

PROSPECTIVE WORK FOR ALMA, HERSCHEL, SOFIA: SUBMILLIMETER-WAVE SPECTROSCOPY OF COMPLEX ORGANIC MOLECULES

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Abstract. Laboratory analysis of spectra of potential interstellar molecules from the radio-frequency to the THz range is a prerequisite for their subsequent identification by radioastronomical techniques. The spectral analysis allows us to derive molecular parameters that are able to model the frequency and intensity patterns of the transitions, as well as to predict with a high degree of precision the frequencies of transitions not measured in the laboratory.

1 Introduction

This paper summarizes the recent results obtained in Lille on the laboratory spectroscopy of the most abundant isotopologues species of methyl formate and glycolaldehyde, two isomers of $C_2H_4O_2$. We mainly focus on the experimental devices. The astrophysical study of molecular isotopologues of complex organic molecules is important for several reasons. First it gives access to the isotopic abundances 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 the present Herschel sub-mm facilities will provide large amounts of high precision ($\Delta\nu \leq 1$ MHz) spectroscopic data in the wavelength range down to $150 \mu\text{m}$ (or up to 2 THz). The interferometer 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 provide a wealth of data 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

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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 Flowers problem”. For an optimal science exploitation of ALMA and Herschel it is necessary to cut down the weeds and to recognize the flowers. Methyl formate and its isotopologues are classified as “weed, class I” species due to their abundance in observations. Third, the observation of isotopologue 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.

2 Experiment

2.1 Microwave spectroscopy

A new molecular beam Fourier Transform Microwave spectrometer has been developed in Lille (Tudorie *et al.* 2011). The main improvement of the present experimental setup over the old one (Kassi *et al.* 2000) is an increase of the mirrors diameter from 0.4 to 0.7 m leading to an improved signal-to-noise ratio at low frequencies and to less diffraction losses. Signals can be recorded in the 2 – 20 GHz spectral region. The sample vapors at a pressure of about 10 mbar are mixed with neon carrier gas at a backing pressure of 1 – 2 bar. The mixture is introduced into a Fabry-Perot cavity at a repetition rate of 1.5 Hz. Molecules are polarized within the supersonic expansion by a 2 μ s pulse generated by an Agilent E8257D synthesizer and the free induction decay signal is detected and digitized at a repetition rate of 120 MHz. After transformation of the time domain signal, molecular lines are observed as Doppler doublets, with a signal point every 0.46 kHz corresponding to a data accumulation of 2^{18} points. Each average spectrum is obtained by coadding about 100 – 1000 signals. Transition frequencies are measured as the mean value of the two Doppler components and for most lines the uncertainty of the measurements is estimated to be less than 1 kHz. The Doppler width is a few kHz.

2.2 Millimeter-wave and submillimeter-wave spectroscopy

The millimeter- and submillimeter-wave measurements (75 – 990 GHz) are mainly performed using the Lille spectrometer based on solid-state sources (Motiyenko *et al.* 2010). The frequency of an Agilent synthesizer E8257D (12.5 – 18.4 GHz) is first multiplied by six and amplified by a Spacek active sextupler, providing an output power of +15 dBm in the W-band range (75 – 110 GHz). This power is high enough to use passive Schottky multipliers ($\times 2$, $\times 3$, $\times 5$, $\times 3 \times 2$, $\times 3 \times 3$) from Virginia Diodes Inc. in the next stage of the frequency multiplication chain. As a detector we use an InSb liquid He-cooled bolometer from QMC Instruments Ltd. To improve the sensitivity of the spectrometer, the sources are frequency modulated at 10 kHz and phase-sensitive detection at 2f is employed. The absorption

cell is a stainless-steel tube (6 cm diameter, 220 cm long). The sample pressure during measurements is about 2 Pa and the linewidth is limited by Doppler broadening. Measurements are performed at room temperature. The accuracy of the measurements for isolated lines is estimated to be better than 30 kHz. However, if the lines are blended or have a poor signal-to-noise ratio, they are given a weight of 100 kHz.

3 Theoretical models

Like many others complex organic molecules, methyl formate exhibits large amplitude motion, *i.e.* the internal rotation of the methyl group with respect to the molecule. As the molecule is light and as the barrier to internal rotation is moderate ($V_3 \approx 389 \text{ cm}^{-1}$ for the normal species), the internal rotation splittings are relatively large, and reach values up to a few MHz in the torsional ground state. Therefore an appropriate theory is needed to model and calculate with accuracy the transition frequencies, especially at high J values. Also the assignments and analysis of the spectra are not obvious.

The description of the theories used for modeling our spectra can be found in (Carvajal *et al.* 2009) and (Margulès *et al.* 2009) respectively for the symmetric (CH_3) and asymmetric (CH_2D or CHD_2) methyl rotor.

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

Glycolaldehyde is an asymmetric top containing an hydroxyl (OH) group, which is stabilized by an intramolecular hydrogen bond. Therefore any spectrum can be modelled with a set of molecular parameters containing the principal rotation constants, and centrifugal distortion parameters, up to the octic terms.

4 Results

4.1 Laboratory spectroscopy

Concerning methyl formate, several isotopologues have been characterized in our Laboratory. The $\text{H}^{13}\text{COOCH}_3$, $\text{HCOO}^{13}\text{CH}_3$ (Carvajal *et al.* 2009), DCOOCH_3 (Margulès *et al.* 2010), $\text{HC}^{18}\text{OOCH}_3$, $\text{HCO}^{18}\text{OCH}_3$ (Tercero *et al.* 2012), HCOOCH_2D (Margulès *et al.* 2009), and HCOOCHD_2 (Coudert *et al.* 2012) ground state spectra have been analyzed and modeled with high accuracy, in order to predict any transition frequency within 100 KHz.

Concerning glycolaldehyde, we have measured the spectra of deuterated isotopologues in the laboratory: the three mono-deuterated ones ($\text{CH}_2\text{OD-CHO}$, CHDOH-CHO and $\text{CH}_2\text{OH-CDO}$) and one dideuterated derivative (CHDOH-CDO) in the ground vibrational state (Bouchez *et al.* 2012).

4.2 Detection in Orion

Several isotopologues species of methyl formate have been detected in the interstellar medium so far. Indeed the $\text{H}^{13}\text{COOCH}_3$, $\text{HCOO}^{13}\text{CH}_3$ (Carvajal *et al.* 2009), DCOOCH_3 (Margulès *et al.* 2010), $\text{HC}^{18}\text{OOCH}_3$, and $\text{HCO}^{18}\text{OCH}_3$ (Tercero *et al.* 2012) species have been detected toward Orion KL (B. Tercero, N. Marcelino and J. Cernicharo, CSIC-INTA, Madrid, Spain).

5 Conclusion

The PhLAM Laboratory has developed over the years a unique set of instrumentation dedicated to the microwave, millimeter-wave and submillimeter-wave spectroscopy of astrophysical molecules. Our very high resolution spectrometers cover the 2 – 990 GHz range. Future developments include a new multiplier chain based on solid state sources in order to cover the 1.1 – 1.7 THz spectral range. The AILES beam line at the third generation synchrotron radiation SOLEIL was recently proven to be highly complementary to our spectrometers, as shown for the NH radical study by Bailleux *et al.* (2012).

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