ORAL SESSION n°9

« THz Spectroscopy & Spectrometers »

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Chaired by :

Dr. Neal Erickson & Dr. Wolfgang Wild

High resolution Terahertz spectroscopy of species of astrophysical interest

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Abstract—**We developed a high resolution Terahertz spectrometer relying on optically-pumped molecular lasers referenced to an absolute frequency standard and mixed with tunable microwave generators on Schottky diodes. The spectrometer is coupled to a cell for gas-phase production of light radicals, ions or floppy molecules that may be detectable with the future instruments Herschel, Sofia and ALMA. We observed the rotational spectrum of urea and of the isocyanic acid in the range of 875-901 GHz.**

Index Terms—**Submillimeter wave spectroscopy, Submillimeter wave lasers, Submillimeter wave technology, Schottky diode frequency converters, Frequency measurement**

I. Introduction

MOLECULAR lasers are powerful tools for high resolution terahertz spectroscopy. The approach used from a number of years to generate tunable Terahertz radiation is to couple fixed frequency laser with tunable microwawe to Scottky diodes and the resulting sidebands are reradiated and can be easily tuned by tuning the microwave source. For accurate spectral measurements, the laser frequency can be further referenced to an absolute frequency standard. We set up a sideband laser spectrometer in order to characterize the high amplitude motions of large flexible molecules (*e.g.* polycyclic aromatic hydrocarbons, prebiotic species) and the rotational spectrum of light radicals or molecular ions. These astrophysically relevant species may be detectable with the future instruments Herschel, Sofia and ALMA that will investigate the Terahertz Universe with high spectral resolution and sensitivity.

II. A Terahertz Molecular Laser Sideband Spectrometer

A. THz optically-pumped molecular laser

The carbon dioxide pump laser is a commercial device (Edinburg Instruments, model PL6) using a DC-discharge, flowing gas technology that delivers up to 200 W on the strongest lines. The CO_2 laser could be precisely tuned over some 100 rovibrationnal lines of the 9 μm and 10 μm bands using a grating in zero-order autocollimation and a piezoelectric transducer. The CO_2 laser pumps coaxially a lab-made Terahertz laser. The laser cavity consists of an input coupler for the CO_2 radiation and an output coupler for the Terahertz radiation, separated by a 2.7 m long, 38 mm diameter bore Pyrex tube which acts as a waveguide for both THz and CO_2 radiation. The input coupler is a flat gold-plated brass mirror with a 2 mm central pin-hole. The output coupler is a flat gold-plated brass mirror with 6 mm diameter central hole. It can be moved with a stepper motor in order to tune the cavity into resonance with the THz laser modes.

We operated the laser with HCOOH, CH_2F_2, CH_3OH, CH_3CH_2F as gain media, which provided more than 20 emission lines in the range 0.6-2.5 THz [1, 2] with power in the range 10-100 mW.

B. Mixing elements at terahertz frequencies

Non-linear mixing at terahertz frequencies has been demonstrated [3,4] with Schottky barrier diodes with ultra-high cut-off frequencies thanks to their femto-farad junction capacitance and low series resistance. We developed in our lab a triple-arm open mixing structure with whisker-contacted Schotky diodes using Virginia Diodes 1TXX diode chips. It allows mixing of THz radiation with microwaves coupled either through a coaxial Bias-Tee or a rectangular waveguide [5]. The lower part of a L-shaped whisker, defined by the bend of the whisker, contacts the sub-micron Schottky diode anode and acts as an antenna for THz radiation. A dihedral corner reflector positioned behind the antenna allows enhanced coupling of the laser beam at the diode. An off-axis parabolic mirror focuses THz radiation on the diode. Optimal coupling of a 4λ antenna mounted at 1,2λ from each face of the dihedral angle is reached when the waist size of the laser beam at the diode is w_0=1,28λ [6].

C. Frequency stabilisation system

The frequency accuracy of the measurement of the molecular lines depends on the frequency accuracy of the terahertz laser. Thermal drift of the THz laser cavity and the CO_2 laser cavity can induce a slow variation of the THz laser frequency. Locking the CO_2 laser frequency against the far-infrared emission lines [7], or against the CO_2 saturated fluorescence lines [8] - although the last technique provide better frequency stability of the CO_2 laser [9] - allowed to control the THz emission frequency via a Doppler pulling effect. Direct locking of the THz laser frequency against an absolute frequency standard was performed by heterodyne mixing of THz radiation with stabilised CO_2 lasers on point-contact MIM diodes in the frequency measurement chains [10], or by mixing of THz radiation with a harmonic of a microwave standard [11] that can lead to millihertz-level

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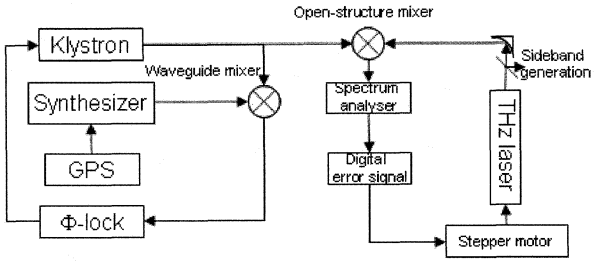

Figure 1: Frequency stabilisation system

spectral purity of the phase-locked THz laser when associated with pump laser frequency stabilisation [12].

For measuring Doppler-limited THz molecular lines with a Megahertz-level spectral linewidth, this phase-lock accuracy of THz molecular laser is not really necessary. We set up a THz laser stabilisation scheme, shown in Figure 1, for measuring THz laser against an absolute frequency standard (10 MHz signal from the Global Positioning System) and controlling its slow frequency drifts.

A 77-83 GHz klystron radiating 50 mW in a WR-12 waveguide is coupled, through a 3-port 20 dB directional coupler, to a harmonic mixer and heterodyned with the 8th harmonic of a microwave synthesizer referenced to the GPS. The intermediate frequency signal at 320 MHz is separated by the DC bias signal, filtered (bandwidth 10 MHz) and amplified with a broadband LNA and shows a typical signal at 30 dB above noise (RBW 1 kHz) that allows efficient phase-locking of the klystron to the synthesizer harmonic. The main line of the directional coupler goes though a power attenuator to the waveguide input of our THz mixer using a 1T12 Schottky diode. THz laser radiation is heterodyned with successive harmonics of the klystron and the intermediate frequency at 525 MHz is extracted through the Bias-Tee coaxial coupling of the mixer, filtered and amplified. Thanks to high LO power, the beatnote is detected with a small fraction of THz laser radiation (providing typical 20 mV video response of the Scottky diode biased at 0,7 V) which is extracted with our optical setup (Figure 2) by convenient adjusting of the waveplate, while the essential of the laser power is used for sideband generation.

The beatnote recorded on 1-s timescale (Figure 3) with 889 GHz laser line shows a 5 kHz FWHM linewidth that demonstrates high intrinsic spectral purity of our THz laser. The beatnote recorded with 1838 GHz laser line shows a broader linewidth (75 kHz FWHM) that could be associated

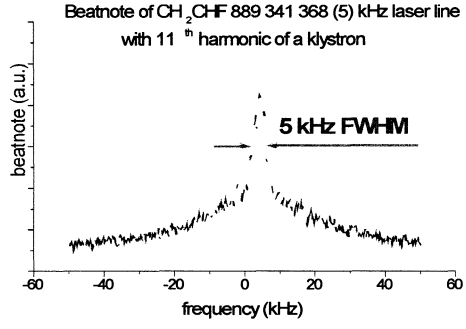

Figure 3: Spectral purity of the free-running THz molecular laser

to increased phase noise due to high harmonic frequency multiplication or specific phase noise of the pump laser induced by the optical feedback from THz laser cavity.

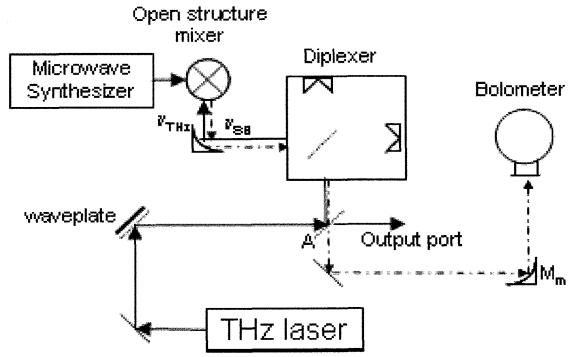

Figure 2: Optical setup of sideband generation. A: wiregrid analyser, M_m movable mirror. The Output port is used either for frequency stabilisation of the laser or for power calibration by conveniently aligning M_m

The free-running laser shows slow frequency drifts up to 400 kHz over 10 minutes with up to 40 kHz rms. The offset between the beatnote frequency and 525 MHz is recorded by a computer that generates a digital error signal with 1 s integration time and drives the stepper motor that control the laser cavity length. The frequency stability of the locked laser is better than 40 kHz rms over an hour that demonstrates efficient correction of slow frequency drifts.

D. Sideband generation and bolometric detection

The terahertz optical system allowing sideband generation is shown in Figure 2. It makes use of low dispersion polarising or reflecting optics that ensures broadband operation of the spectrometer.

The laser beam with linear polarisation impinges on a wire-grid polarizer which is rotated at 45° to the vertical direction and backed by a plane metallic mirror fixed on a micrometer translation mount. This device acts as a reflective waveplate and allows modifying continuously the laser polarisation from vertical to horizontal by adjusting the distance between polarizer and the mirror.

Vertically polarized THz radiation is reflected by a wire-grid polarisation analyser to a Martin-Puplet diplexer [13] which is essentially a Michelson interferometer with a polarisation-dependent beamsplitter (a wire-grid polarizer rotated at 45° to the vertical direction), two rooftop dihedral metallic reflectors and a Schottky diode mixer. The mixer preferentially couples vertically polarised radiation to the diode. The re-radiated power by the mixer at ν_{THz} is coupled through the same optical path in the diplexer as the incoming laser beam and is reflected back to the laser. The sidebands emitted at $\nu_{THz}+\nu_{MW}$ undertake a different phase change in the interferometer, thus a different polarisation status when reaching the analyser. If L is the pathlength difference and there are m,n integers such as: $2L = 2m\lambda_{THz} = (2n+1)\lambda_{SB}$, sidebands emerge with a polarisation crossed to the polarisation of the incoming laser and are transmitted through the analyser. If $\nu_{THz} >> \nu_{MW}$, the previous condition can be meet accurately when $L=\lambda_{MW}/2$ and both sidebands are extracted from the diplexer with equal efficiency.

We operated the sideband generator with a 2-20 GHz synthesizer coaxially coupled to the diode through a Bias-

Tee and with guided-wave in the range of 50-110 GHz from Militech active multipliers.

This system allow in principle very efficient separation of the sidebands from the laser power. Non-ideal operation

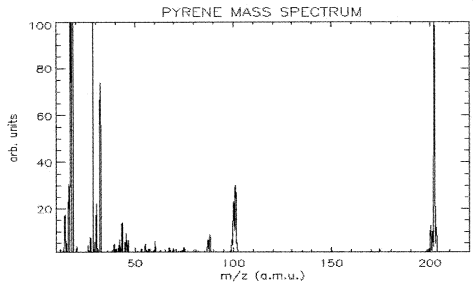

Figure 6: Mass-spectrum of laser-ablated pyrene

with low separation efficiency appear when polarisation state of the laser is changed, that obviously come out when incoming laser beam is reflected back by the corner cube of the antenna. However, one can precisely discern the part of sidebands in the radiation transmitted by the analyser by applying, for example, 100% full amplitude modulation of the RF power on the synthesizer that drives the mixer and using a lock-in detection scheme.

We performed a direct measurement of the efficiency of sideband generation. A QMC bolometer is used as detector providing a linear response for THz power up to a mW level with the calibration data granted by the manufacturer. The analyser, fixed in a kinematic mount, was removed and incoming laser radiation was focused with a movable mirror directly on the bolometer. That allowed us to estimate the THz laser power $P_{laser} = V_{laser} / S$ from the bolometer voltage response V_{laser} and its responsivity S. The pressure of the lasing gas and the current of the DC-discharge of the CO_2 laser were lowered providing a THz laser emission at a mW level that doesn't saturate the bolometer response. We set up the analyser afterwards and we aligned the movable mirror in order to focus on the bolometer the radiation exiting the diplexer. The AM detection technique allowed us to estimate the power in one sideband

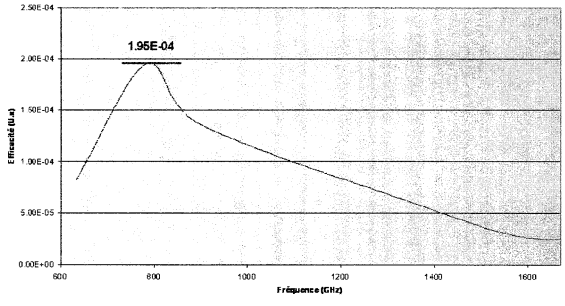

Figure 4: Sideband generation efficiency

$P_{SB} = V_{SB} /(S.C_{AC-DC}.C_{SSB})$ where V_{SB} is the lock-in output voltage and the last conversion factors, equals to 2, are determined by the AC to DC signal processing with the lock-in and by the detection of both sidebands.

Figure 4 shows the values of the sideband generation efficiency for different laser lines. We used an 1T21 Schottky diode biased at 0,7 V. The mixer was driven at 4 GHz with a synthesizer providing 8 dBm of microwave power. The diplexer pathlength was optimised for each laser line as well as the optical alignment of the corner cube mixer. The mixer has broadband operation, while the best sideband generation efficiency, that is around 2.10^{-4}, is reached on the 783 GHz laser line. Its wavelength corresponds to a quarter of the 1.6 mm whisker-antenna that allows optimal coupling of the laser power to the mixer. When the synthesizer that drives the mixer is swept from 2 to 20 GHz, the optimal values of sideband generation efficiency do not vary more that 15% of the listed values, that point out efficient broadband coaxial coupling of the microwaves to the diode. The sideband generation efficiency is typically one order of magnitude lower with a less efficient waveguide-coupling of 50-110 GHz microwaves to the mixer.

The detector is a two-channel QMC InSb cyclotron-resonance assisted hot electron bolometer with an improved spectral response up to 3 THz. The manufacturer specified a responsivity S=4230 V/W and a noise-equivalent power NEP=2 pW.Hz$^{-1/2}$. These values determinates the sensitivity of the spectrometer since the THz power level is not enough strong in order to overcome the detector noise. Absolute power calibration of the 783 GHz laser line [14] allow us to estimate the maximal sideband power at 10 μW, thus the minimum detectable fractional absorption of the spectrometer is 2.10^{-7}. This value neglect specific baseline problems of the THz spectrometer setup – the coupling of the sidebands to the THz laser cavity and the power

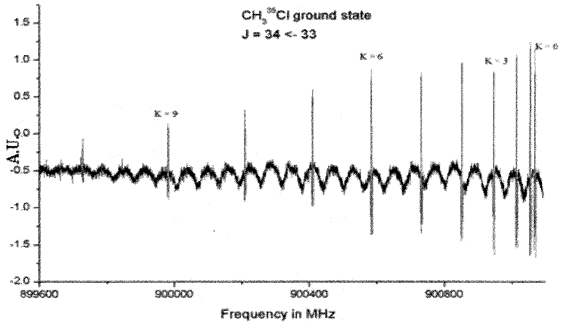

Figure 5: Fine structure of a rotational line of CH_3Cl

fluctuations of the CO_2 laser, induced by optical feedback – that could limit the ultimate sensitivity of the spectrometer.

The system allows broadband scans for molecular lines, improving the previous heterodyne detection scheme [2]. Figure 5 shows a rotational spectrum of the ground state of methyl chloride, a key-molecule for aeronomy that was studied extensively in our group [15 and references therein]. The spectrum shows the K rotational structure of J:34<-33 line over 1,2 GHz that was recorded with excellent SNR with 100 ms acquisition time per point in 10 minutes, using a frequency-modulation technique of the sidebands and 2-f lock-in detection. The spectrum baseline is determined by interference fringes in the 3 m long absorption cell.

III. Gas-phase production of astrophysically relevant molecules

We have coupled to the spectrometer a new cell for the gas-phase production of molecules that are astrophysically

relevant for the observation missions of the Terahertz Universe. A quadrupole mass spectrometer (Pfeiffer-QMG422, mass range 1-512 a.m.u.) in a differentially-pumped vacuum chamber is used to monitor the composition of gas-phase generated neutral or ionised species.

The laser desorption/ablation technique allows us to study a large range of species having low vapor pressure and/or which decompose or polymerize upon heating. The desorption of solid samples (pellets of thin films) is realized with a 10 ns Q-switched Nd:Yag laser wich delivers 4-25 mJ at 1064 nm and its 532, 355, 266 nm harmonics. This set up has been tested on different species such as pyrene, glyceraldehyde, urea. The pyrene mass spectrum shown in Figure 6 has been obtained using the 2nd harmonic at 532 nm at maximum laser energy (25 mJ) with a repetition rate of 15 Hz.

The supersonic beam technique allows the production of intense cold molecular samples from the adiabatic expansion through a nozzle. Our setup uses a 1 mm diameter pulsed-nozzle with two stainless steel electrodes placed directly in the front of the nozzle that allow operating a high-voltage discharge of the molecular beam. Light hydrides, like OH [16], or molecular ions, which are the tracers of the ISM chemistry, will be investigated with this setup.

IV. The Terahertz spectrum of urea

Urea is a prebiotic molecule of astrophysical interest. It is involved in the formation of pyrimidines which have been detected in the Murchinson meteorite [17]. Urea have been temptatively detected in icy grains [18] by comparison of the laboratory spectrum of VUV photolysed HNCO and NH_3/H_2O ice mixture with spectroscopic observations from ISO at 6 μm of the protostellar object NGC7538IRS9. Urea could then be released to the gas phase via thermal desorption. Urea rotational transitions might thus be detected in the gas phase around protostars.

The rotational spectrum of urea and its isotopic species in their groud vibrationnal state have been studied in the 8-19 GHz frequency range [19,20]. Recent measurements was performed in the millimeter-wave range at the Institute of Radio Astronomy (Kharkow, Ukraine) around 200 GHz [21]. These results allowed us to predict the urea spectrum in the 870-910 GHz range with an accuracy better than 30 MHz.

The detection of the Terahertz absorption spectrum of urea ablation plume is challenging because of the ultra-low density of the molecular population in a specific rotational level and the direct detection scheme which is used.

To overcome this problem we have heated urea in a temperature-stabilised brass oven coupled to the cell. The pressure in the cell was typically 5.10^{-2} Pa when the oven was maintained at 373 K. The spectrum shown in Figure 7, recorded with 1 s acquisition time per point, displays two near-resonant transitions where one may be due to urea while the other is most probably a line of the isocyanic acid (HNCO), an urea thermal decomposition product. We measured many HNCO lines that are shifted up to 6 MHz from the predicted line frequencies provided by the JPL molecular spectroscopy database [22]. A new analysis of the spectroscopic constants taking into account our

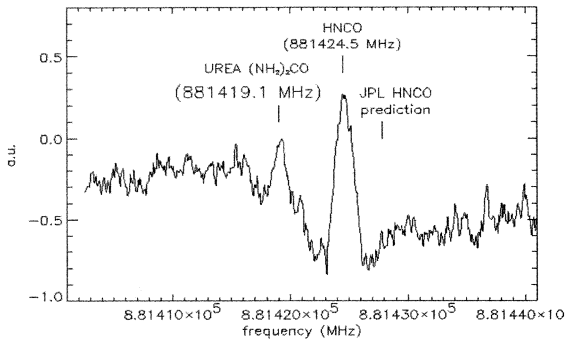

Figure 7: Absorption lines of urea and HNCO

measurements should improve the accuracy of the prediction of HNCO Terahertz spectrum. Further work for increasing the efficiency of urea gas-phase generation, by avoiding its condensation on the cold walls of the cell and its thermal decomposition, will allow the measurement of other terahertz urea lines.

Acknowledgment

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References

[1] N. G. Douglas, *Millimeter and Submillimeter Wavelength Lasers.* New York: Springer-Verlag, , 1989.

[2] D. Boucher, R. Bocquet, J. Burie, W. Chen, "A far-infrared heterodyne sidebands spectrometer," *J Phys. Ill France*, vol. 4, pp. 1467, 1994

[3] H. R. Fetterman, P. E. Tannenwald, B. J. Clifton, W. D. Fitzgerald, N. R. Erickson, "Far-ir heterodyne radiometris measurements with quasioptical Schottky diode mixers," *Appl. Phys. Lett.*, vol. 33, pp. 151, 1978

[4] D. D. Bicanic, B. F. J. Zuidberg, A. Dymanus, "Generation of continuously tunable laser sidebands in the submillimeter region," *Appl. Phys. Lett.*, vol. 32, pp. 367, 1978

[5] L. Margulès, L. F. Constantin, "Spectroscopie Térahertz en phase gazeuse," *Revue de l'Electricité et de l'Electronique*, Dossier Les ondes Térahertz , vol. 1, pp. 50, 2003; H. Krautle, E. Sauter, G. V. Schultz, *Infrared Phys,*.v ol. 18, pp. 705, 1978

[6] E. R. Mueller, J. Waldman, "Power and Spatial Mode Measurements of Sideband Generated, Spatially Filtered, Submillimeter Radiation," *IEEE Trans. MTT*, vol. 42, pp. 1891, 1994

[7] C. R. Pidgeon, W. J. Firth, R. A. Wood, A. Vass, B. W. Davis, "Two-Photon Light Shift and Autler-Townes Splitting in Optically-Pumped FIR Lasers," *Int. J. IR MMW*, vol. 2, pp. 207, 1981

[8] C. Freed, A. Javan, "Standing-wave saturation resonances in the CO_2 10.6 μm transitions observed in a low-pressure room-temperature absorber," *Appl. Phys. Lett.* 17, pp. 53, 1970

[9] B. Frech, L.F. Constantin, A. Amy-Klein, O. Phavorin , C. Daussy, C. Chardonnet, M. Mürtz, "Frequency measurements of saturated-fluorescence-stabilized CO_2 laser lines: comparison with an OsO_4-stabilized CO_2 laser standard," *Appl. Phys. B*, vol. 67, pp. 217, 1998

[10] G.D. Rovera, O. Acef, "Absolute frequency measurement of mid-infrared secondary frequency standard at BNM-LPTF," *IEEE Trans. Instr. Meas.*, vol. 48, pp. 571, 1999

[11] T. Sakurai, "Frequency Stabilization of CH_3OH Laser at 469 μm to Millimeter-Wave Standard," *Japanese Journal of Applied Physics*, vol. 25, pp. 124, 1986

[12] G.D. Rovera, "Low frequency noise optically pumped FIR laser with frequency stabilized pump," *Opt. Comm.*, vol. 143, pp. 247, 1997

[13] D. H. Martin, E. Puplett, "Polarised interferometric spectrometry for the millimeter and submillimeter spectrum," *Infrared Phys.*, vol. 10, pp. 105, 1969

[14] W. Chen, "Techniques d'hétérodynage dans l'infrarouge lointain. Quelques applications en spectroscopie de rotation," Ph.D. dissertation, USTL, Villeneuve d'Ascq, 1990

[15] L. F. Constantin, J. Demaison, L. Féjard, M. Litz, H. Bürger, P. Pracna, "Rovibrational and rotational spectroscopy of the v_2=1, v_5=1 and v_3=2 levels of $^{13}CH_3{}^{37}Cl$," *Mol. Phys.*, vol. 102, pp. 1717, 2004
[16] H.J. Lewandowski, E. R. Hudson, J.R. Bochinski, Jun Ye, "A pulsed, low-temperature beam of supersonically cooled free radical OH molecules," *Chem. Phys. Lett.*, vol. 395, pp. 53, 2004
[17] P. G. Stock, A. W. Schwartz., "Nitrogen-heterocyclic compounds in meteorites: significance and mechanisms of formation," *Geochim. Cosmochim. Acta*, 45, pp. 563, 1981
[18] S. Raunier, T. Chiavassa, F. Duvernay, F. Borget, J.P. Aycard, E. Dartois, L. d'Hendecourt, "Tentative identification of urea and formamide in ISO-SWS infrared spectra of interstellar ices," Astronomy&Astrophysics, vol. 416, pp. 165, 2004
[19] U. Kretschmer, D. Consalvo, A. Knaack, W. Schade, W. Stahl, H. Dreizler, "The ^{14}N quadrupole hyperfine structure in the rotational spectrum of laser vaporized urea observed by molecular beam Fourier transform microwave spectroscopy" *Mol. Phys.*, vol. 87, pp. 1159, 1996
[20] S. Kassi, D. Petitprez, G. Wlodarczak, "Microwave spectrum of isotopic species of urea $(NH2)_2CO$," *J. Mol. Spec.*, vol. 228, pp. 293, 2004
[21] E.A. Alekseev, private communication
[22] http://spec.jpl..nasa.gov/