# White paper for the Planetary Decadal Survey:

# Laboratory Spectroscopy to Support Remote Sensing of Atmospheric Composition

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**Recommendations**

- **Develop standardized spectroscopy databases tailored to planetary needs**
- **Train young scientists in laboratory spectroscopy (experimental and theoretical)**
- **Invest in infrastructure**
- **Facilitate effective communication between laboratory providers and planetary users**
- **Prioritize spectroscopic data needs for planetary science**
  **(determined periodically by consensus of astronomers)**

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## 1. Preface and background

Planetary astronomers depend primarily on spectroscopic remote sensing to determine the compositions of the comets, moons and planets (including extrasolar planets) *because almost every physical phenomenon that influences the radiative transfer of a planetary body can be detected and quantified from the variation of specific spectral features* [**1**]. With spectroscopic remote sensing, astronomers detect new species (atoms, molecules, ions, radicals present in gas, liquid and solid phase) and determine their abundances. Theoreticians use these observations to formulate and validate theoretical models which provide fundamental insight into the various processes that occur in planetary atmospheres. For example, in the Giant planets, mixing ratios of primordial species constrain the models of planetary formation and evolution. Thus, the atmospheres of planets have been probed by spectroscopic techniques (in radio to x-ray wavelengths) using numerous ground-based observatories (**VLA**, **Keck**, **Subaru**, **IRTF**, **VLT**, **ALMA …**), from aircraft (previously *the Kuiper Airborne Observatory* (**KAO**) and currently **SOFIA)** and with instruments on spacecraft (**Voyager, Galileo**, **ISO**, **Cassini, Mars and Venus Express, MRO**) and orbiting telescopes (**ISO, Hubble, Spitzer, Herschel**). In some aspects, these observations are more difficult to interpret if the data are at low, not high, resolution.

Spectroscopic remote sensing is a mature technology, but the effectiveness of this powerful tool depends directly on the reliability of the fundamental spectroscopic data.

The **relevant** information must be

a. complete (with all species and their isotopologues)
b. accurate (enough for specific applications)
c. organized (in a standard format, accessible and well documented)

The interpretation of planetary spectra requires extensive knowledge of the spectral line parameters for every species that contributes to the remote sensing signals. For gaseous species, the crucial line-by-line parameters are **frequencies** (line positions), transition **intensities** (line strengths), **lower state transition energies** and **partition functions**. In high pressure environments, spectral **line shape functions** must be applied to characterize pressure broadening effects (typically half widths, pressure-induced frequency shifts, etc. which vary as a function of transition quantum numbers). These parameters also vary as a function of temperatures that can range from 50 K (for outer planets) to 800 K (for Venus) and perhaps up to 2500 K (for extrasolar planets). Additional essentials are the spectral coefficients of collision-induced absorptions and continua of various spectral features of gases and gas mixtures, as well as the spectroscopic signatures of liquids and solids at the relevant planetary temperatures.

The design of future remote sensing instruments and the planning of observational strategies require *complete* knowledge of the spectral parameters associated with the observed spectral features. Each application has specific needs that depend on the wavelengths selected and the targeted species to be observed (for example, detecting $CH_4$ on Mars requires full knowledge of the $CO_2$ spectrum). A million ro-vibrational transitions can contribute line-by-line to the observed spectral signature of a particular atom, molecule, radical etc. depending on the wavelength and sensitivity of the monitoring system. The increasing sophistication now available in observing instrumentation poses a greater demand for better accuracy in the various spectral line parameters mentioned above.

The degree of completeness and accuracy required is determined by the specific spectroscopic application. The dynamic range of *strong* vs *weak* transition intensities varies from 3 to 20 orders of magnitude, depending on the planetary abundances and temperatures. For example, a database consisting of ~ one million $CO_2$ transitions will be sufficient for analysis of most planetary objects, but the corresponding list needed for Venus is over 15 million transitions because its atmosphere is hot (over 700 K) and dominated by $CO_2$. Many planetary applications need $CO_2$ intensities and broadening coefficients accurate to only 5%, but Earth global warming studies require at least *an order of magnitude better accuracy* for these parameters.

**Spectroscopic parameters for gas phase species are obtained from**

1) Quantum mechanical Ab initio predictions
2) Quantum mechanical Hamiltonian calculations
3) Empirical lists retrieved line-by-line directly from high quality laboratory studies

Ab initio theory can be applied to predict nearly complete compilations with millions of transitions and provide the lower state energies needed to calculate intensities at different temperatures. However, the parameter accuracies are not as reliable as those obtained with successful Hamiltonian methods when extensive measurements are reproduced within experimental accuracies. However, the Hamiltonian models tend to break down for higher values of quantum numbers and can become nearly intractable in the near infrared and visible regions. The empirical measurements can be used to correct the predicted positions, intensities and pressure broadening coefficients on a line-by-line basis, but only for several thousand stronger transitions in a region [e. g. see ref. **2**]. Empirical equations are sometimes developed when theoretical models fail to reproduce measured pressure broadening values. These approaches are all very time consuming, requiring months to years of analysis before sufficient information is produced to meet planetary needs.

It is important to note that the laboratory studies must be done *at the high resolution* sufficient to discern the line-by-line features in order to determine quantum assignments, *not at the low resolution of planetary observations*; the high resolution database permits absorption coefficients to be computed via radiative transfer models for a variety of pressure-temperature-abundance conditions encountered in many different planetary atmospheres.

When theoretically-predicted line parameters are not available, astronomers turn to absorption coefficients (cross sections) obtained point by point from recorded laboratory spectra [**3**]. These data are generally used for liquids, solids (ices and aerosols), gases whose spectra are congested even at Doppler-limited resolutions and for the shorter wavelengths of many common molecules (e. g. $CH_4$). In desperation, astronomers have even used absorption coefficients obtained directly from *planetary* spectra [see ref. **3**]. These are often processed as *band models and correlated-K coefficients* to permit detection of species, but these representations are not reliable if planetary opacities, pressures and temperatures differ greatly from the original recorded spectra.

## 2. General findings and recommendations

### ● Develop standardized spectroscopy databases tailored to planetary needs

Interpretation of planetary spectra requires detailed lists of quantum-mechanical line parameters at all relevant wavelengths as primary input into radiative transfer calculations [**3**].

Existing spectroscopic databases for astrophysics [**4,5**] contain hundreds of species and cover the microwave to far-IR wavelengths while Earth remote sensing databases [**6,7**] include dozens of species in the microwave through visible wavelengths. These public databases typically have spectral line parameters for a few million transitions. *A corresponding planetary database does not exist;* it would contain billions of entries to characterize the spectroscopy of all the atoms, molecules, ions, radicals etc. in the spectral regions (0.000001 to 100,000 $cm^{-1}$) being utilized.

At present, the information required for such a planetary database is incomplete, inaccurate and fragmented. Most planetary astronomers rely on Earth–oriented public databases [**6,7**] supplemented with proprietary *private collections* which are neither openly distributed nor documented. *The first essential step is to collect existing spectroscopic parameters into a single database and render them into a common format tailored to planetary science.*

A general spectroscopic database for planetary applications should be maintained by a permanent staff advised by an International (volunteer) Committee composed of expert users and providers (as is done for HITRAN [**6**]). This effort would require a dedicated staff (at least 4 full time employees [FTE]) with access to large computing capabilities. Their primary function would be to collect, evaluate, merge and organize, document and distribute new available laboratory data; we emphasize that this information must be in a standard electronic form as input into radiative transfer software, not just information to be viewed only by human eyes. However, user-friendly software must be maintained for users to understand the database contents easily (See *websites mentioned in the references)*. Agencies supporting laboratory research would require that new results be given to the database in proper electronic form.

### ● Train young scientists in laboratory spectroscopy (experimental and theoretical)

To have adequate e-databases, there must be new laboratory studies (measurements and theoretical modeling) that can address the dearth of information. Planetary science is being pursued with ever improving spectroscopic instrumentation **(**newer telescopes equipped with better sensitivity spectrometers), but there are too few active researchers available to correct even the many well-known deficiencies. The laboratory science community devoted to providing critical information has shrunk and is now dominated by senior personnel who will retire within a decade; indeed some individual laboratories that previously provided essential detailed spectroscopy for planetary science have already closed their doors. Some agency-funded programs provide support to graduate students and post-doctorates to perform *small scope studies*, but these efforts often do not provide the depth and breadth of information needed to satisfy planetary needs. These potential replacements trained in spectroscopy (and quantum mechanics) are often drawn into related applications (with more stable funding in the long term). It is very important that *fresh-out spectroscopists* be hired in time to learn from the experienced leaders in the field. *One metric: for every senior who retires, support two replacements (theorists and/or experimentalists) to continue spectroscopic research.*

● **Invest in infrastructure**

Experimental spectroscopy of gases produces precise measurements of the line-by-line structure in order to apply quantum mechanical models successfully. The ideal experiment for this is performed using 1) high signal to noise ratios for sensitivity, 2) high spectral resolution, and 3) sufficient band width to capture all the spectral features needed; often only two of these conditions are achieved simultaneously.

Two mature technologies for this research in the infrared and visible are Fourier transform interferometers (FT) a*nd laser spectrometers. The first provides wide spectral coverage but sacrifices resolution to maintain* signal to noise, while lasers can produce both high resolution and sensitivity but for only relatively small selected wavelength intervals. There are several methods for extracting spectroscopic information from the millimeter/sub-millimeter/THz and far-infrared spectral regions. The most comprehensive technique for spectral coverage is an extension of FT-IR in which the entire interferometer is operated under vacuum conditions. However, this technique is not nearly as sensitive as any approach that uses tuned oscillators (either fundamental or multiplied) since the source temperature of a tuned oscillator can be many orders of magnitude larger than a heat lamp. This is similar in principle to Laser Spectroscopy, however the bandwidth of the source is often better. Liquid helium-cooled detectors are common, but they provide poorer signal to noise than is achieved with near-IR detectors (e. g. InSb). Synchrotron sources hold great promise for general use throughout the electromagnetic spectrum [e.g. **8].**

At the longest wavelengths, cavity-enhanced methods which allow extended path lengths are currently limited to the millimeter to centimeter range where radiation can be coupled through electrical antennae. Therefore much of the millimeter and sub-millimeter is probed with 1-10 m path length multipass cells. The few Cavity RingDown Spectrometer (CRDS) type systems developed in the mm/submm/THz thus far suffer from massive injection losses. In the near-IR, the CRDS can cover wider spectral intervals than the typical Tunable Diode Laser systems, and much greater optical path lengths (5 km) are achieved using shorter chambers than is typical with interferometers coupled to multipass cells. More recently, techniques using mode-locked lasers matched to optical-cavity cells (i. e. cavity-enhanced, direct-comb spectroscopy) have simultaneously achieved wider spectral coverage, fast acquisition, and high signal to noise [**9-11**]. *Advancing the high sensitivity capabilities for laboratory studies over a wider range of wavelengths, particularly for the mid-IR, would enable experimentalists to characterize the weakest features arising in very high opacity atmospheres.*

*Funding agencies invest in better technologies for planetary applications, but the successful innovations should also be implemented for laboratory studies in order to supply the corresponding improved spectroscopic information.* Instead, the labs serve as test-beds for new technologies, but the resulting devices are left to die because the continuation funding is lacking. One example: early technology funding for the Herschel Space Telescope seeded the development of the photomixer in the late 1990's as a coherent and frequency-agile source of CW terahertz light [**12**]. This technology proved itself as a valuable laboratory tool for spectroscopy in the terahertz/sub-millimeter/far-IR [**13,14**], at the time a well known *gap region* in the E-M spectrum. However, lack of continued investment led to the shelving of this instrumentation.

Some problems in the spectroscopic information are nearly intractable and must be attacked with a range of spectroscopic techniques. Unfortunately, all the sophisticated instrumentation is rarely available to the researchers most familiar with the problem being addressed, and interpretation of existing laboratory spectra languishes for years (or decades in the case of near-IR $CH_4$, $NH_3$, $H_2S$…). In parallel to observatories, *supporting a network of staffed general user laboratory facilities* would be a relatively inexpensive way to advance these difficult studies.

**● Facilitate effective communication between laboratory providers and planetary users**

Traditionally, the essential interaction is expected to happen at conferences organized to bring the two groups together, but the alternative approach would be to *create a Web-based mechanism through which Laboratory Researchers and Planetary Scientists (observers and modelers) can continually communicate (i. e.* revive the *'Giver Newsletter').* Planetary astronomers could request specific new spectroscopic research. Laboratory providers could briefly showcase their new work as it became available, and they could learn what is important to study.

To implement this, personnel must be funded to create and operate an interactive Website. An interface would be needed to permit easy browsing; the functionality of the site could be determined through recommendations from both user and provider communities. Start-up costs: ¼ FTE to develop software and launch it; ¼ FTE to manage it, plus cost of computer facilities. A volunteer Committee could be established to provide feedback and guidance to program managers as to what future laboratory studies are important to support. Logistically, this task could be performed by the personnel managing a planetary database.

**● Prioritize spectroscopic data needs for planetary science**
**(determined periodically by consensus of users)**

Most planetary scientists can detail many specific shortfalls in current spectroscopic knowledge that seriously hinders or even prevents their ongoing research. In general, the present information is best (more complete and accurate) for already-detected species at frequently-utilized wavelengths. For example, extensive astrophysics research has led to good characterization of many species in the microwave region, while Earth and planetary missions have provided good information in the mid-infrared region for the common molecules composed of five atoms or less. *Many more serious deficiencies exist for heavier species and for the near – infrared in that parameters are missing and/or highly inaccurate for many important species.* The particular list of needs varies from planet to planet (or moon or comet etc…), but some ubiquitous species (e. g. $H_2O$, $CO_2$, $CH_4$, $H_2$, He, $N_2$, air) dominate the spectra of many planetary bodies; astronomers can make false detections or obtain corrupted abundance retrievals or be prevented from any analysis at all if the basic spectral parameters (positions, intensities, lower state energies, broadening coefficients) are not characterized through the full range of temperatures, abundances and pressures encountered in planetary bodies.

In high pressure atmospheres, the quality of the abundance retrievals depends directly on accurate knowledge of pressure-broadened line shape effects and their temperature dependences. Some theoretical models for calculating broadening parameters reproduce lab measurements to within experimental accuracies (2 to 25%), but for each species, the available shape measurements to validate the quantum mechanical calculations are very limited to just a relatively few (dozens or hundreds) stronger transitions. Moreover, recent investigations **[15]** demonstrate that Voigt shapes are inadequate, and other effects must be applied to interpret atmospheric spectra correctly (such as line mixing, speed dependence and Dicke narrowing). *More laboratory and theoretical studies are needed to provide the coefficients for the five dominant broadeners ($H_2$, He, $CO_2$, $N_2$, air) and for these important line shapes. The existing radiative transfer models (e. g. [**3**]) would then be modified to use a selection of line shapes and different broadeners to achieve proper analysis of planetary observations.*

***Finally, the recommendations here are presented in the context of Atmospheric Composition needs, but in fact they apply to many different planetary applications.***

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