Spectroscopy of interstellar internal rotors: An important tool for investigating interstellar chemistry.

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Abstract

This paper is a review of molecules with internal rotors detected or tentatively detected with upper limits in the interstellar medium. Internal rotor molecules containing one or two methyl groups are present at each of the different phases leading to stellar and planetary formation, from the molecular clouds to the star and its planets. They are also found in comets and asteroids. They represent a ubiquitous hydrogen-rich substituent in many complex organic molecules. This paper shows how high resolution spectra (mainly in the microwave, millimeter and sub-millimeter wave range) are analyzed in the laboratory and what theoretical methods can be used to properly reproduce the spectra. We also present a range of examples of important methyl rotors studied and how they can be used as tools to study the chemistry of interstellar medium.

Keywords: internal rotation, spectroscopy, methyl groups, astrophysical molecules, prebiotic molecules, biomimetics

Dedicace

This paper is dedicated to the memory of Dr. Jon T. Hougen (National Institute for Standards and Technology, NIST, Gaithersburg, USA, 1936-2019) and Dr. Li-Hong Xu (New Brunswick University, Canada, 1957-2019). Without their passion and dedication to spectroscopy many of the results discussed here would not exist.

Dr Jon T. Hougen (left) and Dr. L.-H. Xu (right) during one of the high resolution spectroscopy meetings. The picture captures the spirit of our meetings with intense discussion and interaction between all participants (published with the authorisation of family members).

1. Introduction

Internal rotors are molecules containing an atom or a group of atoms which can turn relative to the other parts of the molecule. This motion is hindered by a potential barrier so the internal rotation is not “free”. Internal rotation or torsion is often referred as a “Large Amplitude Motion” (LAM) because the internally rotating group of atoms goes far away (compared to the bond lengths) from equilibrium positions. The present review is mainly dedicated to interstellar asymmetric top molecules containing one or two internal rotor(s) with C_{3v} (or close to C_{3v}) symmetry. Methyl (CH_3), trifluoromethyl (CF_3) or silyl (SiH_3), groups are typical examples for which internal rotation is hindered by a three-fold potential. The rest of the atoms of the molecule may lie down in a plane of symmetry or not. The existence of a three-fold finite potential barrier in a molecule induces a quantum chemical tunneling effect and leads to splittings of the energy levels into the so-called A and E levels. In turn, these splittings result in the observation of A-E doublets in the spectra. The rotational or the rotation-vibration spectra of non-rigid molecules containing such large amplitude motions are often complex and cannot be analyzed using the traditional methods valid for rigid or semi-rigid asymmetric top molecules¹.

Internal rotors play an important role in our environment and particularly in astrophysical studies. Many complex molecules with internal rotors are not only detected in the interstellar medium (ISM)², but also in comets, meteorites and asteroids³⁻⁵. An excellent review of interstellar, circumstellar, extragalactic, protoplanetary disk, and exoplanetary molecules was recently published.⁶ For each molecular species, this 2018 census presents a summary of its first detection, along with the observatorial facility, spectral range, transitions, as well as the laboratory spectroscopic work. Internal rotor molecules are present in the different phases leading to stellar and planetary formation from the molecular clouds to the star and its planets, see Fig. 1 and Table 1. The millimeter-wave spectrum of hot cores such as the Orion molecular cloud or Sagittarius B2 (Sgr B2) is dominated by the rotational-torsional spectra of small internal rotors, such as methanol (CH_3OH) and methyl formate (HCOOCH_3). They are also observed in comets and meteorites⁷. In 2016, methanol was observed in the protoplanet disk TW Hydrae⁸. In 2018, two teams took advantage of the rapid increase in disk temperature of the FU Ori outburst surrounding the young star V883 Ori to detect and analyze in spatially-resolved sub-millimeter observations different complex organic molecules. Among those molecules, four were internal rotors: methanol CH_3OH , acetone CH_3COCH_3 , acetaldehyde CH_3CHO , and methyl formate HCOOCH_3 (see Fig. 2)⁹⁻¹⁰.

Protoplanet disks are the birth place of planets, including the Earth. Some of the major questions in astrochemistry are related to the origin, the evolution and the transfer of interstellar molecules. Are complex molecules formed in the proto-solar nebula by the same processes as those existing in the

interstellar clouds, or do some of them come directly from the ISM? Were they altered? To answer these questions, and to find the missing link between protoplanetary disks and the early Earth composition, it is important to study complex molecules, and thus internal rotors, from many different sources, i.e. in the regions of formation of both low and high mass stars and in protoplanetary disks.

Fig. 1. Artist view showing the different phases for the stellar and planetary formation. From left to right and up to down: molecular cloud, prestellar core/protostar embedded in a gas and dust cocoon, star with its disk rich in volatile species (protoplanetary disk) and Star with its planets. Credit: NRAO.

Table 1. Internal rotors detected so far in the ISM^a.

6 atoms	7 atoms	8 atoms	9 atoms	10 atoms	11 atoms	12 atoms
CH ₃ OH	CH ₃ CHO	HC(O)OCH ₃	CH ₃ OCH ₃	CH ₃ COCH ₃	CH ₃ C(O)OCH ₃	C ₂ H ₅ OCH ₃
CH ₃ SH	CH ₃ NH ₂	CH ₃ COOH	CH ₃ CONH ₂	CH ₃ CHCH ₂ O		
	CH ₃ NCO	CH ₃ CHNH	CH ₃ NHCHO ^b	CH ₃ OCH ₂ OH		

^a We considered here interstellar asymmetric top molecules containing one or two internal rotor(s) with C_{3v} (or close to C_{3v}) symmetry.

^b Tentatively detected (upper limit available).

Fig. 2. The background is an ALMA image of the V883 Ori protoplanet system. On the upper left is an artist's image of the ice dust grains found in the colder, outer regions of the disk. The molecules forming within the ice, such as methanol cannot be detected by ALMA because they are trapped in the ice's layers. The right upper side illustrates what happens when the inner disk gets warmer and temperature are high enough to melt the ice and release the molecules which go in the gas into the disk. These liberated molecules can then be detected with ALMA as shown in the lower panel. The peaks emerging in the sub-millimeter spectrum correspond to different molecules, among which are several internal rotors like methanol, methyl formate and acetaldehyde, Credit: Merel van't Hoff Univ. Leiden and NRAO.

It is thought that comets contain material from the origin of the solar system, condensed directly out of the pre-solar nebula¹¹. Comets may have even delivered some of the water and organic matter found on the Earth via impacts¹². Over 22 molecules have been identified in comets by radio observations, including internal rotor organic species such as acetaldehyde, methanol, acetic acid and methyl formate.

All the recent progress in observations in the last few years is mainly related to the advent of large sub-millimeter facilities (ALMA, SOFIA, Herschel) with their unprecedented spatial and spectral resolutions ($\Delta\nu < 1$ MHz). Not only have these telescopes allowed the astronomers to make new observations, they also permit them to set up chemical spatial distribution maps. At the same time, they have urged the need for very precise spectroscopic data up to the THz and far-infrared. In this spectral range, which was not much studied before in astrophysics, it turns out that internal rotors and their isotopologues have many transitions. As a consequence, the limit of line confusion is often achieved in the new astronomical

surveys¹³. Complete and precise spectral identification of the known species, together with their isotopologues and their excited torsional and vibrational states, is therefore required, otherwise they will prevent the detection of new species. This problem is well-known by the astronomers as the “*weed problem*”¹⁴. It is particularly true for a number of interstellar internal rotors such as methanol, methyl formate and dimethyl ether, which have many lines in astrophysical surveys.

However interstellar rotors are not just “weeds” one wants to “get rid of”. First, they are excellent indicators of the physical conditions of the environment from which they come. Second, they reveal the chemical structure of the molecule they belong to, and third they are important for detecting potential prebiotic molecules at the origin of life.

The first point comes from the fact that internal rotor spectra carry valuable information about *the physical conditions* occurring in dense molecular clouds. Spectra involving highly excited torsional states are excellent probes of the temperature existing in the various environments studied. The pure rotational transitions occurring within one excited state (i.e. $v_t = 1 - 1, 2 - 2$ etc.) usually appear as satellites of the ground torsional $v_t = 0 - 0$ transitions in the microwave or (sub)millimeter-wave ranges. Their intensities can be relatively strong since they are driven by the permanent components of the electric dipole moment¹, and since the excited torsional state energies are low, their population factors are usually not negligible. The torsional transitions between two different torsional states (i.e. $v_t = 1 - 0$) usually occur in the far-infrared range, typically around 100-200 cm^{-1} . Their intensities are driven by the out-of-plane component of the dipole moment induced by the torsion of the methyl group, but also by the permanent in-plane dipole moment components. For certain molecules, like methanol or acetaldehyde, their intensities can also be rather strong.

Moreover, spectroscopic studies of isotopologues for abundant interstellar internal rotors are also of interest as they give access to the isotopic abundances of the environments in which they are found, and eventually help to understand how complex organic molecules were formed, a still challenging topic in astrochemistry. In particular, the isotopic abundance typically provides a history of the cold processing of the molecules as well as some indication (although complicated by history) of the initial conditions. An example is the relative abundances of CH_2DOH , CHD_2OH and CD_3OH to CH_3OD . In cold material, CD_3OH has been observed, but in other environments, CH_3OD can be enriched for reasons that are not understood. Finally, an internal rotor can be a very sensitive sensor for testing the possible time-variation of the proton mass to the electron mass ratio in the universe.

¹ The dipole moment components of an internal rotor molecule is described as a cosine series depending on the torsional angle.

The second point is related to the fact that internal rotors are excellent (and sometimes unique) indicators of the *chemical structure* of any complex organic molecule. Studying their spectra will bring quantitative information on the tridimensional structures of the molecules, on the isomers or conformers observed in space, on the steric and electronic effects of groups attached at the other part of a molecule, and eventually in the case of conjugated bonds, on the transfer of information through those bonds. Internal rotors are “sensors” for what is going on at the other part of the molecule, sometimes several bonds away.

Finally, internal rotors and in particular methyl groups are also important building blocks, allowing an increase in the size and the complexity of organic molecules. They are present in many prebiotic molecules, e.g. molecules that are assumed to be likely at the *origin or precursor of life*. For biologists, the addition of a methyl group makes a molecule more hydrophobic and more prone for binding to biomolecules, because the added methyl group increases the hydrophobic surface area. In pyrimidine nuclear bases, one difference between DNA and RNA is the exchange of a thymine for an uracil, two pyrimidine bases for which the only difference is a methyl group at the fifth position of the pyrimidine ring. It is postulated that the dynamics of methyl groups plays a role in the evolution of biomolecules from an initial “RNA-dominated world,” lacking methyl dynamics, to the presently existing “protein/RNA/DNA world,” which contains many methyl groups (and thus increased plasticity)¹⁵. This shows the influence of the internal rotation methyl groups in the beginning of life.

In recent decades, a substantial number of asymmetric top molecules containing one methyl internal rotor have been detected in the interstellar and circumstellar media, e.g. methanol CH_3OH ¹⁶⁻¹⁷, methyl formate HCOOCH_3 ¹⁸⁻¹⁹, acetaldehyde CH_3CHO ²⁰⁻²¹, acetic acid CH_3COOH ²²⁻²³ and acetamide CH_3CONH_2 ²⁴⁻²⁵. On the other hand, fewer molecules containing two internal methyl groups such as acetone $(\text{CH}_3)_2\text{CO}$ ²⁶⁻²⁷, dimethyl ether CH_3OCH_3 ²⁸⁻³¹ and methyl acetate $\text{CH}_3(\text{CO})\text{OCH}_3$ ³² have been studied in the laboratory and subsequently detected in the interstellar medium. The list above is far from being exhaustive and more internal rotors have been detected, as discussed in the present review.

For all of the above reasons, the spectroscopic studies of interstellar molecules containing one (or more) internal rotor(s) have gained considerable importance in astrophysics. Not only have the astronomical telescopes acquired unprecedented spatial and spectral resolution this last decade, but laboratory spectroscopy has also achieved experimental advancements. Examples are the development of spectrometers based on chirped pulses in the microwave or millimeter-wave range with unprecedented speed for acquiring highly complex broadband spectra³³ and the development of quantum-cascade lasers in the infrared region with precise tunability over a range of wavelengths³⁴.

In addition to these technological developments, a number of theoretical methods based on different axis systems as well as different computer codes are available to model the spectra of internal rotors. The goal of this paper is to guide the astronomers to find the most appropriate method(s) and software(s) for the types of internal rotors and spectra they want to detect. For spectroscopists, the goal is to give them guidelines to understand the needs and requirements of astrophysicists.

In the present review we will restrict our study of astrophysical internal rotors mainly to the microwave, (sub)millimeter-wave, THz and, to a smaller extent, to the infrared spectral ranges.

Section 2 gives the general strategy to go from interstellar observations to astrochemistry using laboratory spectroscopy and databases. Section 3 is dedicated to a description of the basic theory needed to understand the spectra of internal rotors. Fitting and producing predictions for astrophysics is also described in this section, as well as the various available computer codes. Section 4 shows how internal rotors can be interesting tools to probe the ISM. Finally, Section 5 is concerned with the near future and new programs for future molecular systems to be detected.

2. General strategy to detect internal rotors in space

2.1 Getting the astrophysical spectra

The general strategy to detect internal rotors (or any astrophysical molecule) in the ISM is illustrated in Fig. 3. On the left upper side of Fig. 3, astronomers record electromagnetic spectra using ground-based telescopes or space telescopes. In order to detect and measure the relative abundances (or column densities) of the molecular species, they need to access various spectroscopic data on those molecules. They also need other molecular data such as thermodynamics, reaction rates, collision rates, photodissociation threshold, etc., but in the present paper we only concentrate on the spectroscopic line parameters given in the center of Fig. 3. In the microwave, (sub)millimeter-wave and THz ranges, which correspond to the rotational motion of the molecules, the spectroscopic data mainly consist of line frequencies, line intensities, and energy levels. In the infrared range, which corresponds to the vibrational motions, line profiles are also needed. In the visible and UV or VUV ranges, which we will not detail in the present paper, bands are observed rather than separate lines so absorption cross sections are mostly used.

Fig. 3. General strategy for collecting and using spectroscopic data in astrophysical applications.

2.2 Building up databases

In the microwave spectral range through the THz, all the data are in general efficiently accessible to the astronomy community thanks to the well-known spectroscopic databases (JPL³⁵, CDMS³⁶, SPATALOG³⁷, the Lovas NIST databasis³⁸, the Toyama databasis³⁹ etc). In the infrared spectral range, the HITRAN⁴⁰ and GEISA⁴¹ databases also provide line-by-line spectroscopic data.

As an example of astronomical use of these databases, let us mention the CASSIS (Centre d'Analyse Scientifique de Spectres Instrumentaux et Synthétiques) software developed by Centre d'Étude Spatiale des Rayonnement (CESR)/Institut de Recherche en Astrophysique et Planétologie (IRAP) since 2005⁴², which allows astronomers to produce synthetic spectra, to identify molecular lines and to adjust the source parameters. It retrieves any interstellar spectra (Hubble, Corot, Splatalogue, ISO, etc.,) and also accesses some useful information for the modeling or identification from databases (CDMS, JPL, ...) through the VAMDC (Virtual Atomic and Molecular Data Centre) TAP protocol (Table Access Protocol) bases. The VAMDC⁴³ is a European e-infrastructure project devoted to building a common electronic infrastructure for the exchange and distribution of atomic and molecular data.

Databases are built up from intensive spectroscopic studies both experimental and theoretical.

2.3 Recording laboratory spectra

Spectroscopic laboratories around the world collect experimental data on astrophysical “isolated” molecules, as shown in the right upper corner of Fig. 3. In the present paper, we will concentrate on high resolution spectroscopic data, where a line by line resolution is achieved and which allow us to observe internal rotation splittings.

In the microwave spectral range, for a long time, traditional narrow-band resonator (or cavity-based) spectrometers have been used⁴⁴. Coupled with a supersonic jet, the Molecular-Jet-Fourier-Transform MicroWave (MJ-FTMW) spectrometer allows the rotational temperature to cool down and to simplify the spectrum so that only the lower states or lower conformers are populated. The resolution of a MJ-FTMW spectrometer can be as low as 1 kHz, which permits the study of very small internal rotation splittings and/or nuclear quadrupole splittings, for example. The Chirped-Pulsed (CP) technique developed by B. Pate³³ in 2008 offers a slightly lower resolution (10-30 kHz) but it allows the user to record the spectra several orders of magnitude faster than the cavity-based spectrometer. Broadband spectra can thus be obtained for complex organic molecules containing LAM, including internal rotation(s) with several conformers, isomers, clusters, and if electric discharges are produced, ions or radicals. Furthermore, CP-FTMW spectroscopy produces experimental line intensities, which are more reliable than in the classical resonator version, which is of importance for astrophysics. The Chirped-pulse technique has also been demonstrated to work well into the millimeter and submillimeter wave ranges.

In the submillimeter-wave range, estimated uncertainties for measured line frequencies are usually around 30 kHz and 50 kHz, depending on the observed signal-to-noise ratio and the frequency range⁴⁵.

In the infrared range, besides the traditional high resolution Fourier Transform spectrometers commonly used today around the world, the Quantum Cascade Lasers (QCL)³⁴ have different advantages over the previous Lead Salt Laser (LSD). They can be tuned from one wavelength to the other in a precise manner. They have higher optical power than other types of infrared lasers. They can operate in continuous wave mode at room temperature and can be coupled with a supersonic jet. Another important technology development of the last few decades is the use of the bright synchrotron radiation for high resolution spectroscopy, which allows the users to record very weak bands, such as some torsional bands⁴⁶. The spectral resolution is limited to the Doppler width of the molecular lines (unless sub-Doppler techniques are used). Internal rotor spectroscopy has been significantly advanced by all of these technological and experimental improvements.

2.4 Assigning, fitting and predicting spectra: *ab initio* methods versus “effective” Hamiltonians

Once the spectrum of a given molecule has been recorded, it needs to be analyzed using theoretical tools (right bottom corner of Fig. 3). Molecules are described quantum mechanically as quantized energy levels (E), which can be obtained after solving the Schrodinger equation $H \Psi = E \Psi$. H designated the Hamiltonian of the system, including kinetic and potential energy terms. Ψ describes the wavefunction of a given state and depends on the quantum numbers, which unambiguously characterize this state.

Analyzing and fitting a spectrum requires the following steps (see Fig. 4):

(1) First, we select a theoretical model and the corresponding code, which will be appropriate for the molecule under study, taking into account the available level of experimental resolution (if the internal rotation splittings are not resolved we do not need to use a complicated model which takes into account internal rotation). Choosing a quantum mechanical model (or developing one if it does not exist), which sets up the appropriate Hamiltonian describing all the effects observed in the spectrum is a crucial step in analyzing an internal rotor spectrum.

(2) Second, we “guess” the initial values for the molecular parameters needed for the selected theoretical model. These initial values can be based on either previously published values or, if those do not exist, on density functional theory (DFT) and “*ab initio*” calculations using the commonly available softwares (i.e. *GAUSSIAN*⁴⁷, *GAMESS*⁴⁸). *Ab initio* techniques can calculate rotational constants as well as the internal rotation potential function hindering the torsion and quadrupole hyperfine constants. They also can predict from the potential energy surfaces the relative energies of different conformers or isomers. This procedure is very helpful to start the problem, but unfortunately, the differences between the calculated and experimental transitions are often a few thousands of MHz or even larger in the case of internal rotors, which is not sufficiently accurate. In studies of some large molecules with many conformers separated by less than 100 cm⁻¹, *ab initio* methods may also wrongly predict the lowest energy conformer, if the appropriate levels of theory are not carefully chosen.

For these reasons, “effective Hamiltonians,” which are power series of quantum mechanical operators multiplied by molecular constants or parameters such as rotational constants, quadrupole coupling constants, internal rotation parameters etc., are developed.

(3) Based on the first two steps we generate an initial prediction of a spectrum. This means that the energy levels, the transition frequencies and the line intensities of the molecule have to be calculated using the selected code and molecular parameters. The calculated frequencies of the molecular transitions have to be compared to the observed ones. This step is much less obvious than thought because, as mentioned above, the initial parameters may not be accurate enough, or because the theoretical model chosen may not be appropriate. So, if we do not see any correspondence in the spectral features we have to step back and revise either the theoretical model and/or our guesses on the initial values for the molecular parameters. At this step we also need to “assign quantum numbers” for each rotational transition, which characterize its initial energy level and its final one.

(4) If we do see a correspondence of the spectral patterns between the experiment and the prediction, and have assigned the selected range of quantum numbers to the transitions, we go to the fitting stage. A least-squared fitting procedure automatically adjusts and refines the molecular parameters so that the observed minus calculated residuals are minimized. if the fit does not reach experimental

accuracy, the process is iterated until it does so. The problem can be either in the measurement(s) (blended transitions leading to large measurement errors, wrong reading of the frequencies, etc.), or in the assignments of the quantum numbers, or in the choice of the parameters in the model (high order terms in the Hamiltonian missing).

(5) if the fit “converges” and achieves the experimental accuracy, then the “best” set of deduced parameters can be used to produce a prediction of all the allowed transitions occurring in a given spectral range. In a prediction (also sometimes called line-list), not all lines need to be measured. However, extrapolating to higher quantum numbers than the measured ones is often not recommended because the model and the set of parameters may no longer work well. The prediction is finally transformed into a line-list format, which is submitted to the databases for astronomical use, containing the line frequencies, the quantum numbers of the energy levels of the transitions, the line strengths and the partition function, which can be used to calculate the intensities at any temperature or pressure conditions.

Fig. 4. Predicting and fitting spectroscopic data for internal rotors using effective Hamiltonian methods and codes. 1: selecting the appropriate theoretical model and code corresponding to the molecule under study. 2: making initial guesses for the molecular parameters from literature or from *ab initio* calculations. 3: predicting (calculating) a first spectrum based on steps 1 and 2 and making hypotheses on assignments in the observed spectrum. 4: fitting is performed using the selected model and codes including internal rotation effects in the Hamiltonian. 5: determining a set of refined molecular parameters. 6: producing a new prediction of line frequencies and intensities, and comparing the calculated frequencies with the observed ones. 7 If the « fit » of the observed data does not achieve the experimental accuracy, the procedure repeats by changing/increasing the number of assignments and/or adding new parameters in the model. 8: if the “fit” achieves the experimental accuracy, the procedure stops and the prediction for the astronomers is ready.

For internal rotors, the bottle neck of this procedure is often step 1), i.e. building up an appropriate theoretical Hamiltonian and writing up the code if it does not exist, and/or step 2) assigning-fitting-predicting “loop,” which is time-consuming because the complexity of the spectra, which often requires this process to be repeated a number of times until convergence is achieved.

2.5 “Inverting” the interstellar spectra

As shown in the bottom of Fig. 3, the relative abundances or column densities for the various species and the excitation temperature are fitted from the interstellar spectrum, after fixing the sources and the observational constraints (e.g., source size, FWHM and velocity position). This process is called “inversion” of the spectrum. Once the relative abundances of the astrophysical species are determined from the spectrum, those values can be used as constraints in astrochemical models to confirm certain hypotheses.

In the next section, we will concentrate on describing the theoretical model and spectral analysis for astrophysical internal rotors.

3. Fundamental theory for internal rotors

3.1. Effective Hamiltonians, methods and codes for one internal rotor with C_{3v} symmetry

In this review, we consider an asymmetric top molecule containing two nearly rigid groups connected by a bond. One of these groups (typically the methyl group, called the “top”) is almost symmetric, and close to C_{3v} symmetry. Deviations from C_{3v} symmetry will then be taken into consideration later by introducing appropriate higher-order terms describing the torsion-rotation interactions. The other part of the molecule called “the frame” may or may not present a plane of symmetry. A typical example is the astrophysical molecule acetaldehyde CH_3CHO , represented on the right part of Fig. 5.

Fig. 5. Potential Barrier for acetaldehyde, v_t is the principal torsional quantum number and m is the free internal rotor quantum number. The height of the barrier is V_3 . Top right : the acetaldehyde molecule; bottom right: a schematic view of internal rotation with the “top” part and the “frame” part.

Many papers exist in the literature describing the Hamiltonian and methods dealing with internal rotation¹. Therefore, we only give here a summary of the commonly used approaches and softwares developed to analyze the internal rotor spectra. A more complete description and comparison between methods and codes can be found in Ref.⁴⁹. The PROSPE website, created by Kisiel, presently provides a number of internal rotation codes together with input data files and examples⁵⁰.

Most of the spectroscopic papers divide the theoretical models depending on the axis system in which the Hamiltonian is set up: Principal Axis System (PAS) or Rho Axis System (RAS). However, it is also relevant to classify the methods and codes into “local” methods, which treat separately each torsional v_t state (or sometimes even each A and E species states separately) and “global” methods, which take into account all the interactions between the different v_t states. The “global” methods deal with the total set of states (to a certain truncation level) associated with the given large amplitude motions using one Hamiltonian, whereas the “local” methods separate these states into groups (for example, by symmetry species) and then treat each group of states using its own Hamiltonian and its own set of parameters.

A list of available internal rotation codes is shown in Table 2 with the name of the code, the number of internal rotors and quadrupole nuclei it can deal with, some characteristics of the codes and some examples of internal rotors studied.

3.1.1 Principal Axis Method (PAM)

3.1.1.a. Effective PAM Hamiltonian

The principal axis system (PAS) is commonly used by almost all spectroscopists. Provided that small amplitude vibrations are neglected, the rigid frame-rigid top Hamiltonian in the PAS, which is valid for an asymmetric-top molecule (with no other symmetry requirement), is¹:

$$\begin{aligned}
 H &= T + V(\alpha) \\
 &= A J_a^2 + B J_b^2 + C J_c^2 + F (p_\alpha - \rho_a J_a - \rho_b J_b - \rho_c J_c)^2 + V(\alpha) \\
 &= J_a^2 + B J_b^2 + C J_c^2 + F p_\alpha^2 + F (\sum_g \rho_g^2 J_g^2) - 2 F p_\alpha (\sum_g \rho_g J_g) + V(\alpha)
 \end{aligned} \tag{1}$$

The Hamiltonian for rotation and torsion can be described as the sum of two terms, the kinetic energy (T) and the potential energy $V(\alpha)$. The kinetic energy contains the three components of the total rotational angular momentum J_g ($g = a, b, c$) in the principal axis system, and p_α , which is the internal

rotation angular momentum conjugated to the torsion angle α . These angular momentum components are multiplied by the rotational constants A, B, C , and the internal rotation constant F , which are the inverse of the principal moments of inertia of the molecule $I_g = I_a, I_b, I_c$, and the top I_α . The ρ_g components of the ρ vector are also related to the principal moments of inertia of the molecule as defined below:

$$\begin{aligned} A &= \frac{\hbar^2}{2I_a}, B = \frac{\hbar^2}{2I_b}, C = \frac{\hbar^2}{2I_c} \\ F &= \frac{\hbar^2}{2rI_a} \\ r &= 1 - \sum_g \lambda_g^2 \frac{I_\alpha}{I_g} \\ \rho_g &= \frac{\lambda_g I_\alpha}{I_g} \end{aligned} \quad (2)$$

where λ_g are the direction cosines of the internal rotation axis i of the top in the principal axis system, i.e. $\lambda_g = \cos(\langle i, g \rangle)$. The ρ_g components represent a measure of the coupling between the internal rotation motion p_α and the rotational angular momentum J_g .

$V(\alpha)$ is the internal rotation potential function, which has a $2\pi/3$ periodicity for a methyl rotor top. As shown in Fig. 5, it can be expressed in the following Fourier series:

$$V(\alpha) = \frac{1}{2} V_3 (1 - \cos 3\alpha) + \frac{1}{2} V_6 (1 - \cos 6\alpha) + \dots \quad (3)$$

As can be seen from Fig. 5, the presence of a potential barrier is responsible for the splitting of each torsional level, due to a quantum chemical tunneling effect through the barrier. For a C_{3v} top, the two components are called A and E levels. The splitting of the two energy levels is an indicator of the speed of tunneling and depends on the reduced barrier $s = 4V_3/9F$. It increases when the energy of the molecule gets close to the top of the barrier height V_3 .

If the barrier is infinite, a good approximation of the physical model would be a harmonic oscillator centered in each minimum of the potential. The quantum number to use is the torsional quantum number of the harmonic oscillator, v_t (left hand side of Fig. 5). Once the molecule's energy gets close to the barrier top or higher, the model to use is that of a free rotor. The "good" quantum number is then m , the free-rotor quantum number (right hand side of Fig. 5). So the torsional energy levels can occur in three different regimes: 1) below the top of the barrier ("high-barrier" limit), 2) above the barrier ("low-barrier" limit) and 3) close to the top of the barrier ("intermediate" limit).

For our example of acetaldehyde CH_3CHO shown in Fig. 5, which has a barrier height of $V_3 = 407 \text{ cm}^{-1}$, $F = 7.6 \text{ cm}^{-1}$ and $s = 4V_3/9F = 24$, the "high-barrier" regime mainly occurs for $v_t = 0$ and 1, the "low-barrier" regime for levels above $v_t = 3$ and the intermediate region for $v_t = 2$.

3.1.1.b. Examples of PAM fitting codes

It was only last year that a new computer program, ***aixPAM*** (see 2nd row of Table 2), based on the PAM Hamiltonian of Eq. (1) using a direct diagonalisation procedure of the matrix was written in Aachen, Germany. Before that, the size of the matrices to be diagonalized prohibited such calculations. Appendix A gives some details about the early literature⁵¹ and older procedures, in particular the van Vleck transformation, which helps us understand the difference between “global” and “local” approaches.

Due to the limitations explained in Appendix A, the PAM fitting codes are only useful for interstellar molecules if the spectral range studied involves relatively low K values (usually low frequency range), low values for the ρ parameter (usually large molecules with a rather heavy “frame” compared to the “top”) and high barrier regime to internal rotation.

The program called **JB95** (see the 1st row of Table 2), a program originally developed by Plusquellic, Pratt et al. at the University of Pittsburgh and available online⁵²⁻⁵³, is an example of a modern and efficient code based on the “local” PAM approach. The method relies on the PAM perturbation treatment of Eq. (A.1) and has a very useful graphical interface. It has been used in many cases to fit the torsion-rotation perturbations from internal rotation observed in the microwave and UV spectral regions of biomimetic molecules.

3.1.2 Rho-Axis Method (RAM)

3.1.2.a. Effective RAM Hamiltonian

One disadvantage of the “local” PAM approach is the slow convergence of the Hamiltonian from Eq. (A.1), which especially occurs if the barrier is very small and/or the ρ parameter and K quantum number are large. Moreover, the existence of the Coriolis-type term $-2F\rho_\alpha\rho J$ in the Hamiltonian of Eq. (1) makes the separation between the torsional calculation and the rotational calculation difficult to achieve. For computational purposes, Dennison, Hecht and co-workers⁵⁵⁻⁵⁸ proposed to use a different axis system which eliminates the $-2F\rho_x\rho_\alpha J_x$ and $-2F\rho_y\rho_\alpha J_y$ Coriolis-type terms, with the x, y, z axis related to b, c, a (a, b, c) for molecules close to the “prolate (oblate) limit,” respectively. Their approach is described by Lin and Swalen in their review article¹. The resultant Hamiltonian operator contains then only the $-2F\rho_z\rho_\alpha J_z$ term. The new coordinate axis system is related to the PAS by a rotation and the new z axis is parallel to the ρ vector, since by definition we then have $\rho_x = \rho_y = 0$. For this reason, the new axis system was called “Rho Axis System”⁵⁹. More details about the RAM Hamiltonian can be found in Appendix B and in refs.⁶⁰⁻⁶².

The RAM model was first developed for molecules containing one internal C_{3v} rotor and a C_s symmetry, but an extension of the RAM model for treating molecules with no plane of symmetry at equilibrium (C_1 molecules) also exists⁶³. The changes affect primarily the group-theoretical symmetry

arguments, as well as the number of terms in the Hamiltonian. These terms can be found in Tables 1 and 2 of Ref.⁶³ and will not be described in detail here.

In the next section, we present the different variations of RAM codes.

3.1.2.b. Examples of RAM fitting codes

SPFIT/SPCAT package:

There are different codes written using purely the RAM or combining the RAM with the PAM. A convenient fitting and prediction program familiar both to the spectroscopic and astrophysical communities is the **SPFIT/SPCAT** package of Pickett³⁵ (see the 3rd row of Table 2). It has been used, for example, in two

Table 2. Available internal rotation codes and capacities to fit internal rotors spectra

N ^o ^a	Name ^b	N° of tops ^c	N° of NQ ^d	Symmetry ^e	Character ^f	Examples
1	JB95	3 C _{3v}	1	C _s /C ₁	Local	Amino acids, Dipeptide alanine, other biomimetics
2	aixPAM	1 C _{3v}	1	C _s /C ₁	Global	<i>m</i> -Methylanisole
3	SPFIT/SPCAT	2 C _{3v}	10	C _s /C ₁	Local/Global	Acetaldehyde, pyruvic acid,...
4	ERHAM	2 C _{3v} /C _{2v}	1	C _s /C ₁	Local	Acetone, dimethyl ether, methyl formate, methyl carbamate,...
5	XIAM	3 C _{3v}	1	C _s /C ₁	Local/Global	Pyruvic acid, N-methylformamide, metoxymethanol
6	BELGI-C _s	1 C _{3v}	0	C _s	Global	Acetaldehyde, methyl formate, acetamide, acetic acid, vinyl acetate...
7	BELGI-C _s -hyperfine	1 C _{3v}	1	C _s	Global	3-Nitrotoluene
8	BELGI-C _s -methanol	1 C _{3v}	1	C _s	Global	Methanol, methyl mercaptan
9	BELGI-C ₁	1 C _{3v}	0	C ₁	Global	Allyl acetate
10	BELGI-C ₁ -hyperfine	1 C _{3v}	1	C ₁	Global	N-Ethylacetamide
11	Japan	1 C _{3v}	1	C _s	Global	Methanol, methyl mercaptan, methyl formate, acetamide
12	RAM36	1 C _{3v} /C _{6v}	1	C _s	Global	Toluene, methyl formamide, acetaldehyde, methyl isocyanate, methyl formate..;
13	BELGI-C _s -2Tops	2 C _{3v}	0	C _s	Global	Methyl acetate, dimethyl benzaldehyde, methyl propionate, ethyl methyl ketone
14	PAM-C _{2v} -2tops	2 C _{3v}	0	C _s	Global	Acetone
15	Tunneling	Multi-LAM	1	C _s	Local	Methylamine, water dimer, methyl malonaldehyde
16	Poznan	Multi-LAM	1	C _s	Local	Methylamine, hydrazine
17	BELGI-hybrid	Multi-LAM	1	C _s	Global	Methylamine, methyl malonaldehyde
18	BELGI-2states	1 C _{3v}	0	C _s	Global	Acetaldehyde, methanol
19	BELGI-509	1 C _{3v}	0	C _s	Global	Acetaldehyde
20	Multi-states	1C _{3v}	0	C _s	Global	Acetaldehyde (under progress)

^a ordering by appearance in the text^b See text^c Number of internally rotating groups of symmetry C_{3v} or C_{2v}^d Number of quadrupole nuclei causing hyperfine splitting^e Symmetry of the frame^f Characteristics of the method, see text

popular astrophysical molecular databases, JPL³⁵ and CDMS³⁶. A front-end program **IAMCALC** has been added to the SPFIT/SPCAT package. It uses the Mathieu function to generate a set of parameters that connect torsional sublevels ($v_t = 0, 1, 2, A, E$)³⁵.

In the past, a number of studies used a previous version of SPFIT/SPCAT, where each torsional v_t state and each internal rotor state (A and E) was fitted separately (see for example Ref.⁶⁴). This version of SPFIT/SPCAT belongs thus to the “*local*” method. More recently, a number of molecules were added in the JPL catalogue using the updated SPFIT/SPCAT/IAMCALC package, allowing extension of the dataset analysis for methyl formate, acetaldehyde (both detected in the ISM), methyl carbamate, hydroxyacetone (both searched in the ISM) and propane (possible in the ISM) up to the THz range, as needed for astrophysicists. The use of IAMCALC is described in only one paper, which concerns propane, $\text{CH}_3\text{CH}_2\text{CH}_3$, a two-tops internal rotor with high barriers⁶⁵. For the other cases, the assignments were mostly done with other programs⁶⁶. In this new IAMCALC program, the interactions between the lowest torsional states are taken into account in the theoretical model. In that version, the method has thus more of a “*global*” character

ERHAM:

In this RAM section, we also present other methods used in the internal rotation codes which can be qualified as Combined Axis Methods (CAM) as they set up part of the Hamiltonian in the RAM system, but then perform a transformation back to the PAS. One of those methods has been developed by Groner for one or two-tops and is called the Effective Rotational-torsional Hamiltonian (**ERHAM**) approach⁶⁷⁻⁶⁸. The internal rotors are not restricted to C_{3v} symmetry. The frame symmetry can be C_s or C_1 for single rotors or non-equivalent rotors and C_2 , C_{2v} , or C_s for equivalent rotors. A large variety of internal rotors can thus be studied. The ERHAM code was applied very successfully to many astrophysical molecules including two-top molecules such as dimethyl ether⁶⁹, acetone⁷⁰, and *trans* ethyl methyl ether⁷¹ (see the 4th row of Table 2). More recently, ERHAM was also applied to one-rotor molecules searched for in the ISM like pyruvic acid (CH_3COCOOH)⁶⁴, methyl carbamate ($\text{NH}_2\text{COOCH}_3$)⁷², or detected in the ISM such as methyl formate (HCOOCH_3) and its $\text{H}^{13}\text{COOCH}_3$ isotopologue⁷³⁻⁷⁴.

ERHAM allows for the fitting of each torsional state separately. Matrix elements off-diagonal in the torsional quantum number v_t are thus disregarded. Therefore, we classify the ERHAM method as a “*local*” one. In the ERHAM method, the potential barrier does not appear explicitly. The Coriolis-type interaction terms $-2F\rho_x p_a J_x$, $-2F\rho_z p_a J_z$ ($2F\rho_y p_a J_y$ is zero for a planar molecule) are felt only through the Fourier series expansions in $2\pi q(\sigma - \rho K)/3$ of the tunneling matrix elements within one torsional state (see Eq. (9) of Ref.⁶⁷). The information about the barrier is thus hidden in the tunneling coefficients of the internal rotation energy. Currently, all off-diagonal matrix elements in any vibrational quantum number are ignored. The high speed and efficiency of ERHAM, which allows it to compute very fast and accurately line positions and intensities up to high J (up to 120) for moderate to high barriers, is a very big advantage for interstellar

internal rotor molecules studied in the millimeter-wave and sub-millimeter-wave spectral range. Rotational spectra belonging to excited (isolated) vibrational states other than methyl torsional states can be fitted relatively easily with ERHAM⁶⁷.

The ERHAM code has been applied many times in astrophysics. One example is the first detection of the ¹³C isotopologue of ¹²CH₃O¹³CH₃ dimethyl ether in a large submillimeter-wave line survey of the high-mass star forming region G327.3-0.6 performed with the Atacama Pathfinder EXperiment (APEX) telescope. This detection was based on a study of the rotational spectrum up to 1.5 THz performed in the Cologne laboratory, Germany³¹.

XIAM:

Another CAM method, historically called the Internal Axis Method (IAM), was developed by Woods⁷⁵⁻⁷⁶. It was later extended for two top molecules by Vacherand et al.⁷⁷. The Woods method is used in the **XIAM** code written by Hartwig and Dreizler at Kiel, Germany (see the 5th row of Table 2), which can calculate line positions and intensities for one, two or three internal rotors⁷⁸. It can also calculate nuclear quadrupole splitting for one nucleus and spin rotation in first order (diagonal in the rotational quantum number J).

Because of its ease of use and speed, the XIAM code is widely used for many internal rotors⁷⁸⁻⁸¹, including interstellar molecules. It is a “CAM” method as the Hamiltonian is set up in the PAS for the entire molecule, but for each top, the internal rotation operator is set up in its own rho axis system. After diagonalization, the resulting eigenvalues are transformed (or rotated) back into the PAS. The advantage of the XIAM code is that the main parameters of the Hamiltonian are directly related to the molecular structure. Apart from the rotational constants A , B , C , and the centrifugal distortion constants up to the 6th order, the floated parameters are for each methyl top, the direction of the top axis in the PAS, the internal rotation constant F and the potential barrier height V_3 . Only a limited number of higher (4th order) coupling terms between internal rotation and overall rotation are implemented⁷⁹, and each torsional state is fitted separately. These characteristics make XIAM a very fast and useful code, especially in the first stages of the assignment process. A global fit of A and E torsional states is possible with XIAM. However, in cases with rather low barriers, E species transitions are not always satisfactorily predicted. This problem probably occurs because in XIAM (like in ERHAM) torsional interactions between different v_t states are not taken into account explicitly. The situation can be improved by fitting the A and E states separately, using two sets of rotational constants, but taking the same set of centrifugal distortion and internal rotation constants. This method, which we qualify as “*local*” reduces the uncertainties of the residuals in the fit, however the physical meaning becomes somewhat unclear. The XIAM fit is thus more appropriate in general for high or intermediate barrier cases.

An example of the recent use of XIAM in astrophysical detection is the study of methoxymethanol CH₃OCH₂OH, which has a potential barrier of $V_3 > 545 \text{ cm}^{-1}$ for its three stable conformers. The

spectroscopic study by Motiyenko et al.⁸² performed in the Lille laboratory, France allowed for the first interstellar detection of the lowest conformer of $\text{CH}_3\text{OCH}_2\text{OH}$ using Atacama Large Millimeter/submillimeter Array (ALMA) data in Orion⁸³. Methoxyacetaldehyde ($V_3 = 860 \text{ cm}^{-1}$) and methoxyamine ($V_3 = 855 \text{ cm}^{-1}$) were also the subject of an intensive laboratory work in Valladolid⁸⁴⁻⁸⁶. Their spectra were also analyzed with XIAM. Spectral features of methoxyacetaldehyde were searched in the high-mass star-forming regions Orion Kleinmann–Low (Orion KL) and Sgr B2 but no lines above the detection limit were detected.

BELGI- C_s and BELGI- C_1 :

Another code using the RAM method is the **BELGI- C_s** code for C_s ⁵⁹ or its variant **BELGI- C_1** for C_1 molecules⁶³, which are both based on a two-step diagonalization procedure first introduced by Herbst and collaborators (see the 6th and 9th rows of Table 2). This two-step procedure is quite powerful since in the first diagonalization stage, the torsional Hamiltonian H_T of Eq. (B.1 and B.2) is diagonalized in a rather large torsional basis set (typically the size is 21 wavefunctions), which is then truncated in the second diagonalization stage (to typically the lowest 9 or 11 torsional eigenfunctions). Those torsional eigenfunctions obtained by the first step are stored and, after multiplying them by the symmetric top rotational wavefunctions, are used to set up the rest of the Hamiltonian, i.e. the rotational terms H_R (Eq. B.3) and the interactions terms H_{int} . It is quite interesting that Herbst et al. applied it initially to important astrophysical molecules such as acetaldehyde⁸⁷, methyl mercaptan⁸⁸ and methanol^{62,89}. The “*global*” method is well adapted to modern computing techniques and is quite efficient in fitting spectra within experimental accuracy. The BELGI- C_s code was applied to many internal rotors, i.e. to acetaldehyde CH_3CHO and to its deuterated isotopologues CD_3CHO and CD_3CDO ⁹⁰⁻⁹³, acetic acid CH_3COOH ⁹⁴, acetamide CH_3CONH_2 ⁹⁵ allowing its first detection in Sgr B2²⁴, and various isotopologues of methyl formate HCOOCH_3 ⁹⁶⁻¹⁰¹.

A modified version of BELGI- C_s by Xu et al. (designated hereafter as **BELGI- C_s -methanol**, see the 8th row of Table 2) was applied successfully to methanol CH_3OH in its first three torsional states $v_t = 0, 1$ and 2 and eventually provided a THz database¹⁰². It was also used for the isotopologues $^{13}\text{CH}_3\text{OH}$ ¹⁰³, CH_3OD ¹⁰⁴, CD_3OH ¹⁰⁵, as well as for methyl mercaptan CH_3SH ¹⁰⁶.

The BELGI- C_1 code (see the 9th row of Table 2) has been applied to a number of acetates or ketones with no plane of symmetry⁶³ but none of them have been detected in space yet. In fact, the only C_1 symmetry molecule detected so far is propylene oxide¹⁰⁷, which is a chiral molecule with a high barrier ($V_3 = 895 \text{ cm}^{-1}$).

The TOYAMA code (Japan):

The same global method is used by the **Toyama** group in Japan who called it “IAM” (referred to as the “**Japan**” code, see the 11th row of Table 2). It was applied to several internal rotors of astrophysical interest such as methanol CH_3OH ¹⁰⁸, acetamide CH_3CONH_2 ¹⁰⁹, methyl formate HCOOCH_3 and its

isotopologues. For the latter species, compilation of many lines into an atlas allowed them to detect the first excited torsional state of this molecule in the ISM¹¹⁰⁻¹¹¹.

RAM36:

Ilyushin et al. developed a “new generation” of RAM codes, called **RAM36** (see the 12th row of Table 2) written initially for internal rotors with a V_6 barrier like toluene¹¹² but which can also deal with V_3 barriers. The speed of the code is faster than the original BELGI version, so higher J values can be fitted efficiently and faster. It implements a general form for the Hamiltonian (see Eq. (4) of Ref.¹¹²):

$$H = \frac{1}{2} \sum_{pqnkstl} B_{pqnkstl} [J_z^{2p} J_x^q J_y^n J_y^k p_a^s \cos(3t\alpha) \sin(3l\alpha) + \sin(3l\alpha) \cos(3t\alpha) p_a^s J_y^k J_x^n J_z^q J^{2p}] \quad (4)$$

RAM36 also has the advantage of allowing the user to choose almost any symmetry allowed terms in the Hamiltonian by choosing appropriate sets of k, n, p, q, l, s, t integers in Eq. (4).

Methyl formate HCOOCH_3 was the second one-top molecule (with a V_3 barrier) fitted successfully with RAM36¹¹³, with a standard deviation close to experimental accuracy. Using RAM36 Ilyushin et al. were able to fit all the $\nu_t = 1$ transitions excluded from the fit using ERHAM. A total of 10533 transitions were fitted with rotational quantum numbers $J \leq 62$ and $K_a \leq 26$ in the $\nu_t = 0$ state and $J \leq 35$ and $K_a \leq 23$ in the $\nu_t = 1$ state¹¹³. In a latter paper, extension to the far-infrared spectral range with transitions in the $\nu_t = 1 \leftarrow 0$ band, was performed. This was experimentally challenging because, as explained in more detail in Ref.⁴⁶, molecules with small ρ ($\rho < 0.1$) often have very weak torsional fundamentals in the infrared. For methyl formate, the very bright beamline radiation from the synchrotron SOLEIL (France) had to be used⁴⁶.

The RAM36 code was also applied successfully to acetaldehyde CH_3CHO ¹¹⁴ and acetic acid CH_3COOH ¹¹⁵ by extending the spectral range compared to previous studies, and to the ^{13}C isotopologues of acetaldehyde¹¹⁶. Finally, RAM36 allowed the first tentative detection of methyl formamide CH_3NHCHO ¹¹⁷ and the first detection of methyl isocyanate CH_3NCO ¹¹⁸.

3.2 Available methods and codes for two-top internal rotors

For a one-top internal rotor, each line of a rigid rotor splits into an A and an E transition (see Fig. 6). For a molecule with two non-equivalent tops (called rotor 1 and 2), five transitions are expected: the A species splits into two components, AA and AE, where the first letter represents the internal rotation of rotor 1 and the second letter represents the internal rotation of rotor 2. The E species splits into three components, EA, EE and EE*. The EE and EE* species are due to the coupling of motion of rotor 1 with rotor 2, which somehow “feel” each other even at distance. In the case of a two equivalent tops, the components AE and EA are degenerate and therefore only four transitions are observed in the spectrum.

Fig. 6. Splittings due to internal rotation in the rotational spectrum of molecules with one rotor, two non-equivalent rotors or two equivalent rotors

An example of laboratory spectrum for a two-non-equivalent-top internal rotor (methyl acetate $\text{CH}_3\text{COOCH}_3$) is shown in Fig. 7, which shows the five internal rotation components and the magnitude of the splittings, up to 2000 MHz for this transition with $J = 2 \rightarrow 3$. The components are labeled in the G_{18} permutation-inversion group of the molecule (with the correspondence $AA \rightarrow A_1$ or A_2 , $AE \rightarrow E_2$, $EA \rightarrow E_1$, $EE \rightarrow E_3$ and $EE^* \rightarrow E_4$). The spectrum was recorded using the MB-FTMW spectrometer in Aachen, Germany with an accuracy of 4 kHz¹¹⁹.

Fitting the spectra of a two-top internal rotor with intermediate or low barriers is usually rather complex and requires adequate codes. In particular, apart for some exceptions, fitting their excited torsional states still represent a real challenge.

ERHAM and XIAM:

A number of two-top internal rotor codes exist. We have already mentioned ERHAM (see section 3.1.2.b). **XIAM** can also deal with two rotors⁸⁰, especially if both rotors have high barriers.

BELGI-C_s-2Tops:

Two-top internal rotor programs built in the same manner as BELGI also exist. A program for molecules containing two inequivalent methyl tops with a plane of symmetry (C_s) is **BELGI-C_s-2Tops** (see the 13th row of Table 2) particularly efficient if the barrier heights are small¹¹⁹. The method is based on the theory developed by Ohashi and Hougen who applied it for the first time to N-methylacetamide ($\text{CH}_3\text{-NH-C(=O)-CH}_3$)¹²⁰. BELGI-C_s-2Tops was applied to methyl acetate ($\text{CH}_3\text{COOCH}_3$) for which one barrier height is 102 cm^{-1} (for the C-CH₃ group) and the other one is 422 cm^{-1} (for the O-CH₃ group), see Fig. 8. Dimethyl

sulfide CH_3SCH_3 which has two equivalent tops was also fitted using BELGI-C₅-2Tops. Even though the code was written more explicitly for two inequivalent tops, two barrier heights as well as a number of other internal rotation parameters can be set equal to each other, yielding $V_{31} = V_{32} = 736 \text{ cm}^{-1}$ ¹²¹.

Fig. 7. Example of the tunneling components of the $J_{KaKc} = 3_{03} - 2_{12}$ asymmetric rotor transition measured with the FTMW spectrometer in Aachen, Germany, with a measurement accuracy of 4 kHz¹¹⁹. The two upper panels are the A and E₁ tunneling components (see text for the labeling). The three lower panels are the E₂, E₃ and E₄ tunneling components. The splitting indicated by the brackets is caused by the Doppler effect and the frequency for each component is measured in the middle of these two Doppler components.

Fig.8 Methyl acetate molecule with the two internal rotation barrier heights.

PAM_C_{2v}_2tops:

Another code written by Ilyushin (**PAM_C_{2v}_2tops**, see the 14th row of Table 2), which conveys the same advantages of speed and easiness as for the RAM36 code mentioned above, deals with two equivalent methyl tops in a C_{2v} molecule. It was applied successfully to the interstellar rotor acetone

CH_3COCH_3 ¹²² in its ground and first excited states, and more recently to higher excited torsional states of CH_3SCH_3 ¹²³.

3.3 Internal rotation and ^{14}N hyperfine quadrupole effects

If the molecule has in addition to the methyl top a nucleus with the electric quadrupole moment larger than $\frac{1}{2}$ (for example a ^{14}N nucleus with $I = 1$), hyperfine splittings will occur in the spectrum. The combination of a methyl internal rotation and ^{14}N quadrupole coupling can be handled with the RAM36 code for molecules with a C_s symmetry¹¹² frame, and with the BELGI- C_1 code for molecules with C_1 symmetry (or C_s symmetry if all the C_1 symmetry terms to zero)¹²⁴.

In the BELGI and RAM36 codes, to deal with the hyperfine splittings, a first order perturbation approach is used similar to that described in Ref.¹²⁵ for acetamide (see also Eq. 1 of Ref.¹¹³). It was extended later by including terms allowed by the C_1 symmetry (**BELGI- C_1 -hyperfine**, see the 10th row of table 2). The procedure is detailed in Ref.¹²⁴ and will not be repeated here.

As in the RAM36 and BELGI codes, XIAM treats nuclear quadrupole interactions of up to one coupling nucleus in a first order approximation, which is sufficient to fit the hyperfine structure of nuclei with relatively small quadrupole moments like ^{14}N . However, as explained earlier the program XIAM has its disadvantages at treating internal rotations with low barrier heights, since only a limited number of parameters can be fitted.

3.4. Coupling two (or more) different LAMs

Effective tunneling-rotational Hamiltonians, where all low-order terms allowed by group theory are considered in the Hamiltonian operator, are relatively successful in fitting measured frequencies nearly to experimental error for a wide variety of molecules with two or more LAMs, i.e. hydrazine or methylamine¹²⁶⁻¹²⁷. They are referred to in Table 2 as the **“Tunneling”** code (see the 15th row of Table 2) or the **Poznan code** (16th row of Table 2). They are very fast, efficient and can be applied to excited vibrational states. On the other hand, they are “local” methods where each of the LAM states are fitted separately. Like all “local” methods they suffer from the following weak points: (i) Near or above the top of the barrier to the tunneling motion, the energy levels cannot be treated by the tunneling Hamiltonians. (ii) It is almost impossible to relate the tunneling parameters for one vibrational state to those for another vibrational state, therefore the tunneling-rotational levels belonging to different large-amplitude and/or small amplitude vibrational states must be treated separately. (iii) The physical meanings of the various coefficients in the phenomenological tunneling Hamiltonian are often obscure.

Recently, a new hybrid effective-Hamiltonian formalism was developed for methylamine-like molecules, the **BELGI-hybrid** code (see the 17th row of Table 2). In this hybrid formalism the back-and-forth (oscillatory) umbrella motion is described by a tunneling formalism, while the internal rotation motion is

treated using a formalism containing explicit expressions for the kinetic energy operator and the three-well potential energy operator. Such a formalism allows us to calculate all torsional states having the same oscillatory motion quantum number simultaneously. This code has been successfully applied to methyl malonaldehyde¹²⁸ and more recently to methylamine in its excited torsional states¹²⁹.

3.5 Modeling excited vibrational state(s)

Most “local” approaches can deal with excited vibrational states such as SPFIT/SPCAT, ERHAM, the “tunneling” code and the “Poznan”. To our knowledge, XIAM has never been applied so far to any excited vibrational state.

For the global approach, a version of BELGI, **BELGI-2states** (see the 18th row of Table 2) was used in the past to deal with infrared transitions of acetaldehyde¹³⁰ and methanol¹³¹ from the ground vibrational state to a given vibrational state, which was considered as “isolated” from other vibrational states.

In the case of acetaldehyde, where a small amplitude vibrational mode (ν_{10}) is interacting with the rotation energy levels corresponding to torsional states with $\nu_t \geq 3$ of the ground state, another code was developed, named **BELGI-509** (19th row of Table 2)¹³² but i) it was not totally successful to fit all the transitions observed and ii) it was limited to J values of 20.

For methanol, the situation is more problematic than acetaldehyde: the $\nu_t = 3$ state is not yet included in the database¹⁰² since i) it is above the top of the barrier and ii) it strongly interacts with the C-O stretch state. However, Lees et al. has mapped the energies of the CO stretch, OH bending and CH₃ rocking, showing a strong coupling among those three modes as well as with the excited torsional states $\nu_t = 3$ and 4¹³³. More recently the rotational spectrum of methanol in $\nu_t = 3$, as well as the K = 0 A-state of $\nu_t = 4$ has been recorded in the 8-1654 THz¹³⁴ and in the 2.48-2.77 THz¹³⁵ frequency range using the spectrometer at JPL, USA. The data was analyzed and modeled with a power series¹³⁴, but a global fit is still missing.

For methyl formate, assignments were done in $\nu_t = 2$ for the parent species H¹²COO¹²CH₃ but the rotational transitions in this excited state cannot be fitted yet. It is likely that the $\nu_t = 2$ analysis will require an extension of the current model to include perturbation from the two other modes ν_{12} and ν_{17} for this molecule⁴⁶. This has a much more complex interacting scheme than acetaldehyde as it involves three small amplitude states (ground state, $\nu_{12} = 1$ and $\nu_{17} = 1$ states).

A new multi-state vibration-torsion-rotation fitting program for molecules with a C_{3v} top and C_s frame, based on the same procedures as in RAM36, is in progress and is presently being applied by Ilyushin et al. to acetaldehyde as the first “test” case¹³⁶ (see 20th row of table 2).

3.6 Intensities for internal rotors

Intensities are of great importance for astronomers as they will retrieve the column densities or abundances from them.

If one assumes Local Thermodynamic Equilibrium (LTE), which is an assumption often made in astrophysical analyses, the total molecular column density N for a given species and the rotational temperature T is given by¹³⁷:

$$\frac{N_u}{g_u} = \frac{3kW}{g_u 8\pi^3 \nu S\mu^2} = \frac{8\pi k \nu^2 W}{g_u h c^3 A_{ul}}$$

or its logarithm:

$$\begin{aligned} \ln \left[\frac{8\pi k \nu^2 W}{g_u h c^3 A_{ul}} \right] &= \ln \left(\frac{N}{Q} \right) - \frac{E_u}{kT} \\ \ln \left[\frac{3kW}{g_u 8\pi^3 \nu S\mu^2} \right] &= \ln \left(\frac{N}{Q} \right) - \frac{E_u}{kT} \end{aligned} \quad (5)$$

where h is the Planck constant, k is the Boltzmann constant, c is the speed of light in vacuum, ν is the line frequency. N_u is the upper state column density, g_u and E_u are the degeneracy and energy of the upper state involved in the molecular transition, Q is the partition function and W is the integrated intensity given in K km/s. $S\mu^2$ designates the line strength of the transition and A_{ul} represents the Einstein coefficient for spontaneous emission. Since $S\mu^2$ is proportional to A_{ul} the two equations above will lead to the same result. The parameters obtained from the observed spectrum are the integrated intensity (W) and the frequency of the line ν in the observed region while the spectroscopic data provided by the laboratory studies is $S\mu^2$, g_u , E_u and Q . Each one of the internal rotation states, A and E, can be considered as an independent molecular species for the calculation of line intensities.

To determine the column density N and the temperature T from the interstellar spectrum, assuming LTE, one can plot the left side of Eq. (14), $\ln (N_u/g_u)$, as a function of the second term on the right side (E_u/kT). This plot is called a temperature diagram. A linear regression of Eq. (14) will then provide $-1/T$ which is the slope of the temperature diagram and the intercept with the y axis will give $\ln(N/Q)$.

In this process two quantities may cause trouble, especially for internal rotors. The first difficult quantity to get is the line strength $S\mu^2$. Detailed discussions about how to calculate the line strengths for internal rotors exist, but only two aspects will be given here. The line strength ($S\mu^2$) of the torsion-rotation transition between the level L' containing all $(2J'+1)$ M' components and the level L containing all $(2J+1)$ M components is given by the formula⁵⁹:

$$S(L';L) = \frac{1}{\mu_z^2} \sum_M 3 |\langle J', \tau', M, v_t', \sigma' | \mu_z | J, \tau, M, v_t, \sigma \rangle|^2 \quad (6)$$

where μ_z is the instantaneous electric dipole moment along the laboratory-fixed Z axis and $|J', \tau', M, v_t', \sigma'\rangle$ and $|J, \tau, M, v_t, \sigma\rangle$ are the wave functions that represent levels L' and L .

As shown by Ilyushin et al. in Eqs. (1-4) of Ref.¹³⁸, the torsion rotation asymmetric rotor functions $|J, \tau, M, v_t, \sigma\rangle$ can be written as a product of torsional $|K, v_t, \sigma\rangle$ and symmetric rotor basis functions $|J, K, M\rangle$ used to set up the torsion-rotation Hamiltonian matrix of Eqs. (B1-B4). Eq. (6) can thus be rewritten as:

$$S(L'; L) = \frac{1}{\mu^2} \sum_M \left| \sum_{\alpha} \sum_{\substack{K', K = -J, J \\ v_t'', v_t' = 0, N_t - 1}} C_{K', v_t'', \sigma'}^{J', \tau', v_t', \sigma'} C_{K, v_t', \sigma}^{J, \tau, v_t, \sigma} \times \langle K', v_t'', \sigma' | \mu_{\alpha} | K, v_t', \sigma \rangle \times \langle J', K', M | \Phi_{Z\alpha} | J, K, M \rangle \right|^2, \quad (7)$$

where the coefficients $C_{K, v_t', \sigma}^{J, \tau, v_t, \sigma}$ are the eigenvector coefficients obtained after diagonalization of the torsion-rotation Hamiltonian matrix of Eqs. (B1-B4), the $\Phi_{Z\alpha}$ represents the direction cosines and μ_{α} is the electric dipole moment along molecular-fixed $\alpha = x, y, z$ axis. N_t is the number of torsional basis functions kept in the diagonalization of the torsion-rotational Hamiltonian (see section 3.1.2.b for the BELGI code).

An important point can be seen from the last expression that, the μ_x , μ_y and μ_z contributions are added together before squaring. Therefore, the relative signs of the dipole moment components are important for obtaining the correct intensity calculations. Since we sum over μ_x , μ_y and μ_z contributions, the meaning of the traditional *a*-type, *b*-type and *c*-type selection rules for transitions in rigid asymmetric tops is somewhat lost. If energy levels of the same symmetry interact due to rotation-torsion effects, the basis functions will be « mixed », and K ($= K_a$ or K_c) will no longer be a good quantum number. The consequence is the observation of the so-called “forbidden” transitions, which are forbidden in a rigid molecule but are allowed in internal rotors because of the presence of rotation-torsion interactions.

The second quantity difficult to evaluate is the partition function. It is often a confusing issue. The studies on methyl formate HCOOCH_3 by Favre et al.¹⁰⁰ have pointed out the importance of deriving accurate partition functions and therefore molecular densities. In their study, the authors tested the convergence of the partition function for ^{13}C -isotopologues, which ensures that high enough energy levels (i.e vibrationally and/or torsionally excited levels) have been included for a particular temperature. The authors accounted for all torsional-vibrational energy states up to $v_t = 5$. In comparison, in the JPL catalog entry, only contributions of the $v_t = 0$ and $v_t = 1$ level are incorporated into the partition function for the parent species of methyl formate. This results in a higher inferred methyl formate abundance than would be derived using the value in the JPL catalog, since the partition function calculated by Favre et al.¹⁰⁰ is larger by a factor of 1.2 at a temperature of 150 K and by a factor of 2.5 at 300 K than in the JPL tables. A new systematic study showing the necessity of using a complete partition function (in particular including high excited torsional states) to derive reliable interstellar molecular densities and temperatures was also performed¹³⁹.

4. Internal rotors as probes for the study of the interstellar medium (ISM).

4.1 “Hot cores” internal rotors and the grain-gas model

Stars form within interstellar clouds. In these clouds, the gas and dust begin to collapse under their own gravitational attraction. As the cloud collapses, the material at the center starts to heat up. Known as a protostar, the hot core at the heart of the collapsing cloud will one day become a star. Observations of star-forming cores, at centimeter, millimeter, and sub-mm wavelengths, show rich molecular emission spectra², with rotational (excitation) temperatures >100 K. These inner zones at 100K are known as hot cores, in the case of high-mass star formation, or hot corinos, in the case of low-mass protostars.

The molecules responsible for these emissions can be simple species like CO, CS, and HCN, or much more complex organics, among which many are internal rotors. Table 3 shows some internal rotors detected so far in hot cores with their relative abundances.

Table 3: Observed column densities (in cm⁻²) for internal rotors in hot cores^a

Molecules	Sagittarius B2(N)	Orion Hot Core (HC) / Hot Core Southwest (SW) / Compact Ridge (CR)
CH ₃ OH	1.8x 10 ¹⁹ (193) (source size 3’')	9x 10 ¹⁷ - 3x 10 ¹⁸ (143) (HC/SW, source size 3’')
CH ₃ OCH ₃	1.9x 10 ¹⁸ (193) (source size 2.5’')	3.5x 10 ¹⁷ (b) (CR, source size ~1.2’')
HCOOCH ₃	4.4x 10 ¹⁷ (193) (source size 4’')	3-4 × 10 ¹⁷ (100) (HW,CR, source size ~1.2’')
CH ₃ CHO	2.8x 10 ¹⁷ (193) (source size 3’')	1.4-1.6x 10 ¹⁵ (143) (HC/SW, source size 3’')
CH ₃ COOH	1.1x 10 ¹⁶ (193) (source size 4’')	3-12 x 10 ¹⁵ (184) (SW, source size 3’')
CH ₃ NCO	1-2 x 10 ¹³ (118)	4-7x 10 ¹⁵ (143) (HC/SW, source size 3’')
CH ₃ CHNH	7x 10 ¹³ (190) (in absorption.)	

$\text{CH}_3\text{C(O)NH}_2$	$1.4 \times 10^{17} \text{ }^{(117)}$ (source size 0.9'')	$1 \times 10^{15} \text{ }^{(143)}$ (HC, source size 3'')
CH_3NHCHO	$< 1 \times 10^{-17}$ (upper limit) ¹¹⁷	
CH_3NH_2	$6 \times 10^{17} \text{ }^{(193)}$ (source size 3'')	$4 \times 10^{15} \text{ }^{(143)}$ (SW, source size 3'')
CH_3SH	$1 \times 10^{16} \text{ }^{(193)}$ $2.94 \times 10^{16} \text{ }^{(193)}$ (source size 5'')	$5.0 \times 10^{15} \text{ }^{(204)}$ (HC, source size 10'')
CH_3COCH_3	$5 \times 10^{13} \text{ }^{(26)}$	$1.1\text{-}1.4 \times 10^{16} \text{ }^{(143)}$ (HC/SW, source size 3'')
$\text{CH}_3\text{CHCH}_2\text{O}$	$6 \times 10^{13} \text{ }^{(107)}$ (source size 5'')	
$\text{CH}_3\text{OCH}_2\text{OH}^c$		
$\text{CH}_3(\text{O})\text{OCH}_3$		$4.2 \times 10^{15} \text{ }^{(32)}$ HC, source size 15'')
$t\text{-CH}_3\text{CH}_2\text{OCH}_3$		$\leq 4.0 \times 10^{15} \text{ }^{(216)}$ (SW)

^a Single-dish observations for Refs. ^{32, 193, 107, 190, 204}. Interferometric observations for Refs. ^{100, 117, 143, 184}.

^b Interferometric observation, Brouillet et al. *A&A*. 2013, 550, A46

^c Metoxymethanol was detected so far only towards the high-mass star-forming region NGC 6334⁸³

One of the main questions is how those complex organic molecules are formed. For a long time, it was thought that gas-phase processes (mainly ion-molecule reactions) could be responsible for the formation of complex molecules in the hot cores. However, those reactions are usually not efficient enough to explain the column densities observed for those species, including for the internal rotor methyl formate HCOOCH_3 , which is one of the most abundant species in hot cores (sometimes referred as a ‘‘hot core tracer’’).

Therefore, a number of chemical models were developed to explain the formation of complex organic molecules in star-forming region^{140, 141}. These models (gas-grain models) explain the formation of the complex organic molecules on the surfaces or within the ice mantles of dust grains formed in an earlier cold phase. Ultraviolet radiation (UV) photodissociates molecules in the ices, and produces different radicals that react with each other to form new species. The composition of the ice and the abundances of various molecules can be found in the literature, e.g.¹⁴²

Orion-KL represents a unique case: in this near-by star-forming region, a recent explosive event some 500-1000 years ago has occurred. It was proposed that two or more massive stars collided and produced shocks that could have released complex molecules from the grain mantles because of dust heating. This event may have especially affected the relatively large molecules for which no gas-phase-only formation route is satisfactory. Astrochemical models need to take into account this event.

Internal rotors are really at the heart of the issue for testing astrochemical models. Methanol CH_3OH is a very important species in the gas-grain model. The fractional abundance of gaseous methanol (relative to hydrogen) is $\sim 10^{-9}$ in cold clouds and $\sim 10^{-6}$ in hot cores, where ices have sublimated. Methanol is believed to be formed on the dust grains during the cold (early) phase, from the successive addition of atomic hydrogen (H) and CO on the grains. It can then be photolysed by UV radiation, producing radicals such as HCO , CH_3 , CH_3O , and CH_2OH on the ice surface. During star formation the dust is warmed-up, allowing these radicals to become mobile (around 30 K), and to react together (as schematically shown in Figure 9) to produce complex organic molecules. Eventually, at higher temperatures, the complex organic molecules evaporate into the gas phase, which allows us to detect them through their rotational spectra. The grain surface chemical model was successful in predicting the appropriate abundances for methyl formate HCOOCH_3 in hot cores (typically $\sim 10^{-8} \times n(\text{H}_2)$), which could not be explained correctly by gas-phase mechanisms, and dimethyl ether CH_3OCH_3 by using the following surface reactions¹⁴⁰:

But more complex formation mechanisms than simple single-atom addition reactions on grain surfaces occur. Dimethyl ether desorbs strongly around 70 K and its earlier evaporation results in fast gas-phase destruction¹⁴¹. Gas-phase production of dimethyl ether (following methanol evaporation) seems thus to play an important role over grain-surface formation. Calculated abundances for dimethyl ether¹⁴¹ correspond with typical observed values of 10^{-8} – 10^{-7} with respect to H_2 .

Some issues remain tough. Methyl formate HCOOCH_3 , glycoaldehyde $\text{CH}_2(\text{OH})\text{CHO}$ and acetic acid CH_3COOH are structural isomers that have been detected in several star-forming regions. The $\text{CH}_3\text{COOH}/\text{HCOOCH}_3$ abundance ratio of $3\text{--}6 \times 10^{-2}$ reported in the Sgr B2(NLMH) hot core²³ cannot be explained by gas-phase chemistry. Based on the grain surface model, and the simple equations above, their observed abundances should be similar too. So, it was suggested that acetic acid has a different formation route than methyl formate and glycoaldehyde¹⁴¹.

Figure 9. The ice grains model (simplified as other species can be present such as CH_4 , NH_3 ...) ^{140,141}. From upper to lower: Methanol is formed during the early cold phase in the ice grains. UV radiation photodissociates methanol into radicals, which become mobile at temperatures $> 30\text{K}$, and react with each other in the warm-up phase, producing more complex species like methyl formate, glycoaldehyde, ethanol, dimethyl ether.

On the grain-surface, when temperatures are $\sim 30\text{ K}$ or above, acetaldehyde CH_3CHO is formed by the radical-radical association reaction between CH_3 and HCO . However, gas phase reactions must also produce a large amount of acetaldehyde since its abundance exceeds the amount of its isomer ethylene oxide ($\text{c-C}_2\text{H}_4\text{O}$) up to a factor of 3.5. In the gas phase, acetaldehyde is mainly produced by the reaction between O and C_2H_5 and/or by dissociative recombination ¹⁴²:

A revised gas-grain chemical model has thus been elaborated which reproduces the acetaldehyde column density of $1 \times 10^{17} \text{ cm}^{-2}$ observed by Belloche et al. in Sgr (as well as the column densities of other species) fairly well ¹⁴².

Nitrogen-bearing internal rotors are also very important in the chemical understanding of hot cores because they represent key molecules involved in the formation of prebiotic molecules and amino acids. Acetamide CH_3CONH_2 ²⁵, methyl isocyanate CH_3NCO ¹⁴³ and methylamine CH_3NH_2 ¹⁴⁴ were observed towards Sgr B2(N) with a column density $> 6 \times 10^{14} \text{ cm}^{-2}$, $5 \times 10^{17} \text{ cm}^{-2}$ and $4 \times 10^{15} \text{ cm}^{-2}$, respectively. N-methyl formamide (CH_3NHCHO) was tentatively detected towards Sgr ¹¹⁷ with an upper limit to its abundance of $1. \times 10^{-17}$, less than its structural isomer acetamide.

Sulfur(S)-bearing molecules are of great astrophysical importance since they are excellent tracers of early protostellar evolution. Their abundance is particularly sensitive to physical and chemical evolution in hot cores. Although several sulfur internal rotors were searched, methyl mercaptan CH_3SH is the only sulfur containing internal rotors detected so far.

Table 4 summarizes the various interstellar internal rotors detected or tentatively detected in different environments with their theoretical modeling codes used for their analysis.

4.2 Weeds

Methanol CH_3OH , methyl formate HCOOCH_3 , acetaldehyde CH_3CHO , dimethyl ether CH_3OCH_3 correspond to various criteria used to characterize what astronomers called “weeds”: 1) relatively high abundance compared to that of H_2 , on the order of $\sim 10^{-7}$; 2) a dense rotational emission spectrum; 3) found in or associated with regions between 100 and 300 K; 4) a large moment of inertia and/or associated with internal degrees of freedom such as torsion; 5) low-lying vibrational state; and 6) a spectrum that is particularly difficult to predict¹⁴.

We can however take advantage of the observations of the many lines produced by those “weeds” and get a lot of information about the ISM. We will show hereafter that internal rotors are excellent probes for studying the ISM.

4.2.1. Methanol CH_3OH

Methanol is a typical astrophysical molecule for which the rich and dense rotation-torsion spectrum has made this molecule a typical “weed” for radioastronomy. Gas phase methanol is observed in a wide range of interstellar environments, with typical abundances relative to H_2 of 10^{-6} – 10^{-7} in hot cores, 10^{-9} in dark clouds, and $<10^{-9}$ in diffuse molecular gas¹⁴⁵. Its first reported interstellar detection was in 1970 by Ball et al. in the molecular clouds Sgr A and Sgr B2 using the telescope at Green Bank, West Virginia¹⁶.

Various isotopomers have been observed such as CH_3OD ¹⁴⁶ and its ^{13}C -substituted form¹⁷. Methanol was also observed in comet Austin by Bockelée-Morvan et al. in the millimeter wavelengths⁷. It was observed in the infrared spectral range, in the 3 μm features in several comets¹⁴⁷ and the icy mantles of interstellar dust grains¹⁴⁸. The first detection of methanol in a protoplanetary disk was reported in 2016⁸.

The astrophysical detections of methanol and its isotopomers mostly relied on the spectroscopic studies by Xu and Lees and their coworkers. A number of those studies were performed using the RAM approach and the BELGI- C_s -methanol code¹⁰²⁻¹⁰⁵.

Methanol as a probe of the physical conditions

Beside being a “weed”, one can benefit from the many transitions observable for methanol. Methanol is in fact a useful molecular tracer of dense gas¹⁴⁸, very sensitive to the density and the kinetic temperature of the gas. In 2011 Wang et al. observed the methanol emission from molecular cloud Orion KL with the

Herschel/HIFI instrument¹⁴⁹. They studied isolated E-type $v_t = 0$ methanol transitions to explore the physical conditions in the molecular gas. All the chosen methanol lines show asymmetry in their line profiles, indicating the existence of multiple contributions from different kinematic components in Orion KL. Three different spatial contributions from the *hot core*, low velocity flow, and compact ridge can be distinguished.

Methanol as a thermometer

Torsionally excited methanol can be used as a temperature probe, since the first excited torsional state lies near 200 cm^{-1} above the ground state, i.e. about 290 K ¹⁵⁰. By observing transitions of torsionally excited methanol in Orion and simultaneously observing the same transitions in the ground state, Hollis et al. suggested that the ground-state transitions come from a 90 K region, while the torsionally excited transitions may come from a 200 K region¹⁵¹. However, methanol spectra are not well predicted yet in its higher excited state ($v_t > 2$, see section 3.5) so care is urged here.

Methanol exhibits maser activity in the ISM.

Masers are analogous to lasers, which generate coherent electromagnetic radiation at higher energies. In the case of methanol, the maser emission occurs in microwave and submillimeter-wave regions. There are two classes of masers. Class I methanol masers arise from outflows and are found at some distance from the exciting source. They are associated with shocked material in protostellar outflow and thus trace very early stages of massive star formation¹⁵². Class II masers arise in warm gas with significant infrared pumping. The infrared pumping is believed to excite methanol through the excited torsional states. Cragg et al.¹⁵³ have performed several studies of methanol maser action and concluded that probably at a temperature above 300 K , transitions beyond the excited state $v_t = 3$ are required. To perfectly understand the maser activity of methanol we thus need spectroscopic information in higher excited states. However, as explained in Section 3.5, the rotational transitions at $v_t \geq 2$ are not yet determined within measurement accuracy.

Methanol as fundamental physical constant probe

A few years ago, Ubachs, Bethleem and Jensen suggested using the shifts of the methanol frequencies in the microwave range coming from stars located at 7 Gyrs to determine if one of the fundamental physical constants, the ratio of proton mass to the electron mass $\mu = m_p/m_e$, could show a time dependence. Indeed, methanol transitions turned out to be very sensitive to the variations of this ratio μ ¹⁵⁴. Jensen et al. used the very precise modeling of the rotation-torsion energies by the RAM/BELGI approach to predict how frequencies vary as a function of the nuclei mass and calculate sensitivity coefficients, which measure this variation¹⁵⁴. Based on those coefficients, and from radio-astronomical observations of the star PKS1830-211, Menten et al. deduced a constrain of $\Delta\mu/\mu = (0.0 \pm 1.0) \times 10^{-7}$ at redshift $z = 0.89$, which corresponds to a look-back times of 7 billion years . Obviously, this fundamental property μ has almost not changed since that time¹⁵⁵.

Table 4. Examples of interstellar internal rotors and their theoretical modeling for spectra analysis.

Internal rotor	Interstellar source ^a	Spectroscopic particularities	Barrier height ^b	ρ^c	v_t^e	$J_{\max}^f$	Code used ^g	Re f. ^h
One-top (by increasing atom number)								
CH ₃ OH	cc, hc, gc, of, ppd, gl comets maser lines	1 top, light, intermediate barrier, LAM splitting, large coupling between internal and global rotation	$V_3 = 374$ $F = 27.6, s = 6$	0.8	0,1,2 (3, 4) ⁱ v_{CO} stretch	30	BELGI-C _s -methanol BELGI-2-STATES other	¹⁰² 134, 135 131 133
¹³ CH ₃ OH, CH ₃ ¹⁸ OH	yso				0,1,2	30	BELGI-C _s -methanol	¹⁰³
CH ₃ OD	hc,gc ?				0,1	20	BELGI-C _s -methanol	¹⁰⁴
CD ₃ OH	lmp				0,1	20	BELGI-C _s -methanol	¹⁰⁵
CH ₃ SH	hc, gc, cc, msf, lmp	Similar to CH ₃ OH	$V_3 = 441$ $F = 15.1, s = 13$	0.7	0,1,2,3	40	BELGI-C _s -methanol	¹⁰⁶
CH ₃ SD	Tentative lmp		$V_3 = 434$ $F = 10.4, s = 19$	0.5	0,1,2,3,4	53	RAM36	²¹²
CH ₃ CHO	cc, hc, gc,pc	Intermediate barrier, large coupling constant between internal and global rotation	$V_3 = 408$ $F = 7.6, s = 24$	0.3	0,1,2,3,4 0,1,2	26 66	BELGI-C _s RAM36	⁹¹ 114
¹³ CH ₃ CHO CH ₃ ¹³ CHO			$F = 7.6, s = 24$	0.3	0,1,2	60	RAM36	¹¹⁶
CH ₃ CDO CD ₃ CHO CD ₃ CDO			$F = 7.0, s = 26$ $F = 4.9, s = 36$ $F = 4.4, s = 41$		0,1 0,1 0	20 20 14	Elkeurti BELGI-C _s BELGI-C _s	¹⁷⁰ 92 93
CH ₃ NCO	hc	Very low barrier, large splittings, hyperfine splittings	$V_3 = 22$ $F = 8.8, s = 1$	0.4	0	10 41	RAM36 SPFIT	¹¹⁸ 143
<i>cis</i> -HCOOCH ₃	hc, gc	Intermediate barrier, small rotational constant A, 2 excited vibrational states populated at room temperature	$V_3 = 373$ $F = 5.5, s = 30$	0.08	0,1,2 0,1,2 0,1 0,1	62 60	RAM36 ERHAM Japan BELGI-C _s	^{46, 113} 73, 74 177 178
HCOO ¹³ CH ₃	hc		$F = 5.7, s = 32$		0,1	63	BELGI-C _s	^{96, 99}
H ¹³ COOCH ₃	hc, msf		$F = 5.7, s = 32$		0,1	59	BELGI-C _s	^{96, 100}
HC ¹⁸ OOCH ₃	hc		$F = 5.7, s = 32$		0	63	BELGI-C _s	⁹⁸
HCO ¹⁸ OCH ₃	hc		$F = 5.7, s = 32$		0	63	BELGI-C _s	⁹⁸
DCOOCH ₃	hc		$F = 5.5, s = 31$		0	69	BELGI-C _s	^{97, 101}
<i>trans</i> -HCOOCH ₃	hc tentative	Low barrier large splitting, large coupling constant	$V_3 = 13$ $F = 5.6, s = 14$	0.29	0	5	BELGI-C _s	¹⁸⁰

CH ₃ COOH	hc, gc	Low barrier, large splittings	$V_3 = 170$ $F = 5.6, s = 14$	0.07	0,1,2	30 79	BELGI-C _s RAM36	⁹⁴ 115
CH ₃ CONH ₂	hc, gc	Low barrier, large splittings, hyperfine splittings	$V_3 = 25$ $F = 5.6, s = 2$	0.08	0,1,2	20	BELGI-C _s Japan	^{24, 25, 95} 109, 186
CH ₃ NHCHO	Tentative hc	Low barrier, large splittings, hyperfine splittings	$V_3 = 52$ $F = 5.6, s = 4$	0.08	0,1,2	62	RAM36	^{117,}
Two-tops								
CH ₃ OCH ₃	hc,gc, Imp,msf	2 equivalent tops, high barrier	$V_3 = 957$ $F = 6.8, s = 61$	0.2	0,1	70	ERHAM	⁶⁹
¹³ CH ₃ OCH ₃ CH ₃ O ¹³ CH ₃	msf						ERHAM	³¹
CH ₃ COCH ₃	hc	2 equivalent tops, intermediate barrier	$V_3 = 422$ $F = 5.6, s = 33$	0.06	0,1	60 38	ERHAM PAM-C _{2v} -2tops	⁷⁰ 112
CH ₃ COOCH ₃	hc	2 inequivalent tops, low and intermediate barriers	$V_{3,1} = 102$ $V_{3,2} = 422$ $F_1 = F_2 = 5.5$	0.06	0	40	BELGI-C _s -2Tops	^{32, 119} ,219
CH ₃ CH ₂ OCH ₃	hc tentative	2 inequivalent tops, high barriers	$V_{3,1} = 838$ $V_{3,2} = 844$ $F_1 = F_2 = 6.6$	0.15	0,1	92	Tunneling code ERHAM	²¹⁷ 67, 68, 71
Two large amplitude motions								
CH ₃ NH ₂	hc, gc	internal rotation coupled with wagging of NH ₂ group			0,1,2 0,1,2 0,1	40 40 40	Tunneling code Poznan code Hybrid-BELGI	^{127, 198} 126 129
¹³ CH ₃ NH ₂	hc upper limit						Tunneling code	¹⁹⁹

^a Interstellar sources where the internal rotors were detected (or upper limits were determined). Abbreviations (from Table 1 Ref.²): circ, circumstellar envelope around evolved star/protoplanetary nebula; cc, cold cloud core; hc, hot core/corino; gc, galactic center cloud; of, outflow; added abbreviations: ppd: protoplanet disk; gl: galaxie lointaine; yso: young stellar objects, Imp: low mass protostar, pc: prestellar cores; msf: massive star forming region

^b Height of the barrier V_3 , internal rotation constant F , reduced barrier $s = 4V_3/9F$.

^c Coupling constant between internal and global rotation, see Eq. (2).

^d Torsional state (v_t) studied

^e Maximum value of J fitted

^f Name of the code, see Table 1 and text

^g Not exhaustive list of references for laboratory spectroscopy

^h Methanol $v_t = 3$ and 4 transitions were analyzed and fitted using polynomial expansions but a global fit is missing so far

Methanol as an astrobiology probe

Methanol also plays an important role in astrobiology. For example, it is a component of interstellar ices. When ices containing water, methanol and other common molecules such as HCN and ammonia are irradiated in the laboratory, complex mixtures of organic molecules are produced, which may include glycine and other amino acids or their precursors¹⁵⁶.

The role of the isotopologues of methanol

While other species detected in space are formed by gas-phase chemistry alone, or by a combination of both gas- and solid-phase generation, methanol is a complex organic compound which is formed solely in the ice phase via surface reactions on dust grains¹⁵⁷⁻¹⁵⁸.

The present privileged formation path is a successive hydrogenation of solid CO on cold grains, but to establish firmly whether methanol is formed from CO on grains or not, Charnley et al.¹⁵⁹ suggested observational tests. One of those tests is the “isotope labeling” based on the observed effect of ¹³C fractionation into CO at low temperatures due to the reaction:

where $\Delta E = 35$ K. This process is only efficient at 10 K. Therefore, it results in an overabundance of ¹³CO (which is formed on cold grains). Assuming this selective fractionation remains not altered by the processes of adsorption and desorption, then the ¹²C/¹³C ratio in various molecules could be used to distinguish between formation from CO on cold grains and gas-phase formation. **If methanol is formed from CO on grains, the ratios ¹²C/¹³C should be similar to that found in CH₃OH and CO.** Relying on the accurate frequency and intensity measurements of 8 A and E lines of methanol, Wirström et al. showed that the **¹²C/¹³C ratio test is indeed consistent with methanol formation from hydrogenation of CO on grain surfaces**¹⁶⁰.

The detection of deuterated methanol also allows one to study the chemical pathways leading to their formation and to trace the chemical and physical conditions of the observed environment. Methanol exhibits a high deuterium fractionation in hot corinos. Mono-deuterated methanol, CH₃OD and CH₂DOH, are detected in IRAS 16293 with a deuterium fractionation of ~ 1.8 % and 37 %, respectively, doubly-deuterated methanol (CHD₂OH) are observed with a deuteration of 7.4 %¹⁶¹. Triply deuterated methanol CD₃OH was also observed in IRAS 16293 with a deuterium fractionation ratio of 1.4 %¹⁶². These values are much greater than those expected from the cosmic D/H ratio (~ 10⁻⁵). In cold environments, the deuterium molecular enrichment can be explained by gas-phase chemistry, whereas in hot regions it is driven by chemistry on the dust icy surface.

This clearly shows the importance of spectroscopic studies on isotopologues. None of those observations above would have been possible without the intensive work by Xu, Lees and collaborators on $^{13}\text{CH}_3\text{OH}$ ¹⁰³, CH_3OD ¹⁰⁴ and CD_3OH ¹⁰⁵.

4.2.2 Acetaldehyde CH_3CHO

Like methanol, acetaldehyde is also considered to be a “weed” molecule by radio-astronomers because of its dense spectrum, its large dipole moment value and the presence of many low lying excited torsional states. It is a molecule that has been observed in many source types in the ISM: first detected in 1973 by Gottlieb et al. in Sgr B2²⁰, it was observed in cold molecular clouds¹⁶³, in hot cores¹⁶⁴, hot corinos¹⁶⁵, in star-forming regions¹⁶⁶ and in the disk of a high redshift spiral galaxy located near the quasar PKS 1830-211¹⁶⁷. Codella et al. reported the first high-resolution images of acetaldehyde (CH_3CHO) emission towards the chemically rich protostellar shock L1157-B1, with a high CH_3CHO relative abundance, of $2-3 \times 10^{-8}$, similar to what is found in hot corinos¹⁶⁸.

As detailed in Section 3, the combined microwave and far-infrared spectroscopy of acetaldehyde was studied, using the RAM approach and the BELGI-C_s code up to about 590 cm^{-1} which corresponds to the lowest small amplitude vibration of acetaldehyde⁹¹. The published atlas of predictions for acetaldehyde, often used by astronomers, contains transitions from 900 MHz to 500 GHz with $v_t = 0, 1$ and $2, J \leq 26$ and $K_a \leq 14$ ⁹⁰.

In 2013, Smirnov et al. extended the spectral range for acetaldehyde with new laboratory measurements at Lille, France from 49 GHz to 1.6 THz. Using the RAM36 code they were able to fit 18552 transitions in the microwave range and 678 far-infrared transitions, increasing the range of rotational quantum numbers up to $J = 66$ and $K_a = 22$ for $v_t = 0, 1$ and 2 ¹¹⁴.

Various isotopic species of acetaldehyde were also studied with the RAM method. For the deuterated species the analyses do not extend much higher above the millimeter-wave range. On the other hand, there are studies combining microwave spectroscopy with far-infrared high resolution analysis of the $v_t = 1 \leftarrow 0$ fundamental band, which allow us to un-correlate the parameters. CD_3CHO was studied using BELGI-C_s in the ground torsional $v_t = 0$ and excited $v_t = 1$ state up to $J = 20$ ⁹². Acetaldehyde-1- d_1 (CH_3CDO) has been investigated in 1989 by Martinache and Bauder¹⁶⁹ and later by Elkeurti et al. by far-infrared spectroscopy¹⁷⁰. The broadband pure rotational spectrum of the fully deuterated isotopologue CD_3CDO has been recorded using a CP Fourier Transform millimeter wave spectrometer in the 75-110 GHz region⁹³.

The millimeter-wave and submillimeter-wave spectra of mono ^{13}C acetaldehyde ($^{13}\text{CH}_3\text{CHO}$ and $\text{CH}_3^{13}\text{CHO}$) were studied extensively using RAM36 by Margulès et al. up to 1 THz involving $v_t = 0, 1$ and 2 torsional states, with J up to 60 and K_a up to 20 ¹¹⁶.

Acetaldehyde as a tracer of different astronomical objects

Like methanol, acetaldehyde is not only a “weed” but also has an important role as an evolutionary tracer of different astronomical objects^{2,14}. In 2014, Occhiogrosso et al. showed that the chemistry of acetaldehyde is closely related to its isomer ethylene oxide or oxirane¹⁴², both of which are thought to be involved in certain amino acid production. In protostellar environments, the formation of complex organic molecules such as acetaldehyde is however still a question, because the relative importance of the gas phase processes compared to a direct formation of acetaldehyde on the grain surfaces is unknown.

Isotopic ratios, excited torsional states and formation of acetaldehyde

As acetaldehyde might form from both photodissociation-driven radical–radical reactions on grain surfaces and ion-neutral gas-phase reactions¹⁴¹, in principle, the observed isotopic ratios should depend heavily on the chosen pathway. Thus, characterization and detection of multiple isotopologues can provide valuable constraints on models of space chemistry. However, the detection of such isotopic species of acetaldehyde or torsional excited states is only at its beginning. Recent ALMA observations have been performed by Marcelino et al. of the protostellar system Barbad 1b, which is at the earliest stages of low-mass star formation¹⁷¹. They used the MADEX code developed by Cernicharo¹⁷² to reproduce the observed spectra of a number of complex organic molecules in B1b-S, and to obtain column densities and kinetic temperatures of the emitting region. Among the detected species, 15 transitions were found from the main species of acetaldehyde, with energies between 100–300 K. They also detected one transition arising from the deuterated substitution CH₃CDO, and 4 transitions (2 of them blended) from the vibrational state $\nu_t = 1$, with energy levels of ~300–400 K.

In 2019, also using ALMA surveys towards the protostellar binary IRAS 16293–2422 system, Jørgensen et al.¹⁷³ detected the two ¹³C isotopic acetaldehyde species (about 60 and 80 transitions for CH₃¹³CHO and ¹³CH₃CHO respectively, using spectroscopic data from Margulès et al.¹¹⁶). In the same paper the deuterated species CH₃CDO was unambiguously detected for the first time in the ISM.

4.2.3. Methyl formate HCOOCH₃

Methyl formate was first observed in the molecular cloud Sgr B2 in 1975 by Brown et al.¹⁸ and Churchwell and Winnewisser¹⁹ who identified a pair of rotational lines belonging to the A and E species arising from the internal rotation. Methyl formate is one of the most abundant organic molecules in interstellar hot cores. Its column density is of the order of 10¹⁵ - 10¹⁷ cm⁻² depending on the objects. Methyl formate was also detected in the comet Hale-Bopp¹⁷⁴ and in low-mass star-forming regions (hot corinos) such as NGC1333-IRAS4B and IRAS 2A¹⁷⁵. Its large abundance is difficult to account for with a production mechanism based only on gas phase reactions with methanol¹⁷⁶ and grain chemistry should be involved in methyl formate formation. The “success” story in detecting methyl formate and its isotopologues is again due to intensive laboratory work as explained below.

Formation of methyl formate and role of Isotopic species

In 2009, Carvajal et al.⁹⁶ identified for the first time 230 and 234 lines of the two ^{13}C -methyl formate isotopologues ($\text{HCOO}^{13}\text{CH}_3$ and $\text{H}^{13}\text{COOCH}_3$, respectively) in the Orion interstellar molecular cloud. To model the emission of these species, the authors used the MADEX excitation and radiative transfer code¹⁷². These detections have been made possible only through intensive spectroscopic work, involving both experimental laboratory study and theoretical analysis. The spectra were analyzed using the RAM and the BELGI-C_s code described in Section 3⁹⁶.

Based on the APEX observations, Favre et al. reported tentative detections of the ^{13}C -methyl formate isotopologue $\text{HCOO}^{13}\text{CH}_3$ towards four massive star-forming regions: Sgr B2 (N-LMH), NGC 6334 IRS 1, W51 e2, and G19.61-0.23¹⁰⁰. In addition, they used the 1 mm ALMA science verification observations of Orion-KL and confirmed the detection of the ^{13}C -methyl formate species in Orion-KL and imaged its spatial distribution. These detections were based on the spectroscopic work of Carvajal et al. in 2009⁹⁶. Favre et al. also performed LTE modeling of the observed data. Their analysis shows that the $^{12}\text{C}/^{13}\text{C}$ isotope ratio in methyl formate towards the Orion-KL Compact Ridge and Hot Core-SW components are 68.4 ± 10.1 and 71.4 ± 7.8 , respectively, for both of the ^{13}C isotopologues¹⁰⁰. These results are consistent with the $^{12}\text{C}/^{13}\text{C}$ ratio determined for CO and CH_3OH . This suggests thus that grain surface chemistry likely prevails in the formation of methyl formate.

In 2010 the singly-deuterated isotopologue of methyl formate, DCOOCH_3 , was tentatively detected based on eight lines, three of which are blended in IRAS 16293-2422, a hot corino well-known for its high degree of methanol deuteration (see section 4.2.1. above). To search for deuterated methyl formate, the authors used the spectroscopic work using the BELGI-C_s code by Margulès et al.⁹⁷. The derived deuterium fractionation is $\sim 15\%$, consistent with values for other deuterated species in this source and much greater than that expected from the deuterium cosmic abundance.

The spectrum of the ^{18}O isotopic species of methyl formate was also measured in the laboratory and analysed up to 660 GHz using the BELGI code. Following these studies, accurate predictions of line positions and intensities were performed. The line survey of Orion KL with the IRAM 30-m telescope permitted the detection of 80 spectral features that correspond to the first detection of the $\text{HCO}^{18}\text{OCH}_3$ and $\text{HC}^{18}\text{OOCH}_3$ species⁹⁸.

Only a few of the ^{18}O species have been detected up to now. Apart from methyl formate, there are six ^{18}O species detected so far in SgrB2: C^{18}O , $^{13}\text{C}^{18}\text{O}$, HC^{18}O^+ , $\text{CH}_3^{18}\text{OH}$, S^{18}O , and SO^{18}O (see Ref.⁹⁸ and references therein). Studying these species is important to give information about the isotopic ratio and to clean the ISM spectra from “weed’s” isotopic species in order to detect new species.

Excited states of methyl formate

Torsionally excited $v_t=1$ lines of methyl formate were also observed in Orion-KL by Kobayashi et al.¹⁷⁷ and in W51 e2 by Demyk et al.¹⁷⁸. In 2012, Takano et al. reported about 20 emission lines in the second

torsionally excited state ($v_t = 2$) of the methyl internal rotation in Orion-KL as well as lines from $v_t = 0$ and 1¹⁷⁹. Data of these three states was explained by a single vibrational temperature of 124.5 K.

The two ¹³C isotopologues of HCOOCH₃ in their first vibrationally excited state ($v_t = 1$) have also been detected in Orion-KL by means of 135 spectral features (of which 77 are un-blended) with no missing transitions in the 80–280 GHz range¹⁰⁰. Two compact ridge components were enough to model the line profiles with the MADEX code¹⁷², one at 110K, and a hotter and inner compact ridge at 250 K. The vibrational temperature (more accurately “torsional temperature”) $T_{\text{vib}} = 156$ K was obtained for H¹³COOCH₃ and HCOO¹³CH₃ in $v_t = 1$ in each compact ridge component¹⁰⁰. Since this value is similar to the averaged kinetic temperature adopted in the model (180 K), this indicates that collisions are probably the main mechanism to populate the vibrationally excited levels of methyl formate.

The *trans*-conformer of methyl formate – exploring “exotic” chemical reactions which could occur in the ISM

In 2012, Neill et al. reported the tentative detection of the higher-energy *trans* conformer of HCOOCH₃ in the GBT (Green Bank telescope) 100 m telescope observations of Sgr B2¹⁸⁰. They based the identification of seven transitions between 9.1 and 27.4 GHz on laboratory spectroscopy presented in the same work. The analysis of the spectrum was done using the BELGI code as the torsional barrier is very low (12.955 cm⁻¹) and the splitting due to internal rotation very large.

Knowing that the *trans* conformer is less stable than *cis* by 25 kJ mol⁻¹ (3000 K), it means that at typical temperatures of the ISM (100 K), one expects to have at thermal equilibrium a factor of about 10¹³ more *cis*-methyl formate than the *trans*.

This detection is related to another mystery. The abundance of *cis*-methyl formate compared to that of its structural isomers acetic acid (CH₃COOH) and glycolaldehyde (HOCH₂CHO) is very surprising and difficult to explain by the interstellar chemistry models. Methyl formate is found with the highest abundance in many sources, when acetic acid is predicted by quantum chemical calculations to be the most stable isomer (see also the next section on acetic acid)¹⁸¹. How methyl formate is synthesized in ISM is thus a central question.

The derived column density for *trans*-methyl formate was $3.1 (+2.6, -1.2) \times 10^{13}$ cm⁻² with a rotational temperature of 7.6 ± 1.5 K. This excitation temperature is significantly lower than that of the more stable *cis* conformer in the same Sgr source. This difference in the rotational temperatures of the two isomers suggests that they have different spatial distributions in this source and/or that they are produced by different mechanisms¹⁸⁰.

All those hypotheses have to be corroborated by a search of *trans*-methyl formate at higher frequencies in the millimeter-wave range. These experiments are, however, difficult to be done on a room-

temperature spectrometer because the equilibrium population of *trans*-methyl formate is so small. Likely a system using a discharge has to be used.

4.2.4. Dimethyl ether CH_3OCH_3

Dimethyl ether (DME, CH_3OCH_3) was first observed by Snyder et al. in the Orion Nebula molecular cloud in 1974²⁸. It is one of the most abundant interstellar complex organic molecules and considered as a “weed”. It is often detected towards high-mass star-forming regions and has a typical abundance of 10^{-8} – 10^{-7} with respect to H_2 . Bisschop et al. detected the first transitions from the two torsional excited states $\nu_{11} = 1$ and $\nu_{15} = 1$ towards the high-mass star-forming region G327.3-0.6³⁰. Like methyl formate, DME is one of these “hot core molecules” for which the exact formation mechanism is not completely clear. Again, two possible formation mechanisms are suggested: either grain surface reactions, such as the recombination of radicals formed by photodissociation of organic molecules at the surface of those icy grains, or warm gas-phase chemistry. The abundance of DME formed in the gas phase is expected to increase at higher temperatures compared to the grain-surface formation scenario. The observations of Bisschop et al. and models suggest that most dimethyl ether is present in gas that is warmer than 100 K, but a smaller fraction of 5%–28% is present at temperatures between 70 and 100 K³⁰. The DME present in the cooler gas is therefore likely formed in the solid state, while gas-phase formation is probably dominant above 100 K.

Spectroscopic data for this two-top molecule was mainly treated successfully with the ERHAM code as the barrier to internal rotation is high⁶⁹. Not only the parent species but also the ^{13}C species were studied. Based on laboratory work, transitions of $^{12}\text{CH}_3\text{O}^{13}\text{CH}_3$ DME have been detected in a large submillimeter-wave line survey of the high-mass star forming region G327.3-0.6 performed with the APEX telescope³¹.

The $^{12}\text{C}/^{13}\text{C}$ abundance ratio for DME in this interstellar source of about 25 ± 5 indicates the gas-phase formation route to be dominant for DME. Both carbon atoms are equivalent in DME, and thus its $^{12}\text{C}/^{13}\text{C}$ abundance ratio is expected to be less than that of methanol (which is around 50) if gas-phase processes are significant for the formation of DME.

4.3 Other complex organic internal rotors and prebiotic molecules

4.3.1. Acetic acid CH_3COOH

Acetic acid (CH_3COOH) was detected in the molecular cloud core known as the “Large Molecule Heimat” towards the high mass star forming region Sgr B2(N-LMH) by Mehringer et al.²² and towards W51e2 by Remijan et al.²³. A follow-up survey of 12 Galactic hot molecular cores for acetic acid by Remijan et al.¹⁸² resulted in the detection of an additional galactic acetic acid source towards G34.3+0.2, as well as in other hot cores^{165,183, 184}.

Although acetic acid is present in other star-forming regions, it was not detected in Orion-KL until very recently using 37 antennas of ALMA around 215.15 GHz to 252.04 GHz^{84,184}. As mentioned earlier, the Orion hot core region may have resulted from interaction of the surrounding gas with remains of an explosive event, which occurred in the region about 500–700 yr ago. Thus, this history makes Orion-KL an interesting source which however may not be representative of other high-mass star forming regions, to study the production route (at the icy surface of grains and/or in the gas phase) of complex organic molecules¹⁸⁴.

Compared to the previous molecules, acetic acid is a fairly heavy, and asymmetric oblate ($\kappa = +0.38$) internal rotor with a rather low torsional potential barrier ($V_3 = 170 \text{ cm}^{-1}$) and a small ratio of the methyl top moment of inertia to that of the rest of the molecule ($\rho = 0.07$). The available data in the 8–365 GHz range were analyzed with BELGI-C_s⁹⁴. A fit within experimental error for the $v_t = 0, 1, 2$ dataset with J up to 30 was obtained. The frequency range was then expanded in the sub-millimeter-wave range up to 845 GHz using RAM36 to explore the performance of RAM in the high- J region of rotational quantum numbers ($J \leq 79$)¹¹⁵.

A path to the bimolecular synthesis of glycine

In the laboratory, one of the paths to synthesize glycine, the simplest amino acid ($\text{NH}_2\text{CH}_2\text{COOH}$), occurs when acetic acid reacts with NH_2 ⁺¹⁸⁵. So, it is often assumed that a source containing acetic acid may also contain glycine.

Detection of isomeric pairs $\text{CH}_3\text{COOH}/\text{HCOOCH}_3$

The detection of acetic acid and its structural isomer methyl formate are important for the understanding of astrochemical reactions as described in the previous section.

4.3.2. Acetamide CH_3CONH_2

The search for peptide moiety

Proteins are an essential component of all living systems. They are polymers of amino acids ($\text{NH}_2\text{CH(R)COOH}$, $R = \text{H}, \text{CH}_3$, etc.) connected together by the peptide bond, $-\text{NHCO}-$. So far, even the simplest amino-acid, glycine ($\text{NH}_2\text{CH}_2\text{COOH}$), has not been detected unambiguously in the ISM¹⁸⁶, although the chemically related amino acetonitrile (NHCH_2CN) has¹⁸⁷. Only a few species containing the peptide moiety have been detected such as HNCO, formamide (NH_2CHO) and acetamide CH_3CONH_2 ²⁴.

Acetamide (CH_3CONH_2) is an asymmetric top, containing a methyl group internal rotor with a very low ($\sim 25 \text{ cm}^{-1}$) three-fold barrier. Therefore, the spectrum of this molecule is quite complicated. A number of laboratory studies of acetamide have been performed in the past^{109,188}. The authors employed the internal axis method (IAM) to fit the A and E species lines, but the residuals were high. Moreover, the E

state lines above $K_a = 3$ could not be assigned. Measurements for this species were then extended by Ilyushin et al.⁹⁵ with transitions from the first two excited torsional levels $v_t = 1$ and 2, as well as $v_t = 0$, in the range 49–149 GHz. Using the RAM method and the BELGI-Cs code, all available acetamide data with J up to 20 and K_a up to 11 for both A and E species was analysed.

In 2006, Hollis et al. reported the first detection of this molecule towards Sgr B2(N)²⁴. The authors identified eight transitions using the NRAO 100 m GBT in the range 9–47 GHz based on the spectroscopy work done by Ilyushin et al.⁹⁵. They also concluded that acetamide was only found in the cold halo gas (~ 8 K) surrounding the Sgr B2(N) hot core. Though acetamide is a more complex molecule, it has an extremely high abundance similar to that of acetaldehyde, CH_3CHO . In 2011, because of the importance of acetamide in prebiotic chemistry, Halfen et al. carried out a more extensive observational study of this species towards Sgr B2(N) at 1, 2, and 3 mm²⁵ and detected 54 lines. For the colder component of Orion ($E_u < 40$ K), they derived a column density of $N_{\text{tot}} = 5.2 \pm 3.5 \times 10^{13} \text{ cm}^{-2}$, whereas for the higher energy component $N_{\text{tot}} = 6.4 \pm 4.7 \times 10^{14} \text{ cm}^{-2}$.

4.3.3. N-methyl formamide CH_3NHCHO

Search and tentative detection of N-methyl formamide, the second-most stable isomer of the $\text{C}_2\text{H}_5\text{NO}$ family

Based on spectroscopic data produced using the RAM36 code, Belloche et al. searched towards Sgr B2 (N) for an isomer of acetamide, N-methyl formamide (CH_3NHCHO), but only an upper limit could be determined for that species¹¹⁷. Therefore, that study concluded that this species is at least a factor of 5–22 lower in abundance than acetamide. N-methyl formamide is the second more stable isomer of the $\text{C}_2\text{H}_5\text{NO}$ family, the most stable being acetamide. Belloche et al. found five transitions of N-methylformamide to be coincident with spectral lines detected towards the hot molecular core Sgr B2(N2). These lines are not contaminated by other species, and their intensities are well reproduced by the Local Thermodynamical Equilibrium LTE model of N-methylformamide. Therefore, this suggests that this species may be present in the Sgr B2 source¹¹⁷.

4.3.4. Methyl isocyanate CH_3NCO

An important molecule missing in the astrochemical models

In 2015, the Cometary Sampling and Composition (COSAC) mass spectrometer on board the Rosetta spacecraft's Philae lander detected methyl isocyanate, CH_3NCO , in the comet 67P/Churyumov–Gerasimenko, as one of the most abundant molecule at the comet surface¹⁸⁹. This is the only molecule detected on the surface of the comet. Shortly after the detection in the comet, Halfen et al. used the survey recorded with the 12 m telescope of the Arizona Radio Observatory (ARO) to search for methyl isocyanate

towards Sgr B2¹¹⁸. The search was based on a new spectroscopic analysis and new Fourier transform millimeter-wave measurements using the RAM36 program¹¹⁸. Halfen et al. detected all the internal rotation components of methyl isocyanate from five consecutive rotational transitions from 68 to 105 GHz, with 57% of the lines being uncontaminated.

The rotational spectrum of methyl isocyanate has been a challenge for experimentalists for a long time. The barrier to the methyl internal rotation is quite low ($\sim 20 \text{ cm}^{-1}$), creating large A-E splittings. The pure rotational spectrum is quite complex with the presence of strong vibrational satellite lines due to a low-lying C-N-C bending mode ($\sim 172 \text{ cm}^{-1}$). As for acetamide, the RAM method Hamiltonian was particularly useful because it incorporates torsional motion for a nearly free methyl rotor.

Observing a survey towards the Orion cloud, Cernicharo et al. made an extensive characterization of the methyl isocyanate rotational spectrum resulting in a list of 1269 firmly assigned laboratory lines, among which, 399 lines have been unambiguously identified and detected¹⁴³. The column densities for methyl isocyanate were determined to be around $4 \text{ to } 7 \times 10^{15} \text{ cm}^{-2}$ in Orion.

Fig. 10 illustrates selected lines observed for methyl isocyanate in Orion, combining data from the Orion 30m telescope with ALMA data. This figure shows the complexity of the spectrum. Various other species are also observed, and for some of them their torsional excited states are also present. Using their laboratory frequencies, Cernicharo et al.¹⁴³ were able to identify 76 lines (43 unblended and 33 partially blended) in the 3mm Sgr B2(N) data. The derived abundance ratios in Sgr B2 between CH_3OH , CH_3CN or HNCO and methyl isocyanate were not the same as the values derived for Orion KL. This points out the physical and chemical differences based on the evolutionary states of the clouds found in the Galactic centre (Sgr B2) and outer disk of the Galaxy (Orion).

Fig. 10. Selected lines of CH_3NCO observed with the IRAM 30 m radio telescope (2 upper panels) and the ALMA interferometer (2 lower panels). The red lines show the model for the methyl isocyanate emission from 143 , with the quantum numbers of the transitions as J_{Ka} (J is the rotational angular momentum quantum number and K_a is its projection along the a axis) of the lower state. The quantum number m is the free internal rotation quantum number, with $|m| = 0, 1, 3$ corresponding to the $v_t = 0$ A state, $v_t = 0$ E state and the excited torsional $v_t = 1$ A states respectively. Blue labels show the other species observed. The intensity units for the two lower panels (ALMA data) are in Jy/beam which can be transformed into brightness temperature T_{MB} (mean beam antenna in K) by multiplying the intensities by 9. The intensity scale for the two upper panels (IRAM 30m data) is T_{MB} . From Ref.¹⁴³.

4.3.5. Ethanimine CH_3CHNH

A key reaction intermediate required for the formation of alanine detected using broadband rotational spectroscopy

The detection of ethanimine in 2013 by Loomis et al. was achieved by using broadband rotational spectroscopy¹⁹⁰. Using the Chirped-Pulse Fourier Transform Microwave (CP-FTMW) spectroscopy³³, Loomis et al. realized that the spectra of a mixture of molecules produced from an electrical discharge of CH_3CN and H_2S showed several correspondances to unidentified features in the GBT PRebiotic Interstellar MOlecule Surv (PRIMOS) data towards Sagittarius B2 North (Sgr B2(N)). Loomis et al. identified those spectral features as belonging to E- and Z-ethanimine¹⁹⁰.

Apart from the CP-FTMW spectrum, the microwave transitions of ethanimine were measured at higher spectral resolution at the Harvard Smithsonian Center for Astrophysics (USA) between 8 and 40 GHz

with uncertainties of 5 kHz on a Fourier transform microwave (FTMW) spectrometer in order to resolve the nuclear quadrupole hyperfine and methyl group internal rotation splittings. The laboratory data was fit using the XIAM code with standard deviations of 12 kHz and 56 kHz for the E- and Z- ethanimine fits, respectively. A column density of $\sim 7 \times 10^{13} \text{ cm}^{-2}$ was determined with a fixed temperature of 6 K for E-ethanimine. A similar column density was found for the Z-ethanimine¹⁹⁰.

The formation and chemistry of ethanimine is of interest to understand the formation of amino acids and other prebiotic molecules. Ethanamine is the first reaction intermediate required for the formation of alanine. Experiments using UV radiation of simple ices composed of high abundance interstellar molecules have shown that amino acids can be formed when the analogues of ices contain the precursors necessary for a Strecker-like synthesis, with methanol converted to an aldehyde as the first step, as shown in the top panel of Figure 4 of Ref. ¹⁹⁰. On the other hand, Woon¹⁹¹ presented another possible pathway for amino acid synthesis using hydrogen atom addition to the nitrile CN to form an aldimine R-CHNH- (such as methanimine if R = H or ethanimine if R = CH₃), followed with another addition of a hydrogen to form an amine radical. A final radical-radical reaction with COOH (coming from formic acid – a known interstellar species) would then create the amino acid, in this case alanine¹⁹⁰:

The detection of ethanimine by Loomis et al. is therefore very important as the existence of the first reaction intermediate required for the formation of alanine is confirmed.

4.3.6. Methylamine CH₃NH₂

An important prebiotic species

In laboratory experiments where interstellar ice analogues are irradiated by UV photons, it has been shown that methylamine, and also the CH₂NH radical, are involved in reactions forming amino acids, in particular in the synthesis of glycine (NH₂CH₂COOH)¹⁹². Therefore, the astrophysical detection of methylamine being the simplest primary amine- (-NH₂) of prebiotic interest is very important.

For a long time, methylamine was only securely detected towards the high mass source Sagittarius B2 (Sgr B2) located in the Galactic centre¹⁹³. A tentative detection was done in Orion KL by Pagani et al.¹⁹⁴. Non-detections led to upper limit in a number of highmass young stellar objects (YSOs)¹⁹⁵ or in the low-mass Sun-like protostar IRAS 16293–2422B where the abundance of methylamine was determined to be two orders of magnitude lower than in Sgr B2¹⁹⁶.

So, the discrepancy between the abundance found in Sgr2 and the non-detections or tentative detection elsewhere have led astronomers to suggest that the formation of methylamine may depend on

the conditions occurring in the various regions investigated. On interstellar dust grains, two main formation pathways have been proposed:

In the gas phase, the following radical-neutral reaction:

was proposed to be the main formation for methylamine.

In 2019, Bøgelund et al. succeeded in detecting CH_3NH_2 along with other simple pre-biotic nitrogen-bearing species (CH_2NH , CH_3CN and NH_2CHO) towards three dense cores within the molecular cloud complex NGC 6334¹⁹⁷. This detection could only be achieved thanks to the high sensitivity, high angular and spectral resolution observations obtained by the ALMA observatory. Based on the identification of five transitional features (with all their hyperfine components) and on the spectroscopy studies of Motyienko et al.¹⁹⁸, Bøgelund et al. determined the methylamine column density ratios relative to methanol to be of the magnitude of 5×10^{-4} to 5.9×10^{-3} depending of the cores investigated¹⁹⁷.

The good agreement between methylamine derived from their observations and that from the hot core astrochemical models led the authors of Bøgelund et al.¹⁹⁷ to suggest that methylamine formation is more likely to occur via radical reactions on grain surfaces (Eq. 13) rather than through gas phase reactions.

The new modeling of methylamine using BELGi-Cs-hybrid¹²⁸⁻¹²⁹ (see section 3.4) may also allow for the observation of excited states of this species in the future. The spectrum of methylamine has been studied in its ground state in the millimeter and sub-millimeter spectrum using the tunneling formalism¹⁹⁸ as well as its¹³C isotopologue¹⁹⁹.

4.3.7. Metoxymethanol $\text{CH}_3\text{OCH}_2\text{OH}$

The photodissociation products of methanol

The detection of methoxymethanol was performed for the first time in the ISM using ALMA observations towards the high-mass star-forming region NGC 6334⁸³. The astrophysical interest of metoxymethanol is related to the photodissociation of methanol, which by producing various radicals, is an important source of organic species:

H

Methoxymethanol is supposed to form primarily through the direct reaction of CH_3O with CH_2OH in the solid-phase¹⁴¹:

The detection achieved by McGuire et al.⁸³ was based on the spectroscopy work by Motiyenko et al. between 150 and 450 GHz⁸² (see section 3.1.2.b). More than two dozen un-blended transitions for the lower energy conformer were identified. These transitions show identical spatial distributions matching well to that of CH_3OH . A column density of $4(2) \times 10^{18} \text{ cm}^{-2}$ at $T = 200 \text{ K}$ was derived for methoxymethanol about 34 times less abundant than methanol (CH_3OH). However, this column density derived from observations is higher than predicted by astrochemical models, which seems to indicate that other formation pathways exist⁸³.

4.3.8. Propylene CH_2CHCH_3

Propylene (also called propene) was detected in 2007 with the IRAM 30 m radio telescope towards the dark cloud TMC-1²⁰⁰. Dark clouds ($T \sim 10 \text{ K}$) are the sites of low-mass star formation. The authors initially detected a pair of lines, which they tentatively assigned to the A-E splitting of the $5_{05}-4_{04}$ rotational transition of propylene. The barrier height of propylene is rather high so the A-E splitting is of the order of 0.3 to 4 MHz. A total of 13 transitions were finally identified using the spectroscopic study of Włodarczak et al.²⁰¹. Before the study of Marcelino et al.²⁰⁰, propylene was thought to have a too small dipole moment to be detected in space. It was also thought that the best place to search for it was in the hot cores in high-mass star-forming regions, and not in the dark clouds.

Propene illustrates that in astrophysics, surprise is never far away, and discovering new species can take time. A fundamental laboratory spectroscopy study, which was performed in the early nineties was used more than a decade after in order to detect this species.

4.3.9. Methyl mercaptan CH_3SH

A chemical clock

Methyl mercaptan (CH_3SH) was first identified in the high-mass star-forming region Sgr B2 close to the Galactic center in 1979 by Linke et al.²⁰². It was later detected by Gibb et al. towards the warm and dense part of a high-mass star-forming region in the G327.3–0.6 hot core²⁰³, in the Orion KL hot core²⁰⁴, in the low-mass star forming region IRAS 16293–2422²⁰⁵, and in the prestellar core L1544²⁰⁶. Torsionally excited methyl mercaptan was also observed in Sgr B2 by Müller et al. reported in 2016²⁰⁷.

Sulfur-containing molecules can be important in the chemical evolution of hot cores. Their molecular ratios have been previously used as chemical clocks to obtain information about the age of those hot cores²⁰⁸. However, the chemistry of interstellar sulfur is still undetermined. Much less sulfur is found in dense regions of ISM than in diffuse regions²⁰⁹. Therefore, there is some mystery about this missing sulfur and what might be its reservoir.

About 20 sulfur-containing molecules have been identified in space so far. Methyl mercaptan is the only internal rotor detected which exhibits observable internal rotation splittings because of the internal rotation of the methyl group. Ethyl mercaptan ($\text{CH}_3\text{CH}_2\text{SH}$) has been recently detected in the Orion Cloud²⁰⁴, but no A-E splittings could be observed due to the high barrier to internal rotation.

Methyl mercaptan is the sulfur analogue to methanol but contrary to methanol, its first excited state $\nu_t = 1$ is below the top of the barrier and its reduced barrier height is $s = 4V_3/9F = 13$. In consequence, the torsional splitting between the A and E levels in the $K = 0$ state of methyl mercaptan is 0.99 cm^{-1} , an order of magnitude smaller than in methanol, which has a torsional splitting of 9.1 cm^{-1} .

The CH_3SH parent species was the subject of many studies. Early investigations on its rotational spectrum were carried out almost 60 years ago (e.g.²¹⁰). The investigations were extended later into the millimeter- and submillimeter-wave, the THz range (1.1-1.5 THz and 1.790-1.808 THz) as well as into the far-infrared regions ($50\text{-}550 \text{ cm}^{-1}$) using the BELGI- C_s -methanol code¹⁰⁶. The last study also initiated several high-resolution infrared spectroscopic investigations (Ref.²¹¹ and references therein).

In 2019, Zakharenko et al. performed a laboratory study on the deuterated CH_3SD species recording in the 150–510 GHz frequency range using the Cologne millimeter wave spectrometer²¹². More than 4000 transitions up to $\nu_t = 2$ were analyzed and fitted using the RAM36 program. Using these spectroscopic data, the search for CH_3SD in data from the ALMA, Protostellar Interferometric Line Survey (PILS) of the protostar IRAS 16293–2422, was performed²¹².

While methyl mercaptan has not been observed to date on any of the other Solar System planets, it could be used as a biomarker for detecting evidence of Martian life²¹³.

4.3.10 Acetone CH_3COCH_3

Acetone (CH_3COCH_3) is a two-top internal rotor molecule, which was first reported to be in the ISM by Combes et al.²⁶ in Sgr B2. The column density was estimated to be $5 \times 10^{13} \text{ cm}^{-2}$, corresponding to a fractional abundance with respect to H_2 of 5×10^{-11} . In 2005 Friedel et al. also detected acetone towards the star forming region Orion-KL by lines assigned to both the vibrational ground state and the lowest vibrational excited state²⁷.

Acetone was studied by Groner et al. in the ground torsional state using the ERHAM code⁷⁰ in 2002. In 2013 using the PAM_C_{2v}_2tops¹²², Ilyushin and Hougen developed a formalism involving an explicit two-dimensional potential function. Their global approach allowed them to simultaneously fit rotational transitions belonging to different torsional states of the molecule: the torsional ground state the first excited state of the lower torsional mode ν_{12} , and in the first excited state of the higher torsional mode ν_{17} , with J values up to 60, 38, 31 and K_a up to 30, 16, 8, respectively¹²².

The microwave spectra of the two mono-substituted ¹³C isotopologues of acetone were reported with measurements carried out from 11 to 25 GHz with a MJ-FTMW spectrometer²¹⁴ but so far, no detection has been done.

4.3.11. Trans ethyl methyl ether t-CH₃CH₂OCH₃

Trans ethyl methyl ether (t-CH₃CH₂OCH₃ or t-EME) was searched for in the hot cores Sgr B2(N-LMH) by Carroll et al.²¹⁵ and towards W51 e1/e2 by Fuchs et al.⁷¹ but those studies only provided upper limits. In 2016, Tercero et al. tentatively detected t-EME towards Orion KL²¹⁶ by the identification of many lines in the IRAM 30 m line survey and in the ALMA Science Verification data. The derived column density of this species is $\leq (4.0 \pm 0.8) \times 10^{15} \text{ cm}^{-2}$ and the rotational temperature is around 100 K. In the compact ridge region of Orion, an abundance ratio between DME and t-EME was found to be $N(\text{DME})/N(\text{t-EME}) \geq 150$ ²¹⁶.

It is interesting to note that usually molecules containing formate, alcohol or ether groups have been detected in Orion with both the methyl and ethyl groups (methyl formate/ethyl formate, methanol/ethanol, DME/t-EME²¹⁶). Using the ALMA data, Tercero et al. found that the three ethyl species have a reduced spatial distribution compared to the methyl species. This suggests that gas-phase processes may occur after the evaporation of the mantles in hot cores, and also that there is probably a time-dependent chemistry.

From the spectroscopic point of view, t-EME is an interesting molecule with three LAMs which can couple: two inequivalent methyl internal rotations and a skeletal torsion. Since internal rotation barriers are high (1154 cm⁻¹ and 891 cm⁻¹ for the C-CH₃ and the O-CH₃ internal rotations respectively), Fuchs et al.⁷⁰ analyzed the spectrum using the ERHAM code⁶⁷⁻⁶⁸. Tsunekawa et al. also reported pure-rotational transitions in the ground state, using an ordinary asymmetric rotor Hamiltonian. They also prepared a spectral atlas of about 21,000 lines up to 200 GHz²¹⁷. Kobayashi et al.²¹⁸ reanalyzed the three torsionally excited states (the C-CH₃ and the O-CH₃ excited torsional states and the excited skeletal torsional state), by extending the measurements and by using the IAM-like tunneling matrix formalism.

4.3.12. Methyl acetate CH₃COOCH₃

The detection of methyl acetate, $\text{CH}_3\text{COOCH}_3$, is a nice illustration for the success of the strong interplay between laboratory spectroscopy and astrophysical observations. In 2011, Tudorie et al. published a global analysis using the BELGI-C_s-2Tops code and methyl acetate was chosen to test the theoretical method on this inequivalent two-top species¹¹⁹.

Two years later, Tercero et al.³² reported the detection of methyl acetate for the first time in space (see Fig. 11), with 215 lines from the states AA, AE, EA, and EE (E3, and E4) of this molecule at 3, 2, and 1.3 mm spectral range. From the derived velocity of the emission of methyl acetate, it was concluded that this molecule arises mainly from the compact ridge region with a total column density of $(4.2 \pm 0.5) \times 10^{15} \text{ cm}^{-2}$ ³². In 2014, new spectroscopic data were recorded later using a room temperature Chirped-Pulse Fourier transform microwave (FTMW) spectrometer in the frequency range from 8.7 to 26.5 GHz, two molecular beam FTMW spectrometers (2 to 40 GHz), a free jet absorption Stark-modulated spectrometer (60 to 78 GHz), and a room temperature millimeter-wave spectrometer (44 to 68GHz). Approximately 800 new lines with J up to 40 and K up to 16 were assigned and fitted using the BELGI-Cs-2Tops code²¹⁹.

Fig. 11. Detection of the methyl acetate $\text{CH}_3\text{COOCH}_3$ molecule in the interstellar cloud Orion. The x axis is the frequency of the lines in GHz, the y axis is the mean beam temperature antenna ($T_{\text{MB}}(\text{K})$). In black the observed spectrum with the telescope IRAM (Spain), in green the modeling of the spectra for 140 other species detected so far in Orion, and in red the modeling of methyl acetate lines. From Ref.³²

5. Conclusions

The role of internal rotors in the ISM is clearly established. They represent a ubiquitous hydrogen-rich substituent in many complex organic molecules. Internal rotors such as methanol, methyl formate, acetaldehyde, acetone or dimethyl ether and their isotopologues have thousands of rotation-torsion transitions in the spectral range of the astrophysical observations. With the advent of large sub-millimeter facilities (ALMA, SOFIA, Herschel) with their unprecedented spatial and spectral resolutions, the spectra of these species need to be analyzed before observing new species. Besides being “weeds” in the astronomical spectra, internal rotors are also excellent tools to study the ISM. They can be a

“thermometer” for temperatures from 20 K to 500 K. They can be important for detecting certain prebiotic molecules. They can be sensors for possible time-variation of the fundamental constants of physics.

To achieve that goal, new experimental and theoretical spectroscopic data must be recorded and analyzed in the laboratory. Excited torsional states of a number of internal rotors are still a challenge for spectroscopic studies. Interaction with other low frequency modes in complex organic molecules can make the spectral analysis very complex. Theoretical models, which involve a global approach of the vibration-rotation-torsion, are under development¹³⁶, but it is clear we are only at the very beginning of solving this big problem. Many of the astronomical sources discussed in this review are going to cause problems in that regard when observed with ALMA. Human forces as well as computational resources are needed. Regrettably, it has been noted that while very expensive observatory instruments are built, many fewer laboratory spectroscopy studies get financed in general.

A complete review of interstellar, circumstellar, extragalactic, protoplanetary disk, and exoplanetary molecules can be found in Ref.⁶. It is clear that some classes of internal rotors have not been searched for in the ISM yet, such as methyl-substituted aromatic benzene-ring molecules. The recent detection of an aromatic, benzene-ring containing molecule in the ISM: benzonitrile ($c\text{-C}_6\text{H}_5\text{CN}$)²²⁰ opened a new direction which should be pursued. Simple aromatic molecules (and their methyl-substituted analogues) may be precursors for polycyclic aromatic hydrocarbon formation (PAH) and possibly responsible for the still unidentified diffuse infrared bands in the ISM. So far, only one chiral molecule, propylene oxide, has been detected outside of our solar system¹⁰⁷. Other chiral molecules containing internal rotation methyl groups could also be present.

The formation of complex organic molecules in the ISM is still poorly understood. Most of the reaction pathways are not known. The radicals are certainly playing an important role in astrophysical chemistry. So far, only a few radicals containing oxygen have been detected in space: OH, HO₂, HCO, HCCO, and CH₃O²²¹. The existence of LAMs in radicals is a challenge both experimentally and theoretically for spectroscopy. Some of those species are not yet detected due to a lack of laboratory data. This obviously opens a new field of research for both spectroscopy and astrochemistry.

Appendix A: The Principal Axis Method approximations and the van Vleck transformation

In the early literature, the main approximation made in the PAM is that the cross terms from Eq. (1), i.e. $-2Fp_\alpha(\sum_{g=a,b,c} \rho_g J_g)$ are treated as perturbations. Successive van Vleck transformations can then be applied⁵¹, which reduce the matrix elements arising from the cross terms (non-diagonal in the torsion

quantum number v_t) to a sufficiently high order that they can be neglected at first approximation. The transformed Hamiltonian matrix can then be divided into smaller rotational matrices, one for each torsional state v_t and for each internal rotation state $\sigma = 0$ (A state), and $\sigma = \pm 1$ (E state):

$$H_{v\sigma}^{PAM} = H_R + F \sum_n W_{v\sigma}^{(n)} \sum_g (\rho_g J_g)^n \quad (A.1)$$

$$\text{with } H_R = AJ_a^2 + BJ_b^2 + CJ_c^2$$

The $W_{v\sigma}^{(n)}$ coefficients of Eq. (A.1) result from a van Vleck perturbational treatment. They are tabulated⁵¹ and their values depend on the so-called reduced barrier parameter s . This PAM, as described above, typically belongs to what we call a “local” method, because each group of states (A, E states and each torsional v_t state) is treated using its own Hamiltonian. It can be also qualified as a “*perturbative*” method because it is based on van Vleck transformations.

Fig. A.1 shows schematically the van Vleck transformation. This figure allows us to understand better the difference between a “local” method and a “global” method. The “global” method directly diagonalizes the matrix involving all the non-diagonal interactions between various torsional v_t states. The “local” method considers the off-diagonal terms as being negligible and treat each v_t submatrix independently.

Fig. A.1 Van Vleck transformations.

One important limitation of this historical implementation of the PAM is that the perturbation treatment is only valid if the barrier parameter s is not too small. The perturbation coefficients $W_{v\sigma}^{(n)}$ increase rapidly as s decreases⁵¹. Therefore, one often says that the PAM (in its early version) is mostly appropriate for “high barrier” cases. This means that the perturbative or local PAM approach as described above is *not* appropriate if the rotation-torsion A-E splittings are large in comparison with the energy differences between two torsional v_t states, because in that case, the power series of Eq. (4) converges slowly. This situation occurs if i) the barrier to internal rotation is rather low or ii) the torsion v_t state under study is close to or above the top of the barrier.

Moreover, for a given barrier height, the convergence of the perturbation series is also measured by the magnitude of the $\sum_g(\rho_g J_g)$ term, which is roughly given, at the symmetric top limit, by the ratio $K \frac{I_\alpha}{I_{a(c)}}$ where K is the quantum number associated with the projection of the rotational operator J on the a or c symmetry axis of the molecule. The convergence is thus rapid if the value of the ρ parameter is small, i.e., if the frame part of the molecule represented by the moment of inertia I_a or I_c is much heavier than the top I_α and if low values of K are studied.

Appendix B: Details about the Rho Axis Method (RAM)

As a result of the axis system rotation, the cross term in Eq. (1) $-2F\rho p_\alpha J$ reduces to $-2F\rho_z p_\alpha J_z$. Since matrix elements of $-2F\rho_z p_\alpha J_z$ are diagonal in the symmetric-top quantum number K , this operator can be added to the pure torsional terms of the Hamiltonian, which then becomes K dependent. The RAM Hamiltonian may be written as⁵⁹:

$$\mathbf{H}_{\text{RAM}} = \mathbf{H}_R + \mathbf{H}_{\text{cd}} + \mathbf{H}_{\text{int}} + \mathbf{H}_T \quad (\text{B.1})$$

where $\mathbf{H}_R$ is the rotational Hamiltonian, $\mathbf{H}_{\text{cd}}$ the usual centrifugal distortion Hamiltonian, $\mathbf{H}_T$ is the torsional Hamiltonian and $\mathbf{H}_{\text{int}}$ contains higher order torsional-rotational interaction terms:

$$H_T = F(p_\alpha - \rho J_z)^2 + V(\alpha) \quad (\text{B.2})$$

$$H_R = A(\cos\theta_{\text{RAM}}J_z - \sin\theta_{\text{RAM}}J_x)^2 + B(\sin\theta_{\text{RAM}}J_z + \cos\theta_{\text{RAM}}J_x)^2 + CJ_y^2 \quad (\text{B.3})$$

By grouping the terms and if x, y, z become b, c, a we get:

$$H_R = A_{\text{RAM}}J_a^2 + B_{\text{RAM}}J_b^2 + C_{\text{RAM}}J_c^2 + D_{ab}(J_aJ_b + J_bJ_a) \quad (\text{B.4})$$

Note that the values of the rotational constants in the RAM system (A_{RAM} , B_{RAM} and C_{RAM}) are not the same as in the PAS. This often causes confusion. It is easy to establish the relation between the rotational constants A, B, C in the PAS and the constants in the RAM by either equating the coefficients of Eqs (B.2) and (B.4) or by diagonalizing the 3x3 matrix of the RAM rotational constants.

The higher order interaction terms of $\mathbf{H}_{\text{int}}$ can be obtained by multiplying the powers of the rotation angular momentum components J_i with the powers of the torsion operators p_α , $(1-\cos 3\alpha)$, $(1-\cos 6\alpha)$, etc., as schematized in Table 2 of ref.⁴⁹ (see also refs.⁶⁰⁻⁶²).

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