temperature drift. The convolution technique, combined with the stable sources of the frequency multiplication source spectrometer, allow a statistical parametric analysis (Drouin et al. 2004b) of the spectral results. In short, the temperature and pressure dependencies of the linewidth (or shift) are simultaneously extracted from all of the convoluted spectra. Furthermore, new system programming that enables preprogrammed pressure/flow settings allows highly stable and reproducible experimental conditions while simultaneously removing user error and fatigue.

Recently published pressure broadening results include hydrochloric acid (Drouin 2004c) (broadening gases - N_2 , O_2 , air), and ozone (Drouin et al. 2004b) (broadening gas - air). Comparable measurements on bromine monoxide (Yamada et al. 2003) (broadening gas - N_2 , O_2) in collaboration with the Japanese group at Ibaraki. More recently, broadening measurements of hypochlorous acid have been completed that indicate that the N_2 -, Air- pressure-broadened linewidth of rQ_0 branch transitions above $J = 18$ have reached the asymptotic limit (Drouin 2005e). A graph of this data set (Figure 3), normalized to room temperature is shown to indicate the relative precision of the broadening and shift parameters. As yet unpublished broadening measurements of oxygen, isotopic oxygen $O^{18}O$, nitric acid, methyl cyanide, ozone, and sulfur dioxide have all been incorporated into EMLS retrievals.

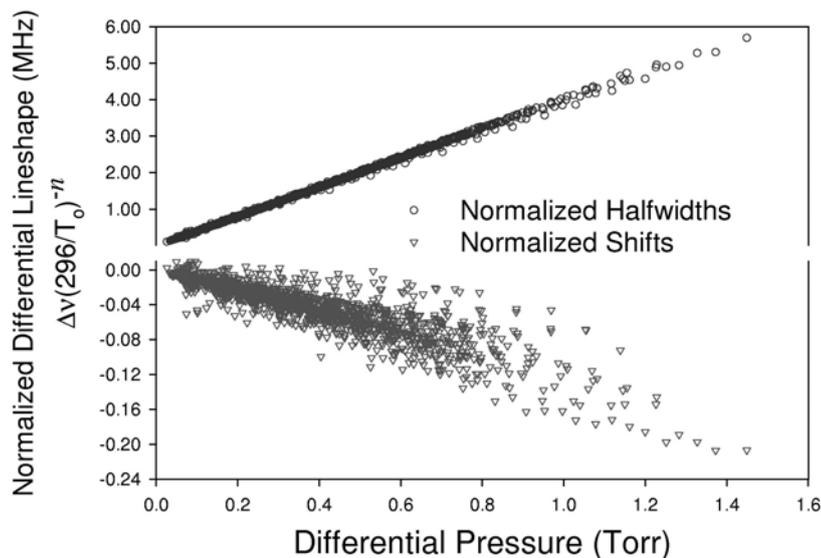


Figure 3. Broadening and shift measurements of HOCl rQ_0 -branch transitions near 630 GHz.

The new ozone and sulfur dioxide linewidth measurements were made with a nearly completely automated spectrometer. After detector and sample preparation a flow of the sample gas and regulated air was allowed to pass through the spectrometer cell. The scanning program utilizes a table of frequencies and pressure settings to scan through small windows (15-25 MHz) encompassing the important transitions within the source bandwidth. After several hours of measurements at the full range of frequencies and pressures the

user can intervene to change the system temperature and repeat the data collection procedure. In this manner data sets of 10-20 transitions measured at 7-12 pressures and 5-10 different temperatures can be recorded in a few days. Fifteen new air-broadening measurements of ozone in the 620-662 GHz range have been performed. Twenty-six new sulfur dioxide air-broadening measurements have also been made in the same frequency region.

2.2. CHEMISTRY EXPERIMENTS

There has been considerable interest in a minor product channel of the OH + NO₂ radical-radical association reaction. Knowledge of the overall rate constant for this reaction is critical to accurate modeling of atmospheric chemistry since catalytic HO_x and NO_x reaction cycles regulate ozone concentrations in the upper troposphere and stratosphere, as well as ozone formation and air quality in the lower troposphere. The major product, HONO₂, or nitric acid is characterized and currently monitored. The minor product, HOONO, or peroxyxynitric acid was first identified in the gas phase through photodissociation spectroscopy (Nizkorodov and Wennberg 2002). Our laboratory reported the first rotationally resolved spectra of the *cis-cis* conformer of this species (Drouin et al. 2004d) and has now completed analysis of the weak field Stark effect (see Figure 4) and the deuterated isotopologue (Drouin et al. 2005b).

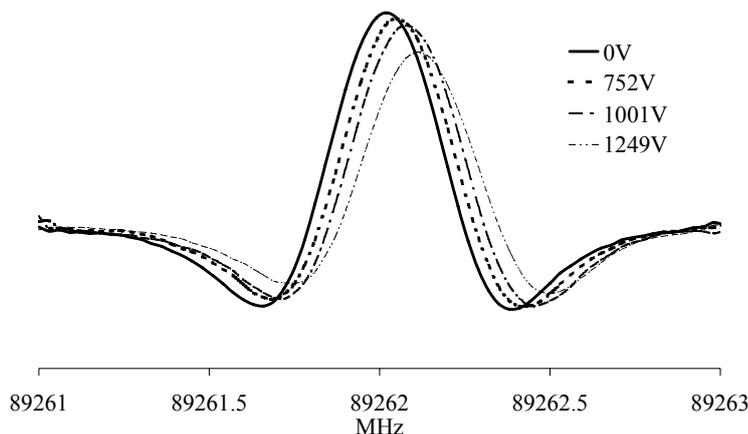


Figure 4. HOONO 18_{5,13} - 18_{4,14} Stark effect

2.3. BROADBAND MEASUREMENTS

The wide-band frequency sources allow much more data collection than was previously attainable using Klystron and Gunn Oscillator sources. Bandwidths are comparable to BWOs, but the computer controlled phase lock of the sweep synthesizer releases the experimenter from the need to continuously monitor the experiment. Unlike the FASSST system (Petkie *et al.* 1997), the wideband sweeps are slow, using the step-and-stare data collection method. The advantages in comparison to FASSST include no post-calibration of the frequency, no external etalon for frequency calibration and only one beam to align and detect.

Complex chemical systems, such as those used to identify HOONO and its various substituted isotopic forms require an intimate knowledge of the chemicals. During searches for isotopic HOONO we collected broadband spectra of isotopically substituted nitric acid. The strong *Q*-branch signatures were easily identified in the survey scans throughout the sub-millimeter. The isotopic nitric acid spectra have now been analyzed up through 800 GHz and reported in the JPL spectral line catalog and the Journal of Molecular Spectroscopy (Drouin *et al.* 2005c).

2.4. CATALOG UPDATES

The JPL catalog is continuously updated as new information becomes available in the literature, and as NASA mission needs require more detail. The perennial atmospheric species that are routinely improved are ozone and water. The most recent updates on these species include new extended frequency measurements of higher *J* and *K* quanta (H₂O - Chen *et al.* 2000, O₃ - DeNatale 1997 and Colmont *et al.* 2005) as well as critical analyses of the dipole moment functions that reproduce Stark measurements to experimental precision (H₂O - Clough *et al.* 1973, Dyke and Muentner 1973, O₃ - Mack and Muentner 1977) and absolute intensity measurements near experimental precision (H₂O - 1.8% absolute, 14.1% relative, (Toth 1998), 0.7% absolute, 5.5% relative, (Brown and Plymate 1996); O₃ 2 σ relative (Birk *et al.* 1994)). In the case of water the previous entry in the JPL catalog (1999) appears to be inconsistent with Stark measurements. Table 2 displays the calculated Stark coefficient before and after the latest update. The previous discrepancy was, on the average, slightly less than 1%. Ozone intensities have significantly changed only at higher *J* and *K* due to the centrifugal distortion corrections. The centrifugal distortion of the dipole moments for H₂O and O₃ are calculated to match a perturbative model of vibrational corrections to the ground state Hamiltonian (Pickett 1990).

Table 2. Stark shift values for H₂O, from ref X, Y and those predicted using SPCAT and the previous and current JPL catalog models. $\Delta\nu_{\text{Stark}} = ({}^0\Gamma + {}^2\Gamma M^2)\epsilon^2$ units of Γ are Hz(V/cm)²

| Levels | | Literature | JPL05 | %Diff JPL05 | %Diff JPL99 | 1 σ %(meas) |
|---|-----------------------|---------------|-----------|----------------|----------------|-----------------------|
| 1 ₁₁ (0 \leftarrow 1) ^x | ² Γ | 0.226644(45) | 0.226678 | 0.02 | -0.80 | 0.04 |
| 1 ₁₀ (1 \leftarrow 0) ^x | ² Γ | 0.407086(81) | 0.407111 | 0.01 | -0.77 | 0.05 |
| 2 ₁₁ (0 \leftarrow 1) ^x | ² Γ | 0.162902(32) | 0.162935 | 0.02 | -0.86 | 0.04 |
| 3 ₁₃ \leftarrow 2 ₂₀ ^y | ⁰ Γ | 0.077514(11) | 0.077389 | -0.16 | -0.63 | 0.14 |
| 3 ₁₃ \leftarrow 2 ₂₀ ^y | ² Γ | -0.042180(17) | -0.042176 | -0.01 | -0.64 | 0.04 |
| 6 ₁₆ \leftarrow 5 ₂₃ ^y | ⁰ Γ | 0.198564(110) | 0.199024 | 0.23 | -0.81 | 0.55 |
| 6 ₁₆ \leftarrow 5 ₂₃ ^y | ² Γ | -0.009598(15) | -0.009607 | 0.10 | -0.97 | 0.16 |

Nitric acid has also been updated with new information (Petkie et al. 2003, Perrin et al. 2004) on vibrational states below 1000 cm⁻¹, and the partition function is given for the entire vibration-rotation manifold. The isotopically substituted forms of nitric acid (Drouin 2005c) are new entries in the catalog.

Other new entries (since 2001) include peroxyxynitrous acid (including a frequency and dipole update), hypochlorous acid (frequency extension, Drouin 2005e), perchloric acid (new species, Oh 2005), propane (new catalog species), acetone (new catalog species), glycolaldehyde, methyl calcium, dihydroxyacetone, aminoethanol, and formyl chloride (new catalog species).

3. Conclusion

Detailed laboratory measurements of controlled chemical systems provides information necessary for critically sensing the Earth environment. The spectroscopic information made publicly available through the literature and through open databases is essential to field mission planning and execution. Space and field instruments capable of measuring pollution, weather, and climate are currently in operation at JPL and the laboratory program directly supports these spectroscopic needs. In a concerted laboratory and field program the science necessary for environmental security is obtained.

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