

ROTATIONAL SPECTROSCOPY ON PLANETARY PROBES

Brian J. Drouin*, John C. Pearson, Frank W. Maiwald

California Institute of Technology, Jet Propulsion Laboratory, 4800 Oak Grove Dr., Pasadena, CA 91016, USA

ABSTRACT

High resolution spectroscopy at long wavelengths has been widely used for characterization of gas-phase species. It is particularly powerful because of the ability to absolutely specify the carrier of the (usually rotational) observed spectrum, including isomers, conformation and isotopic content. The technique has not enjoyed mainstream analytical use due to technological constraints on the source and detector systems and therefore it has been relegated primarily to use in research laboratories. At JPL we have incorporated new source technology developed for the Herschel Space Telescope and commercially available room temperature Schottky diode detectors into the JPL millimeter and submillimeter spectrometer and demonstrated its use for wideband detection of trace gas-phase species. This new system can be configured in a compact, portable design for in-situ measurements. The spectrometer has been tested with a laboratory simulation of the activated Titan atmosphere and shown to be sensitive to trace species such as methyl cyanide, hydrogen isocyanide, ammonia and the cyanide radical. The list of detectable species includes all gas-phase molecules with an electric or magnetic dipole moment. Current detection efficiencies require an absorption pathlength of approximately five meters for a suitable cadre of interesting species to be rapidly detected, i.e. millisecond integration times. The demonstrated room-temperature technique is currently five orders of magnitude above the theoretical detection limit.

Keywords: *in situ* sensing, rotational spectroscopy, catalog, lineshape, linewidth, frequency multiplication

1. INTRODUCTION

Planetary probes are the most direct means of discovering and elucidating the constituents of extraterrestrial environments. Thorough understanding of physics, chemistry, geology, biology and mathematics are all required to understand these systems. Spectroscopy has long served as a tool for probing these environments both remotely and *in-situ*. A focused combination of these methods at the Jet Propulsion Laboratory (JPL) has led to significant advances in remote and, more recently, *in-situ* planetary science. Each of the myriad of available spectroscopic techniques has unique capabilities for planetary sensing; this work will focus on efforts in rotational spectroscopy.

1.1. SENSING TECHNIQUES/REQUIREMENTS

Rotational spectroscopy has several advantages for probing atmospheric systems. Generally, the spectral features are strong, narrow (at low pressures) and unique for each species.

Spectral features are proportional to the square of the permanent electric dipole moment, μ , and inversely proportional to the molecular partition function, $Q(T)$, in general this means all polar gas-phase species can be studied. However, larger species (>100 atomic units) generally have a high degree of partitioning which effectively limits the sensitivity range. Since each molecule (as well as each isomer and isotopolog) has a unique μ and $Q(T)$, the sensitivity of a given spectrometer to a particular species must be tabulated.

*To whom correspondence should be addressed. Brian Drouin, M. S. 183-301, 4800 Oak Grove Dr. Pasadena, CA 91016, USA; e-mail: brian.j.drouin@jpl.nasa.gov

However, a reasonable 'rule of thumb' is that typical strong transitions of a polar molecule with a mass of 100 atomic units and a modest 1 Debye dipole moment have absorptions of 0.01% (1×10^{-4}) in a 1 cm path in a 10 mTorr sample at 100 GHz.

The long lifetimes of rotational states allow the linewidth to be governed principally by pressure broadening or, below ~ 100 mTorr, Doppler broadening. The origin near zero frequency means that the Doppler width is typically $1:10^6-10^{10}$, $\Delta\nu:\nu$.

The spectral features are unique and well separated when pressure broadening can be neglected. The specificity of rotational spectral features is due to the dependence of the rotational energy levels on the inertial moments of the species. Inertial moments depend upon mass and position with respect to the center of mass. The characteristically narrow spectral features allow high resolution techniques to easily discern spectral features that shift several percent upon isotopic substitution. Rotamers or chemical isomers typically have drastically different patterns in their respective rotational spectra.

1.1.1. Emission

Sensitivity to resonant thermal emission enables remote measurements of bulk and trace species: such as O_2 , O_3 , OH and ClO (on earth) [1]; or HC_nN and CH_3CN on Titan [2-4]; or H_2O and HDO on Mars [5] and Venus [6]. This method has line-of-sight measurement capability through cloud/haze particles; and, due to the common origin (at zero frequency) of all rotational spectra, most species are observable in the available spectral windows of Earth's atmospheric absorption. The Earth-Observing-System, Microwave Limb Sounder [1] has been utilizing these aspects of rotational spectra to accomplish continuous global climate monitoring since its launch onboard the Aura satellite in July 2004. The millimeter/submillimeter telescope, IRAM, has been used to remotely probe Titan [2-4], Mars [5] and Venus [6]. With known spectroscopic parameters the required hardware and necessary integration time is well defined for such studies [7].

1.1.2. Absorption

Absorption techniques in rotational spectroscopy are commonly used in laboratories to study samples to characterize and discover molecules. Simple systems utilize a high spectral purity tunable source oscillator coupled through an absorption cell and into a broadband detector. Sensitivities are defined by source and detector characteristics as well as pathlength in the absorption cell.

At JPL these techniques [8] are primarily used to support remote sensing needs. Recent upgrades of the submillimeter hardware have created the possibility for miniaturization and remote operation of the absorption system.

1.1.3. Database

At the outset, much of the required knowledge for 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 Submillimeter Spectral Line Catalog [9], 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 and John Pearson, fills in the gaps of necessary quantitative spectroscopy as field instrumentation progresses. In addition to spectral characterization of many species, this group has also led many new laboratory spectroscopy developments which will be outlined in section 2.

1.2. LABORATORY STUDIES

Remote and in-situ sensing of rotational transitions requires quantitative spectroscopic information including: 1) transition frequency, 2) lower state energy, 3) line intensity, and 4) air-broadened linewidth (in a dense sample). The first three of these quantities are typically derived from high precision measurements of spectral features that are analyzed quantum-mechanically. A transition frequency is reliably determined when a high-resolution sweep through the resonance is completed using a referenced, phase-locked frequency source. Line intensities are best determined through measurements of the dipole

moment using the Stark effect. Use of the measured dipole moment in a quantum-mechanical spectral prediction transfers the Stark measurement precision 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 broadening measurements often remain as the limiting accuracy (typically 3-5%) in a remote sensing measurement.

Improvements in remote and in-situ sensing capabilities require more precise spectroscopy databases, which, in turn continues to drive laboratory spectroscopy to produce the necessary data. 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

High resolution rotational spectra are, in most cases, described exquisitely well by the physics of angular momentum couplings. This allows theoretical models to generally fit spectra to experimental precision and precisely predict the entire spectrum. The compilation of predicted and measured rotational spectra in the JPL Spectral Line Catalog [9] created a single reference model for three of the types of quantitative information mentioned in section 1.2 (transition frequency, lower state energy, line intensity). It also created a need for a procedure that could 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 and others. Quantitative cataloging requires comprehensive inclusion of all of the possible combinations within one framework. For this purpose Herb Pickett developed 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 is used to generate catalog format files. The program is

continuously upgraded [9-13] to include more features important to compelling scientific problems.

2. Quantitative Laboratory Spectroscopy

In the last several years the JPL millimeter and submillimeter spectrometer has been utilized to support NASA and ESA missions in Earth Science (UARP) and Astrophysics (APRA). This research has lead to a number of publications of air-broadened linewidth measurements [14-18]; as well as exploratory searches for new species [19-22]; and extensions of existing models [23-31]. Additionally, the spectrometer system has been utilized as a quantitative gas analyzer to determine concentrations of species in a simulated atmosphere of Titan [32].

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.

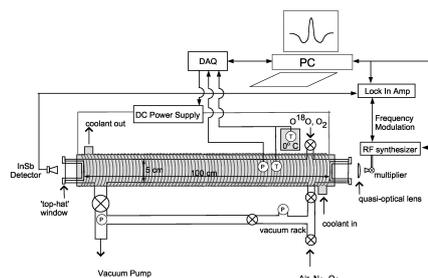


Figure 1. Spectrometer schematic

Secondary windows are added when the cell is below 0°C to prevent condensation, which would absorb the RF signal, 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 control

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. For submillimeter wavelength generation the mm-wave module output is amplified using monolithic-membrane integrated circuit [33] technology prior to injection into a cascaded set of harmonic multipliers [34]. Modulation applied at the sweep synthesizer is transferred directly to the higher frequency radiation.

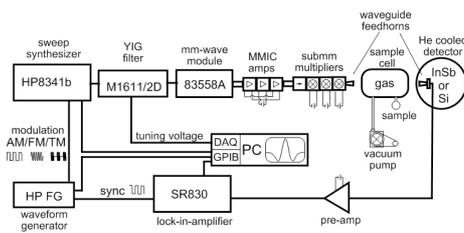


Figure 2. Cascaded frequency multiplier system.

Table 1 shows the frequency range, maximum power, typical power and harmonic content of each source available for the system. In most cases sources can be interchanged with all other system components unchanged.

2.1.1. Lineshape studies

The most difficult to measure lineshape component that has direct impact on remote 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 [35] 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 minimization of systematic errors such as temperature drift. The convolution technique, combined with the stable sources of the frequency multiplication spectrometer, allow a statistical parametric analysis [14] of the spectral results. In short, the temperature and pressure dependencies of the linewidth (or shift) are simultaneously extracted from all of the deconvoluted spectra. New system programming that enables automation of the pressure/flow settings allows highly stable and reproducible experimental conditions while simultaneously reducing user error and fatigue.

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

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

Recently published pressure broadening results include oxygen [18], hypochlorous acid [17], bromine monoxide [16], hydrogen chloride [15] and ozone [14].

The broadening measurements of hypochlorous acid are summarized here as an example. The data indicate that the N_2 -, Air- pressure-broadened linewidth of Q_0 branch transitions above $J = 18$ have reached the asymptotic limit. A graph of the entire N_2 broadening data set ($J = 17-22$, $T = 200-300$ K, $p = 0.1-1.5$ Torr, Figure 3), normalized to room temperature is shown to indicate the relative precision ($2\sigma_{\max}(I_T) = 1.4\%$) of the broadening and shift parameters ($2\sigma_{\max}(\delta_T) = 4.2\%$). The high precision of the broadening parameter over the full temperature range is immediately discernable by the tight correlation of the normalized data set (open circles in Figure 3).

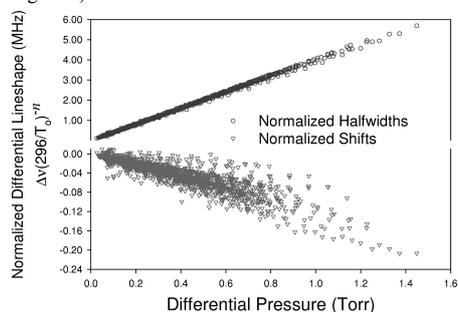


Figure 3. Broadening and shift measurements of HOCl Q_0 -branch transitions near 630 GHz.

Line broadening measurements since 2005 have been made with an automated spectrometer. After detector and sample preparation, a flow of the sample gas and regulated air is allowed to pass through the spectrometer cell. The scanning program utilizes a table of frequencies and pressure settings to scan through spectral windows (15-25 MHz) encompassing the important transitions within the source bandwidth. After several unassisted hours of measurements at the full range of frequencies and pressures the user may 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. With this technique fifteen new temperature

dependent 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.

2.1.2. Frequency Measurements

The measurement of rotational transition frequencies is a highly accurate and precise science, with most measurements reported in the literature with 7-10 significant figures. The transition frequencies represent differences in energy levels given by the moments of inertia of the molecule and perturbations due to spins, centrifugal distortion and/or internal rotation. Laboratory data is collected at Doppler or sub-Doppler resolution and fitted to a quantum mechanical model adequate for the species under study. Often, a single publication includes analyses of isotopologues and thermally excited vibrational states. Many species are 'discovered' through measurement of rotational transitions thanks to the ability of the high resolution technique to resolve species in complex mixtures and unambiguously assign the spectral carrier based on the inertial moments.

The wide-band frequency sources allow much more data collection than previously attainable using Klystron and Gunn Oscillator sources. Bandwidths of the frequency multiplier sources 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.

Since 2005 the laboratory has published rotational transition frequencies and spectral analyses on the following species; HCO⁺[31], D₂O[25], propane[26], hypochlorous acid [16], acetone [27], propargyl alcohol[28], glycolaldehyde[29], nitrous oxide[24], ammonia[30], nitric acid[23], CH⁺ [22], peroxyntrous acid[19,21] and perchloric acid[20]. In most of these species the JPL effort was to extend the frequency coverage of earlier work, however the last three species, peroxyntrous acid and perchloric acid, had never before been analyzed at high resolution. Consequently, these species also required measurements of the Stark effect in order to determine the dipole moment and calculate the rotational transition linestrengths.

2.1.3. *New Species and dipole measurements*

Considerable interest in a minor product channel of the OH + NO₂ radical-radical association reaction led us to investigate peroxyxynitrous acid. 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 peroxyxynitrous acid was first identified in the gas phase through photodissociation spectroscopy [36]. Our laboratory reported the first rotationally resolved spectra of the *cis-cis* conformer of this species [19] and analysis of the weak field Stark effect [22] (see Figure 4).

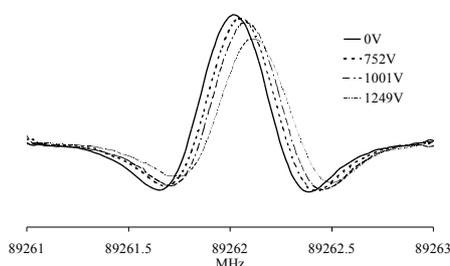


Figure 4. HOONO 18_{5,13} - 18_{4,14} Stark effect

Complex chemical systems, such as those used to identify HOONO and that described in the next section, require an intimate knowledge of all of the chemicals. For example, during searches for isotopic HOONO we also collected broadband spectra of isotopically substituted nitric acid. The strong *a*-R-branch signatures were easily identified in the survey scans throughout the sub-millimeter. Isotopic nitric acid spectra has now been analyzed up through

800 GHz and reported in the JPL spectral line catalog and the Journal of Molecular Spectroscopy [23].

2.1.4. *Simulated Titan Atmosphere*

Proposed missions to Titan's surface involve searches for pre-biotic compounds hypothesized to form from processed atmospheric sediments known as Tholins. A significant gap in this hypothesis can be filled through new laboratory measurements. Experiments simulating the Titan atmosphere have consistently generated tholin compounds when the representative Titan atmospheric mixture (98% N₂, 2% CH₄) is activated in a plasma discharge. However, the constituents of the activated mixture have never been probed directly with a sensitive spectrometer. We have quantitatively determined trace components of a chemically active synthetic Titan atmosphere utilizing the JPL submillimeter spectrometer. Identification of chemical, radical and ionic species involved in the tholin production elucidates specific production mechanisms. Subsequent observation of these trace species in Titan's atmosphere will form a basis for pre-biotic surface chemistry and mitigate risk in mission planning.

The JPL submillimeter spectrometer [8] was fitted with two mass flow controllers, two hollow electrodes, polyethylene windows and a liquid nitrogen trap. The operating temperature of 200 K was maintained through passive cooling with methanol chilled by liquid nitrogen and circulated through an envelope surrounding the discharge region. A 3000 Volt, 0.240 Ampere discharge was maintained within 110 mTorr (0.00014 atmospheres) nitrogen and methane. This pressure was actively maintained using the mass-flow controllers following the gas regulators and the discharged gas was continuously pumped through the system using a vacuum pump. Condensable discharge products were collected in a liquid nitrogen trap in line to the vacuum pump. Plastic (polyethylene) windows were fitted directly onto the cold, grounded hollow cathode and onto an insulated extension near the hot hollow anode.

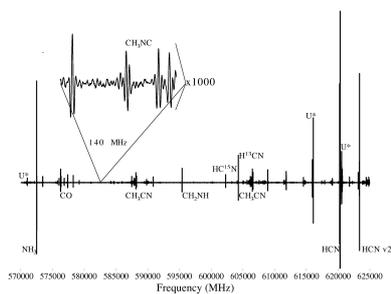


Figure 5. Survey scan of the synthetic Titan atmosphere.

Low sensitivity scans, utilizing the room temperature Schottky diode detector in the 570-625 GHz range, quickly identified chemicals such as hydrogen cyanide (HCN), carbon monoxide (CO), water (H₂O), ammonia (NH₃), methyl cyanide (CH₃CN), methylenimine (CH₂NH) and cyanoacetylene (HC₃N). Quantitative analyses of direct absorption spectra shows that HCN, CH₃CN and HC₃N are present in the cell at concentrations about 200x the mixing ratio at the equivalent pressure in Titan's atmosphere (water, methylenimine and ammonia are not characterized in Titan's atmosphere yet). Water was not added to the system, but is detected at concentrations consistent with its source being the cold cell walls.

The detection system was then improved by utilizing the laboratory's most sensitive detector, a liquid helium-cooled, Silicon bolometer. Survey scans (See Figure 5) in the same spectral window then revealed a number of radical and unstable chemical species present at < 20 ppm. Compounds thus far identified in the survey spectrum include: cyanide radical (CN), hydrogen isocyanide (HNC), amidogen (NH₂), methyleneamidogen (H₂CN), cyanomethylene (HC₂N), methyl isocyanide (CH₃NC), and methylamine (CH₃NH₂). Most of these species have been quantified using direct absorption spectroscopy and known quantum mechanical parameters from the JPL [9] and CDMS [37] databases. During assignment and quantification of the spectra several database/literature spectroscopic deficiencies were identified including: 1) Only extrapolative predictions for CH₃NC and

CH₂NH; 2) no predictions for hydrazine (N₂H₄), or imine (N₂H₂); 3) and no dipole moment measurement for cyanomethylene. The survey spectrum shown here, as well as spectra recorded from 770-930 GHz are sufficient to update the database for CH₃NC and CH₂NH.

This work developed understanding of the minor constituents of the Titan atmosphere and verified that relative chemical concentrations could be reproduced in laboratory controlled plasma as shown in Figure 6. Figure 6 shows experimental data overlaid upon measured profiles in Titan's atmosphere [2-4,38] Titan's atmosphere has been the subject on an increasing number of modeling efforts as well as the hypothesized source for pre-biotic deposits on the surface. The present results show that the characteristics of a synthetic Titan atmosphere can be monitored and directly compared to actual atmospheric measurements.

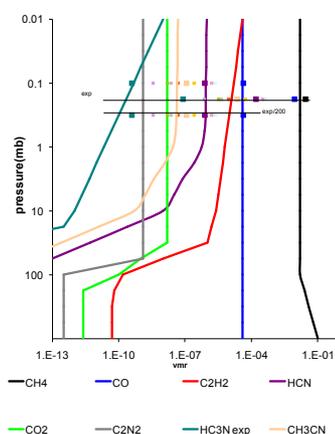


Figure 6. Titan atmospheric profiles with experimental data overlaid.

The results indicate that new observations with higher sensitivity and/or spectral coverage will likely reveal more details of the photochemical activity in Titan's atmosphere. Some of the database issues discovered this far will hamper observational efforts, causing significant wastes of telescope and research time. Improved observations, coupled with validated

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laboratory experimentation will mitigate uncertainties in current and future plans for observations and surface sampling missions.

This work also serves as a proof-of-concept for studying active species *in-situ* with microwave spectroscopic techniques for identifying and quantifying the chemicals in a complex mixture.

2.2. CATALOG UPDATES

The JPL spectral line catalog is continuously updated as new information becomes available in the literature, and as NASA mission needs require more detail.

2.2.1. Recent terrestrial atmospheric entries

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 for H_2O [12] and O_3 [39,40]. Critical analyses of the dipole moment functions reproduce Stark measurements to experimental precision H_2O [41-42] and O_3 [43]. Absolute intensity measurements are reproduced near experimental precision (H_2O – 1.8% absolute, 14.1% relative, [44], 0.7% absolute, 5.5% relative, [45]; O_3 2 σ relative[46]). In the case of water the previous entry in the JPL catalog (1999) was 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%, the new analysis agrees with experimental Stark data to within the measurement precision of ~0.1%. 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 H_2O and O_3 are calculated to match a perturbative model of vibrational corrections to the ground state Hamiltonian [47].

Nitric acid has also been updated with new information [48,49] 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 [23] are new entries in the catalog.

Other new entries (since 2001) include peroxyxynitrous acid [19] (including a frequency and dipole update [21]), hypochlorous acid (frequency extension [16]), perchloric acid (new species, [20]), nitrous oxide (frequency update, [24]), formyl chloride [50] and nitrous acid [51]

2.2.2. Recent planetary and interstellar entries

A re-invigoration of the astrophysical portion of the catalog has been supported during the preparation for the launch of the Herschel Space Telescope and the building of the ALMA array. Furthermore, several species of interest to Titan, or other planetary atmospheres and exospheres have been added to enable sensitivity analysis for mission concepts. These new species include; propane [26], acetone [27], glycolaldehyde [29], dihydroxyacetone [52], methyl peroxide [53], methoxy radical [54], propargyl alcohol [28], tetrasulfur [55], trisulfur [55], sodium monoxide [56], formyl cation [31] and hydroxyacetone [57].

3. Conclusion

Detailed laboratory measurements of controlled chemical systems provide information necessary for critically sensing planetary environments. The same techniques can be developed for application *in situ*. The spectroscopic information made publicly available through the literature and through open databases is essential to science field mission planning and execution. Space and field instruments capable of measuring bulk and trace species are currently in operation at JPL. Instrument development can lead to near-term deployment of the technology

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