

PRELIMINARY WORK TO ALMA, HERSCHEL, SOFIA: SUBMILLIMETER WAVE SPECTROSCOPY OF COMPLEX ORGANIC MOLECULES

L. Margulès¹, M. Goubet¹, R. Motiyenko¹, S. Bailleux¹, T.R. Huet¹ and G. Wlodarczak¹

Abstract. Laboratory analysis of the microwave and millimeter-wave spectra of potential interstellar molecules is a prerequisite for their subsequent identification by radioastronomical techniques. The spectral analysis is used to obtain spectroscopic parameters that are used in the assignment procedure of the laboratory spectra, as well as to predict with a high degree of precision the frequencies of transitions not measured in the laboratory.

Keywords: identification, data analysis, laboratory, observational, molecules, submillimeter

1 Isotopic species of a major weed : Methyl Formate

1.1 Introduction

This huge effort of gathering spectroscopic data is nowadays still pursued in order to prepare the future large sub-millimeter facilities like the ground-based ALMA (Atacama Large Millimeter Array) and the Herschel space observatory. It is expected that the high sensitivity and angular resolution reached by the instruments in these facilities combined with very precise spectroscopic analysis will provide accurate information about the formation of stars in the interstellar molecular clouds.

The astrophysical study of other molecular isotopologues of methyl formate is important for several reasons. First it gives access to the isotopic abundance in astronomical environments. Second it allows the astronomers to discriminate in their surveys the transition lines due to the isotopologues and eventually eliminate them to be able to discover new species. Indeed the upcoming ALMA and Herschel sub-mm facilities will provide large amounts of high precision ($\Delta\nu \leq 1\text{MHz}$) spectroscopic data in the wavelength range down to $150\mu\text{m}$ (corresponding to 2 THz in frequency). The interferometric operation of ALMA, in addition, will provide a so far unprecedented spatial resolution and a sensitivity which reaches the limit of line confusion. Both HIFI/Herschel and ALMA focus on dense clouds with young stars and surrounding material that contain molecular species with numerous and strong transitions throughout the whole sub-mm region. Much of the line emission comes from known species, such as methyl formate and similarly complex molecules. Without spectral identifications, however, the resulting forest of spectral lines will seriously hinder the detection and analysis of new molecular and radical species. This problem is known as the 'Weeds and Grass problem'. For an optimal science exploitation of ALMA and Herschel it is necessary to cut down the weeds and to recognize the grass. Methyl formate and its isotopologues are classified as "weed, class I" species due to their abundance in observations. Third, the observation of isotopologues transitions is needed to derive correct column densities for abundant molecules exhibiting optically thick lines, which could be the case for methyl formate in some hot cores.

This is why we decided in Lille, to do the systematic studies of all the mono-isotopic species of methyl formate.

1.2 Experiment

All the isotopic species were measured from 2 to 660 GHz using different spectrometers. These new measurements were fitted together with those from the literature. Rotational spectra in the 4-20 GHz spectral range

¹ Laboratoire PhLAM, CNRS UMR 8523, Université de Lille1, 59655 Villeneuve d'Ascq Cedex, France

were recorded using a molecular beam microwave Fourier transform spectrometer in Lille. The accuracy of frequency measurements is estimated to be better than 3 kHz. The rotational spectrum was studied in the range 8-80 GHz using the Oslo Stark spectrometer, the accuracy of the spectral measurements is about 0.1 MHz for isolated lines.

Concerning the millimeter-submillimeter wave measurements: in the frequency range 580-660 GHz a Russian Istok backward wave oscillator (BWO) is used. It is phase locked to a harmonic of Agilent E8257D synthesizer which provides in our design large-step (~ 30 MHz) frequency control. High-resolution frequency scan is provided by tuning a reference source of BWOs PLL: HP 3325 synthesizer. In the lower frequency range (150-525 GHz), solid state frequency multipliers are used as a source of radiation. The frequency of the Agilent E8257D synthesizer is first multiplied by six and amplified with a Spacek active sextupler. Then we used passive Schottky multiplier (x2, x3, x5) from Virginia Diodes Inc. In order to minimize frequency determination errors, all the reference synthesizers are locked on a GPS signal. The detector is an InSb liquid He-cooled bolometer from Queen Mary College. In order to improve the sensitivity of the spectrometer the sources are frequency modulated at 10 kHz and lock-in detection with the second harmonic is used. The absorption cell is a stainless steel tube (6 cm diameter, 220 cm length), the pressure used during measurements is 2.6 Pa (26 bar).

We are replacing our old BWO's sources with a multiplier chain based on solid state sources. As shown in Fig. 1, these sources are more compact, easier to use, and we have a larger frequency coverage. We could increase the number of measured lines. The spectroscopic parameters are better determined, so the prediction we make are more reliable. The tests we did are very positive in the lower part of the range (150-525 GHz). Our project is now to increase the frequency of the chain up to 1 THz.

1.3 Theoretical model

Like many others complex organic molecules, methyl formate exhibits large amplitude motion. The assignment and analysis of the spectra is not obvious. Here, it is the internal rotation of the methyl group around the rest of the molecule. As the molecule is light and as the barrier to internal rotation is not so high ($V_3 \approx 389$ cm $^{-1}$ for the normal species), the internal rotation splittings are relatively large, reach values up to a few MHz in the torsional ground state, and the transition frequencies are thus difficult to calculate with accuracy, especially at high J values, without appropriate theory.

We will not go too much into details about the theory in this paper. The description of the theory used could be found in (Carvajal et al. 2009; Margulès et al. 2009) respectively for the symmetric and asymmetric methyl rotor. The need of different theories could be seen in the Fig. 2. The potential energy function is a three fold potential in the case of symmetric CH $_3$ rotor. With a partial deuteration of the methyl group (CH $_2$ D or CHD $_2$) this leads to an effective potential energy function which no longer displays threefold. The spectra observed will also be different.

Concerning the symmetric case, each rotational line is split into a doublet (characterized by the symmetry labels A and E). Concerning the asymmetric rotor, there are three lines: one due to the in-plane conformer, and two others due to the internal rotation splitting for the two equivalent out of plane conformers

1.4 Results

The studies about the isotopic species are finished. The results are published for H 13 COOCH $_3$, HCOO 13 CH $_3$ (Carvajal et al. 2009), DCOOCH $_3$ (Margulès et al. 2010), and HCOOCH $_2$ D (Margulès et al. 2009) species. About the HC 18 OOCCH $_3$, HCO 18 OCH $_3$ and HCOOCHD $_2$, the manuscript are in preparation. The theoretical models used reproduce very efficiently the measurements. Despite the fact that we could reach high quantum numbers values (J up to 70). The H 13 COOCH $_3$, HCOO 13 CH $_3$, and DCOOCH $_3$ were detected without ambiguity in ORION (B. Tercero, N. Marcelino and J. Cernicharo, CSIC-INTA, Madrid, Spain).

1.5 Conclusion

All the mono-substituted isotopic species of a major weed were studied. Due to these new studies more than 500 lines were identified in Orion.

Solid state sources: 150 - 525 GHz

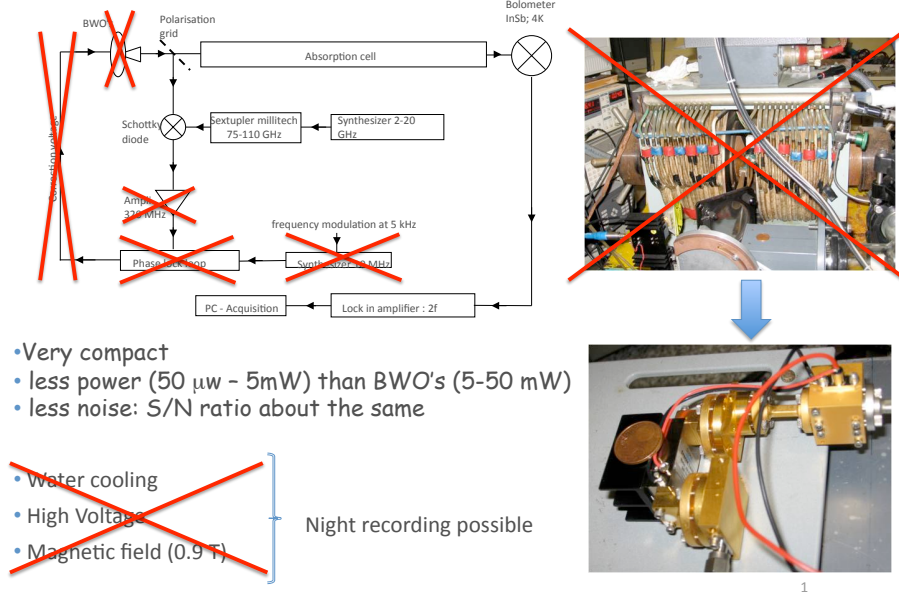


Fig. 1. Potential energy function of methyl formate

Internal rotation in Methyl Formate

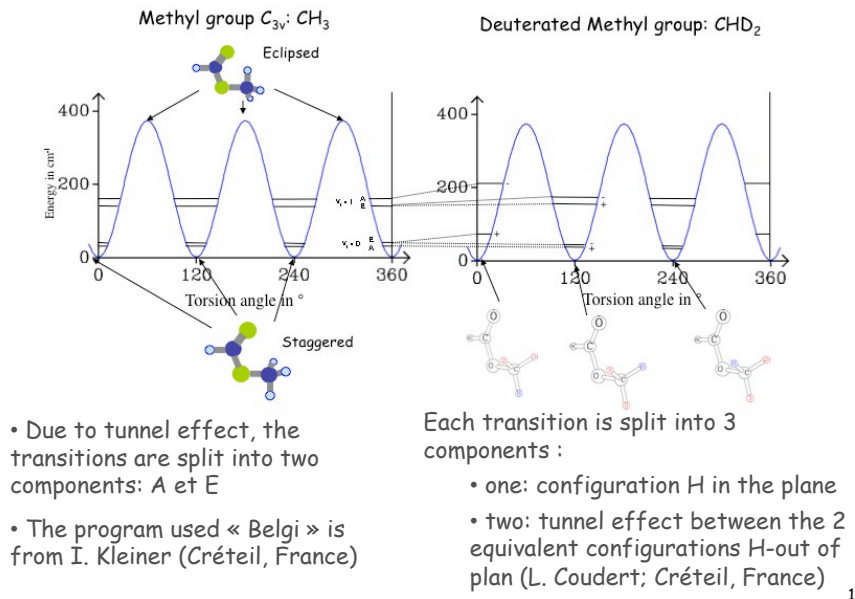


Fig. 2. New solid state submillimeter wave spectrometer in Lille

2 Jet-Ailes

"Jet-AILES" is a consortium including researchers from the PhLAM at Lille 1 University (T. Huet and M. Goubet), the IPR at Rennes 1 University (R. Georges), the LADIR at Paris VI University (P. Asselin and P. Souillard) and the AILES beamline at the SOLEIL synchrotron (O. Pirali and P. Roy). The objective is to take advantage of the brightness of the synchrotron radiation source in the FIR region (Roy et al. 2006) to probe a supersonic expansion. There are two main interests of such a set-up. Firstly, molecules and molecular complexes prepared in a supersonic jet are observed in the gas phase at very low temperature (few tenths of Kelvin) in a very low density environment (of the order of 10^{-10} cm⁻³). Secondly, Signals of large amplitude motions and typical signatures of COMs and hydrogen bond complexes lie in the FIR region. Technically the synchrotron radiation coming from the high resolution spectrometer of the AILES beamline (Bruker IFS125-HR) is transferred to the expansion chamber by bare gold mirrors. Then, a planar expansion is probed by a multi-reflections optical device called SORM (acronym for "Système Optique Rflexions Multiples") (Gross et al. 1989). Finally, the IR beam is redirected to various detectors depending on the studied region (a Si bolometer in the FIR, a MCT photovoltaic detector in the MIR and a InSb detector in the NIR). To our knowledge, it is the unique supersonic jet device successfully coupled to a synchrotron radiation source in the FIR region. Although the set-up is still under optimization, some encouraging results have already been obtained. The Q branch of the out-of-plane bending mode of methylformate, centered at 331 cm⁻¹, has been observed. This detection highlights the good sensitivity of the experiment since the vaporization conditions were not optimal and its calculated intensity is only of about 20 km.mol⁻¹. A high resolution ($2.5 \cdot 10^{-3}$ cm⁻¹) spectrum of (CO₂)_m ($m \leq 5$) complexes as well as a medium resolution (10^{-2} cm⁻¹) spectrum of CO₂-(H₂O)_n ($n \leq 4$) complexes has been recorded for the first time in the ν_3 of CO₂ spectral range (2350-2360 cm⁻¹). Bands of the perturbed OH stretching mode (around 3550 cm⁻¹) of ether-H₂O complexes, ethers being (CH₂)₂O and (CH₃)₂O, have been observed. According to the difficulty in forming small hydrated aggregates, these results show the good efficiency of the adiabatic expansion. Forthcoming runs of experiments will focused on the study of the FIR spectrum of glycolaldehyde and its hydrated complex as well as acetic acid and its dimer. Both molecules are stable isomers of methylformate and are also astrophysically relevant.

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