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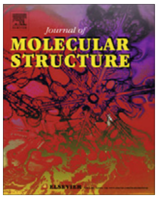

Terahertz spectroscopy for space applications: 2.5–2.7 THz spectra of HD, H_2O and NH_3

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ABSTRACT

At the Jet Propulsion Laboratory (JPL) a vibrant THz development program supports the construction of space-based spectroscopic instruments. The recent successes of the Aura's Microwave Limb Sounder (0.1–2.5 THz) and *Herschel's* Heterodyne Instrument for the Far-Infrared (0.5–1.9 THz) have demonstrated the wide range of molecular astro- and geophysics accessible when remote sensing from a space platform. With access to the THz spectral range these instruments readily observe the rotational spectra of small molecules, and the laboratory spectroscopy of these molecules is then utilized to convert the remote observation into physical quantities such as density and temperature. At the JPL millimeter and submillimeter spectroscopy laboratory we utilize the same technology developed for the space missions in order to make new or improved spectroscopic measurements that support these remote sensing objectives. By virtue of the improvements in technology these new measurements often result in improved structural understanding for the species of interest. We present an overview of the space applications and report a series of improved measurements in the 2.5–2.7 THz range obtained with our most recent hardware under development for sub-orbital/orbital astronomy.

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1. Introduction

The renaissance of far infrared spectroscopy, known today as terahertz spectroscopy, is revolutionizing our view of the universe. Part of the challenge of studying the terahertz (THz) domain is the strong absorption of this radiation in the ambient atmosphere. Therefore, space is the ideal location for sensing of THz radiation, and JPL has led this effort through development and deployment of remote sensing instruments operating at 0.1–2.5 THz. As part of this process the JPL molecular spectroscopy laboratory has improved, refined, or defined the current status of molecular spectroscopy in this frequency range. We present the most recent results of a 2.5–2.7 THz multiplier chain developed for remote sensing of the simplest heteronuclear diatomic, HD. With the laboratory's charter for studying molecules of interest to astronomy, earth and planetary science, we have surveyed the simplest, and most important, species with spectroscopic transitions in this region. These measurements include HD, NH_3 and H_2O. The accuracy of previous measurements was limited in some cases due to instrumental challenges, or lack of sensitivity. We discuss the improvements in our spectrometer which enable the best accuracy, and how these improvements will affect remote observations of these species. Additionally, we discuss the structural aspects of the spectroscopic measurements and how well *ab initio* theory predicts the positions of transitions of small molecules in the THz.

1.1. Astronomy

Light hydride molecules containing the more abundant elements (N, C and O) trace the first steps of interstellar chemistry. These species are often excellent probes of the interaction between atomic and molecular phases of the interstellar medium (ISM). Comprehensive studies of light hydrides require THz spectroscopy, which is difficult or impossible to accomplish from the surface of the Earth due to atmospheric absorption by water vapor. HD, NH_3, and H_2O represent three unique case studies. Observation of HD allows one to directly measure the total column of molecular hydrogen after assuming a D/H ratio. These observations are a science priority for the GREAT instrument on SOFIA. NH_3 was the first polyatomic molecule detected in the interstellar medium from its 24 GHz inversion band [1], but observation of the rotation-inversion transitions and sophisticated models are required to completely explain the non-thermal effects widely observed in its inversion spectrum [2]. Extraterrestrial water, with the exception of a few weaker lines, is nearly impossible to observe from the Earth's surface. Due to a number of space based observatories (ISO, Spitzer, SWAS, and Odin), H_2O is known to be one of the most abundant molecules in the universe. It often features complex line profiles, is rarely if ever in thermal equilibrium, and requires

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sophisticated models to explain its abundance and excitation [3,4]. Astronomical interpretation requires complete laboratory characterization of these species.

The first and most fundamental step in astronomical spectroscopy is the identification of the carrier of a spectral feature. The fundamental parameter is the transition frequency of the spectral line, which, once identified, allows the Doppler shift (red-shift) of the object to be precisely determined. Then the relative velocities of other lines can be studied identifying the carriers and obtaining information about the motions and chemistry along the line of sight. The next step is to determine the physical parameters of the observed object; this requires the transition strength and energy levels for determination of column density, excitation conditions and the role of the radiation field. The THz transitions of many light molecules are not in thermal equilibrium so the observed excitation is usually the result of a complex interplay between coupling to the radiation field, the effective translational temperature, density as a function of object structure, collisional excitation cross sections, and spontaneous emission. It is only with all these parameters that a full understanding of the fundamental exchange of energy in the object can be obtained.

The Heterodyne Instrument for Far Infrared (HIFI), developed by a consortium lead by Space Research Organization the Netherlands, required a radical technical departure from previous generations of submillimeter observational instruments in its bandwidth and operation [5]. The local oscillator for this instrument utilized a synthesizer as the fundamental source along with active multiplication utilizing solid state amplifiers in the 70–106 GHz range and passive multipliers utilizing GaAs Schottky diode technology [6]. The submillimeter wave advanced technology group at JPL designed a series of multipliers fulfilling the HIFI requirements for local oscillators at frequencies greater than 1.1 THz [7–15]. In HIFI local oscillators between 480 and 1272 GHz drive superconductor insulator superconductor mixers which down convert the astronomical spectrum to 4–8 GHz. Local oscillators between 1440 and 1903 GHz drive hot electron bolometer mixers down converting the astronomical spectrum to 2.4–4.8 GHz. Spectral analysis is accomplished in each polarization simultaneously with a 4 GHz bandwidth 1.1 MHz resolution acoustoptical spectrometer and a frequency selectable high resolution autocorrelation spectrometer with up to 134 kHz resolution [16].

The most dramatic early science result from HIFI has been its ability to detect and study a number of light hydride molecules that are both abundant and wide spread through the diffuse ISM. This includes a number of new detections for the diffuse ISM: OH^+ [17,18], H_2O^+ [17–19], H_2Cl^+ [20], SH^+ [21] and HF [22]. Additionally NH, NH_2 and NH_3 are found to be roughly in the same abundance [23]. Other fundamental science results include the first astronomical observations of the para water ground state transition [24,25], the first detections of the CH^+ ion in rotation [26] and observational estimates of the ortho-para ratio in water [27].

The diffuse medium was highlighted in initial results due to its low level of excitation resulting in absorption from ground states. However, the warmer denser phases of the ISM have yielded discovery of over 160 molecules and the spectra of dense clouds such as Orion KL [28] (see Fig. 1) will likely yield many more discoveries upon thorough examination. Data, such as those shown in Fig. 1 must be analyzed using knowledge of the molecular spectra to understand the local conditions. The graphic was chosen to illustrate the complexity of a spectrum of a relatively simple molecule, methanol. The correlation of the astronomical observation with a 300 K laboratory spectrum is surprisingly good and a direct comparison is shown in Fig. 1. Nevertheless, full characterization of the methanol excitation in the HIFI spectrum remains a work in progress. Despite the extensive global spectral analyses in recent years [29], which parameterized methanol spectra with up to two quanta of torsion, even more extensive analyses, such as with the 3*rd* torsional mode in Ref. [30], of the existing laboratory spectra are required to appropriately model the emission features observable in these complex molecular clouds.

THz astronomy requires quantitative spectroscopic information including (1) transition frequency, (2) lower state energy, (3) degeneracy of upper and lower states, (4) line intensity (sometimes referred to as oscillator strength), and (5) collisional cross sections for excitation by H_2. The first three of these quantities are typically derived from high precision measurements of spectral features that are analyzed quantum–mechanically. Transition frequency is reliably determined when a high-resolution line profile of the transition is obtained and compared to a frequency reference, usually by phase-locking the oscillator supplying the radiation to a known master oscillator or by counting the frequency relative to another high precision secondary standard. Line intensities of rotational transitions are usually calculated from 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 as long as centrifugal distortion of the dipole moment is negligible. Collisional cross sections are generally calculated from a full potential surface of the two colliding partners. This computationally involved process becomes very difficult in larger molecules or at higher temperatures, so many rates must be estimated. Experimental benchmarking of these calculations remains a work in progress.

1.2. Earth science

Spectroscopy has long served as a tool for probing the Earth's environment as well as performing controlled experiments. A focused combination of these methods at JPL has led to significant advances in remote and *in situ* earth science. Each of the myriad of available spectroscopic techniques has unique capabilities for environmental remote sensing; here we review efforts in THz spectroscopy.

THz spectroscopy has several advantages for probing the Earth system. These include: sensitivity to terrestrial emission which enables equivalent diurnal measurements; high sensitivity to radical species such as OH; line-of-sight measurement through cloud particles; and, due to the common origin (at zero frequency) of all rotational spectra, nearly all stratospheric species with electric dipoles are observable in the available spectral windows. The Earth-Observing-System, Microwave Limb Sounder (EMLS) [31] 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 basis for EMLS observation is spectrally resolved radiometric observations of the limb in front of the spacecraft's near polar orbit. With four 'GHz' bands (100–650 GHz), and one 'THz' band near 2.5 THz, this instrument has access to emission from the mesosphere, stratosphere, and upper troposphere. Products of EMLS include daily global maps of geopotential height and ozone profile, as well as global coverage of temperature, cloud ice density, and the following chemical species; O_3, H_2O, OH, HO_2, CO, HCN, N_2O, HNO_3, HCl, HOCl, ClO, BrO, SO_2, and CH_3Cl in various altitude ranges. EMLS sensitivity to chemical species is best in the stratosphere, where simultaneous measurements of chemically active and reservoir species provide tight constraints on global climate modeling. In the upper troposphere and lower stratosphere continuum blindness and increased cloud sensitivity hinder space-borne rotational spectroscopic remote sensing instruments. Much of the current research for EMLS is concentrated on analysis of this important region where pollution, weather, and climate interact. This extensive list of