

Rotational Spectroscopy of Biomolecules, Atmospheric Species and Molecules with Astrophysical Interest

Carlos Cabezas

Departamento de Astrofísica Molecular, Instituto de Física Fundamental (IFF-CSIC), C/Serrano 121, 28006 Madrid, Spain; carlos.cabezas@csic.es

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Abstract: Rotational spectroscopy is one of the most outstanding techniques for investigating the structure and dynamics of gas-phase molecules. Pure rotational spectra are primarily observed in the frequency range from 300 MHz to 1 THz, spanning the centimeter to submillimeter wave regions. Over the past five decades, significant advances in radiation sources, detectors, and digital electronics have led to substantial improvements in experimental methodologies in this field. As a result, modern rotational spectroscopic measurements benefit from markedly enhanced sensitivity and resolution, enabling the study of an ever-increasing number of molecular species with growing structural complexity. These developments have expanded the scope of rotational spectroscopy from simple diatomic molecules to moderately large systems containing up to approximately 50 atoms. Rotational spectroscopy is widely applied to the investigation of molecules of atmospheric relevance and astrophysical interest, as well as biomolecules, weakly bound complexes, transient or unstable species, and metal-bearing or ionic clusters. In this work, recent laboratory spectroscopic studies employing rotational spectroscopy to probe biomolecules, atmospheric species, and molecules of astrophysical significance are reviewed. Particular attention is given to the experimental techniques employed, the strategies used to characterize the observed species, and the broader implications of the reported results.

Keywords: rotational spectroscopy; laboratory astrophysics; Criegee intermediates; biomolecules

1. Introduction

Rotational spectroscopy is one of the most precise tools for structure determination of gas-phase molecules. The rotational spectrum of a molecule depends primarily on its moment of inertia, which is determined by the molecule's mass distribution and geometry. This makes the rotational spectrum of each molecule exclusive, and can therefore be considered a fingerprint of the molecule. Small changes in the distances between atoms or in their mass (different isotopes) alter the molecular rotational spectrum in predictable and measurable ways. This characteristic enables rotational spectroscopy to differentiate among conformers, tautomers, and isotopomers. The potential of rotational spectroscopy should attract every spectroscopist. The capability for resolution is remarkable as the rotational frequencies can be determined to an accuracy of 1 part in 10^6 or superior (e.g., achieving a frequency uncertainty of ≤ 10 kHz at a frequency of 10 GHz) during a standard laboratory experiment. A molecular species can therefore be unambiguously identified, even in complex mixtures, as long as it has permanent electric dipole moment that is not zero. As stated by Wilson in his review in 1968 “once a molecule has been caught and fingerprinted by this method, it is forever recognizable” [1].

While rotational spectroscopy has traditionally been associated with molecular structure determinations [2,3], the present advancements in this field are not only reinforcing but significantly enhancing its key role in providing



accurate insights into an array of chemical and physical targets. Some of the most relevant applications of this spectroscopy are described below. In addition to the ability to provide reliable and accurate information about molecular structures, rotational spectroscopy has proved to be a highly effective method of obtaining key properties as the magnitude of the molecular electric dipole moments or the electronic structure of the molecule [2]. These properties play a crucial role in various subjects, including the examination of chemical reactions as well as the quantitative assessment of intricate gas-phase mixtures, including those in chemistry within astrophysical environments. The prevalent experimental approach to ascertain the dipole moments of individual molecules has involved observing the Stark effect that occurs when an external electric field is applied to gas-phase samples [4,5].

Rotational spectroscopy represents one of the leading experimental methodologies utilized for distinguishing between various conformers that may form a molecular system. The first investigation related to conformations using rotational spectroscopy was done in 1962 by Hirota [6]. In this work Hirota determined that the *gauche* conformer of propyl fluoride was more stable than its *trans* counterpart. Today, the number of conformers which can be detected in the rotational spectrum of a sizable flexible molecule has risen significantly: up to fifteen isomers have been identified in a single experiment for the acyclic monoterpene citronellal [7].

Another area of research where rotational spectroscopy has been applied is the studies of weakly bound molecular complexes. A key aim of these rotational studies has always been to achieve a comprehensive understanding of the interactions between molecules. This offers the potential to bridge between the properties of isolated molecules and those of condensed phases. The first observation of a molecular adduct by rotational spectroscopy in 1961 consisted of a series of absorption lines of CF₃COOH-HCOOH [8]. The emergence of the rotational spectroscopy techniques coupled to supersonic expansions in the 80s made possible to form and observe weakly bound complexes more efficiently, allowing to characterize molecular adducts such as the water nonamers and decamers [9] or the benzaldehyde-(H₂O)_{1–6} clusters [10].

However, one of the most important roles of rotational spectroscopy is played in the field of astrochemistry [11,12], with the overwhelming majority of chemical species in the space being discovered via their rotational signatures. Radioastronomical observations are responsible for the detection of more than 90% of the 340 molecules identified so far in the interstellar and circumstellar media (ISM and CSM, respectively) [13–15]. The list of the latest molecular discoveries provided by the interplay between rotational spectroscopy and radio-astronomical observations includes radicals [16], ions [17], sulfur-bearing species [18], metal-containing molecules [19], and polycyclic aromatic hydrocarbons (PAHs) [20–22]. These examples give an idea of the exotic chemistry taking place in the ISM and CSM and provide a clear evidence of the transcendental role that rotational spectroscopy plays in radioastronomy.

As previously stated, the patterns of frequencies observed in rotational spectroscopy are directly linked to the geometry of the molecule, allowing for a direct comparison between the spectrum and theoretical structure calculations. In almost no other type of spectroscopy is the connection between molecular geometry and spectrum so evident and so precise. Therefore, the data derived from the rotational spectroscopy can be used as a benchmark for developments in the field of computational chemistry [23–25]. In fact, new theoretical models can reproduce the frequencies in a rotational spectrum with very high accuracy [26]. Finally, one of the latest applications of rotational spectroscopy is associated to the emergence of broadband experimental techniques [27,28]. Recent instrumental advances led to a number of groundbreaking new experiments in the gas-phase which provide accurate chirality sensitive information [29–31], distinguishing enantiomers and measuring the enantiomeric excess.

A variety of techniques have been developed to measure the spectra of rotational transitions. For most molecules and molecular systems, these transitions happen in the microwave (MW) region, Table 1, which is why we refer to rotational spectroscopy as microwave spectroscopy. The frequency of a rotational transition is primarily determined by the values of the rotational constants, spanning from under 500 MHz for larger molecules to >1339 GHz for a smaller molecule like HD. Therefore, detections in millimeter (mm), and sub-millimeter (sub-mm) wavelength ranges are usually limited to the study of small to medium-sized molecules [32], while measurements in the centimeter (cm) wavelength region allow the investigation of large molecules and molecular complexes, even with more than 40 atoms [33,34]. The first microwave spectrometers operating in the 10–40 GHz range were marketed in the late 1950s and early 1960s. Since that time, significant advances have been achieved in the performance, availability and affordability of microwave instruments, largely attributed to advances in communication electronics. Currently, the vast majority of microwave spectrometers incorporate a combination of standard commercial and custom-built components that users assemble based on their specific requirements. While frequency-domain methodologies continue to prevail in mm wave and sub-mm wave spectrometers, the cm wave sector has been predominantly influenced by time-domain methods. A brief description of the most commonly used microwave spectrometers is given below.

In conventional microwave spectrometers, operating within the millimeter and sub-millimeter wave domains, monochromatic radiation is directed through a sample cell, with the resulting transmitted signal being recorded. Various designs of static gas cells are utilized, contingent on the specific setup of the microwave spectrometer; the primary categories include waveguide cells and free-space cells. The MW radiation in these spectrometers can be produced by different sources like the old klystrons, backward wave oscillators (BWOs), Gunn diodes and active frequency multiplier chains. Broadband spectra may be obtained by sweeping the output of a low-frequency generator serving as the microwave source. Different modulation methods, including Stark effect modulation or frequency modulation paired with phase-locked detection, are frequently utilized to minimize the background characteristics of the cell, consequently reducing the detection limit. Some spectrometers of this type can be found operating at the Max Planck Institute for Extraterrestrial Physics [32], and at the universities of Bologna [35], Valladolid [36,37], Lille [38], Arizona [39] and Prague [40].

Table 1. Estimated extension of the microwave region.

Range	Wavelength (cm)	Wavenumber (cm ⁻¹)	Frequency (GHz)
cm wave	1.0–100.0	1.0–0.01	30.0–0.3
mmw wave	0.1–1.0	10.0–1.0	300.0–30.0
Sub-mmw wave	0.01–0.1	100.0–10.0 ^a	3000.0–300.0

^a This region is frequently described as a segment of the far-infrared (FIR) range.

Rather than continuously directing monochromatic radiation through a sample cell to ascertain the transmitted signal in relation to frequency, modern microwave spectrometers apply the radiation for a brief period of time. When a sample is present, it elicits a radiative response. To achieve the spectrum, the response signal is captured as a function of time and then analyzed using Fourier transformation (FT). Based on this, Balle & Flygare [41] developed in 1981 a pulsed nozzle Fourier transform microwave (PNFTMW) spectrometer which completely changed the scenario of microwave spectroscopy. FTMW spectroscopy on pulsed supersonic-jet expansions gained popularity due to its distinctive capability to provide both high resolution and sensitivity at the same time. Moreover, the environment of a supersonic-jet expansion, where the enthalpy of the sample is converted into the energy of a directed translation, offers the ideal conditions to form weakly-bound complexes. After their formation, these species are isolated within the collision-free environment of the expanding gas, which allow them to persist despite their weak intermolecular bonds. In the same manner, the molecular species formed in a DC discharge or vaporized by laser ablation can survive in a supersonic-jet expansion for their spectroscopic characterization. This converts FTMW spectroscopy an ideal technique for studying unstable and transient molecular species such as closed-shell reactive species [42,43], open-shell radicals [44,45], ions [46,47], weakly-bound complexes [48], low vapor pressure species [49,50], or inorganic clusters [51,52]. Caminati & Grabow [53] offer an excellent overview of the development of these instruments and their applications.

After the emergence of PNFTMW spectrometers in 1981, the most transformative scientific innovation in the field of microwave spectroscopy, and maybe in the field of general spectroscopy, is the development of chirped pulse Fourier transform microwave (CP-FTMW) spectroscopy by the Pate group at the University of Virginia in 2006 [54,55]. This technique permits the acquisition of a spectrum with a bandwidth of ≥ 10 GHz in a single shot of the spectrometer, facilitating the capture of broadband, high-resolution microwave spectra at speeds many times greater than those achievable before. Thus, it is feasible to gather individual broadband spectra while preserving phase stability to achieve an optimal signal-to-noise ratio. This aids in enhancing broadband accessibility in molecular systems, which encompass molecular adducts [34], isotopologues in natural abundance [56], and also allows for the analysis of chemical reaction dynamics [57] or chirality properties [31]. In addition, this type of spectrometers can be coupled to methods to generate new species like laser ablation sources [58], electric discharges nozzles [59] or flash pyrolysis microreactors [60]. This, combined with the fact that these spectrometers can cover spectral ranges between 2 and 110 GHz [61–63], makes microwave spectroscopy one of the most versatile techniques available.

This manuscript examines recent studies that have utilized rotational spectroscopy to investigate the molecular structures of biomolecules, atmospheric constituents, and molecules significant to astrophysics. These investigations have taken place over the past decade at both the University of Valladolid and National Yang Ming Chiao Tung University. The paper elaborates on the experimental methods, the approach taken to analyze the various species identified, and the conclusions drawn from these investigations.

2. Experimental Techniques

The studies revised in this work have been conducted using two different PNFTMW spectrometers. The spectroscopic investigations of biomolecules and some of the molecules of astrophysical interest were done using a laser ablation Fourier transform microwave (LA-MB-FTMW) spectrometer [64] developed at the University of Valladolid. An extensive description of this type of experimental setup has been given elsewhere [65–67]. The spectrometer is composed by a laser ablation system, a vacuum chamber with a Fabry-Pérot resonator and all the electronic components of the FTMW spectrometer. The laser ablation system consist in a picosecond Nd:YAG laser, usually working in the third harmonic (355 nm), and a homemade laser-ablation nozzle (Figure 1) placed inside of the vacuum chamber and in the backside of one of the mirrors of the Fabry-Pérot resonator. The laser-ablation nozzle consists of a commercially available solenoid valve equipped with an extended channel designed to accommodate the solid sample shaped like a rod, which is rotated and moved linearly after each laser pulse by a motorized micrometer. The molecular content formed during the laser ablation are diluted into a carrier gas (either argon or neon) and expanded forming a supersonic jet between the two mirrors of the resonator cavity. This resonator is contained within a cylindrical high vacuum chamber made of stainless steel, measuring approximately 85 cm in length and 45 cm in diameter, which is evacuated with a diffusion pump. One of the mirrors remains fixed while the other is attached to a motorized support that allows for fine adjustments in translation to facilitate automatic tuning during scans. The molecular species present in the chamber are probed using Fourier-transform microwave spectroscopy. A brief microwave pulse, typically lasting around 0.3 microseconds, is utilized to generate a macroscopic polarization among the species in the jet (refer to Figure 1). After the excitation pulse, the molecular emission signal, known as free induction decay (FID), is recorded in the time domain. Applying a Fourier transformation to this data results in the molecular rotational transitions, which manifest as Doppler doublets due to the parallel travel of the supersonic jet relative to the resonator's axis. The accuracy of the frequency measurements is estimated to be within 3 kHz, with a resolution of better than 5 kHz. The LA-MB-FTMW spectrometer operates within a frequency range of 4 to 14 GHz.

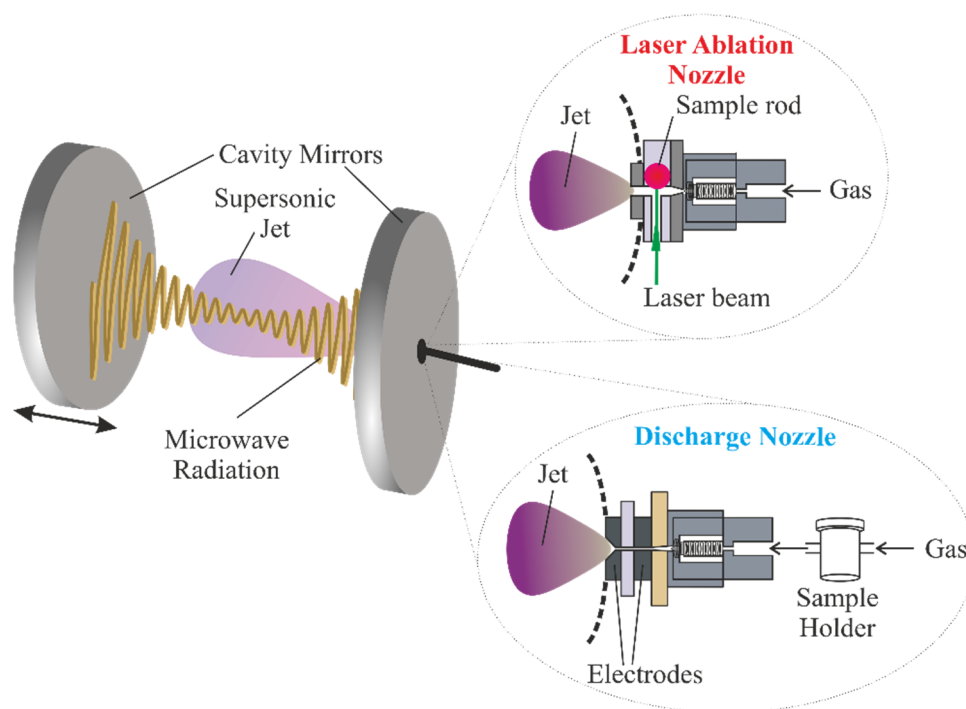


Figure 1. Schematics of the FTMW spectrometers employed in the investigations presented in this work. The cavity resonator and the designs of the laser ablation and pulse discharge nozzles are shown.

The spectrometer employed to investigate the molecules with atmospheric and astrophysical interest is a PNFTMW spectrometer with an electric discharge source incorporated, now at the National Yang Ming Chiao Tung University of Taiwan [68,69]. The PNFTMW setup consists of a narrow-band Balle-Flygare type Fourier-transform microwave (FTMW) spectrometer [41] covering the 4–40 GHz frequency region [68,69]. This spectrometer allows one to extend the frequency measurements up to 85 GHz by the double-resonance techniques FTMW-MW and FTMW-mmW [70]. These measurements methods are ideal for validating the assignments

gathered through FTMW spectroscopy. The molecular species under study are formed in a supersonic expansion by a pulsed electric discharge over a gas-phase mixture containing different chemical precursors, usually diluted in argon. To form new chemical species, the spectrometer is equipped with a pulsed discharges nozzle [71], which consists in a holder of electrodes mounted in a commercial solenoid valve. An anode, an insulator, and a cathode are attached in this order from the outlet of the pulsed valve on this holder with its center hole forming a smooth taper shape to guide sample gas into the chamber as shown in Figure 1. The nozzle is allocated in the back side of the fixed mirror of the Fabry-Pérot resonator. The electrodes are made of stainless steel and the insulation is made of Teflon. A pulsed voltage, usually lasting for 450 μ s and ranging from 800 to 1200 V, is applied between two stainless steel electrodes to create an electric discharge that initiates chemical reactions in the precursor mixture. Immediately, the products formed in the discharge are supersonically expanded and quickly cooled to about 2 K between the mirrors of the Fabry-Pérot resonator for analysis via Fourier-transform microwave spectroscopy. The frequency measurements are estimated to have an accuracy of less than 3 kHz, while the resolution is better than 5 kHz.

3. Probing Biomolecules by Rotational Spectroscopy

Studies dedicated to discerning the structure-property relationship of biomolecules cover a wide range of molecular sizes, from molecules with discrete sizes such as amino acids, monosaccharides or neurotransmitters up to macromolecules such as proteins or polysaccharides. Interest towards this field of research has increased over the past several years, leading to a variety of experimental and theoretical techniques that are constantly evolving. Although gas-phase conditions differ greatly from the condensed-phase environment in which biomolecules act and biological reactions occur, it offers perfect conditions for observing intrinsic molecular properties. This is why gas-phase studies of biomolecules constitute the first step toward understanding molecular behavior in more complex media. The majority of biomolecules exhibit significant torsional flexibility, leading to numerous conformational variations that possess similar energy levels. Given that studies in condensed phases are largely influenced by intermolecular interactions, the conformational preferences of biomolecules may be skewed due to the surroundings. In contrast, studies carried out in the gas-phase can uncover the inherent structural minima of isolated biomolecules.

3.1. Revealing the Conformational Flexibility of the Neurotransmitter Dopamine

Dopamine, a catecholamine neurotransmitter, functions as a hormone within both peripheral and central nervous systems. Its roles pertain to various cognitive processes, including emotional reactions and the capacity to feel pain and pleasure [72,73]. In its role as a neurotransmitter, dopamine is discharged by neurons at synaptic junctions and adheres to designated receptors, facilitating the transmission of signals to the intended target cell. Similar to other catecholamines, it exhibits significant flexibility, resulting in numerous stable conformations. Understanding its preferred forms is therefore highly valuable, as the configuration is crucial in the key-and-lock recognition mechanism that takes place at the receptor site [72]. However, only X-Ray diffraction in solid-phase [74,75] and in solution nuclear magnetic resonance [76,77] studies of dopamine have been reported. To date, there have been no experimental investigations concerning dopamine in the gas phase, where it exists in its neutral state, likely because of challenges associated with its vaporization (melting point 130 °C).

The conformational landscape of dopamine has been first explored using quantum chemical calculations. Eighteen structures were then optimized using the Møller-Plesset second-order perturbation method (MP2) with the 6-311++G(d,p) basis set (see Table 2). Only the conformers in which both hydrogen atoms of the hydroxyl groups lie in the plane of the aromatic ring and are oriented in the same direction were considered. The G or A labelling relate to the arrangement of the alkyl chain, with gauche (G, folded) or anti (A, extended) referring to each configuration, respectively. The use of Roman numerals indicates the energetic hierarchy of various conformations linked to the rotation of the NH₂ group. A third index (a, b, c, and d) specifies the various orientations of the catechol OH groups in relation to the side chain.

The rotational spectrum of dopamine was studied within the 4–10 GHz frequency range using a LA-MB-FTMW spectrometer at the University of Valladolid [67]. A number of sets of *a*-type R-branch transitions were identified, corresponding to seven distinct rotamers labelled from I to VII (refer to Table 3). Beyond the instrumental Doppler splitting, all transitions exhibited division into a noticeable hyperfine structure due to the interaction of the nuclear quadrupole of ¹⁴N (*I* = 1). The identification of each conformation was accomplished by comparing the molecular parameters obtained through experimentation, as outlined in Table 3, with those predicted by the quantum chemical calculations (Table 2). Given that the constants for all different conformers display similarity, distinguishing each conformer requires a thorough examination of the rotational constants in addition to the quadrupole coupling constants, and ultimately the type of the transitions that are detected.

The rotational constants offer insights into the mass distribution within each conformation and are typically definitive in the assignment of spectra. Nevertheless, the variations in the measured values of the rotational constants for all the detected species are insufficient for effective differentiation. Conversely, the nuclear quadrupole coupling constants exhibit considerable sensitivity to the chemical surroundings of the ^{14}N nucleus as well as the orientation of the NH_2 group in relation to the principal axis system. In compounds that contain nitrogen, these molecular constants have demonstrated remarkable significance for identifying conformers, enabling the differentiation between entities that possess closely resembling molecular geometries, and consequently, nearly identical rotational constants [78,79]. Analyzing the quadrupole coupling constants presented in Tables 2 and 3 permits the recognition of the rotamer pair I/II in association with the conformer duo GIc/GId. However, pinpointing specific rotamers as distinct conformers is not feasible through the examination of the quadrupole coupling constants, as the values for these entities are quite similar. The conformers GIc and GId are distinguished solely by the arrangement of their hydroxyl groups, leading to distinct variations in their rotational constant values: $\Delta A = 4$ MHz, $\Delta B = -2$ MHz and $\Delta C = -2$ MHz. These measurements correspond well with the observed constants ($\Delta A = 2.491$ MHz, $\Delta B = -1.473$ MHz and $\Delta C = -2.066$ MHz). Consequently, this information allows for a clear determination of rotamers I and II, identifying them as conformers GIc and GId, respectively. Employing a similar approach, the seven species that were observed (refer to the molecular structures displayed in Figure 2) were identified as shown in Table 3. It is important to highlight that rotamer VII can initially be assigned as a conformer of both GIIa and GIIb. Nevertheless, the definitive classification as GIIb was determined by the identification of both *a*- and *b*-type spectra in accordance with the significant values of the predicted dipole moment components (Table 2).

Table 2. Theoretical spectroscopic parameters and relative energies for the eighteen low-energy conformers of dopamine at the MP2/6-311++G(d,p) level of theory.

	<i>A</i> ^a	<i>B</i>	<i>C</i>	χ_{aa}	χ_{bb}	$ \mu_a $	$ \mu_b $	$ \mu_c $	ΔE ^b	ΔG ^c
GIa	2113	675	580	1.93	-1.79	1.5	1.1	0.6	0	0
GIb	2118	675	577	1.85	-1.47	0.8	3.4	0.9	126	131
GIc	2168	658	575	0.99	-1.76	0.9	1.3	0.1	35	54
GId	2172	656	573	0.95	-1.53	0.6	3.1	0.1	100	156
GIIa	2132	657	574	-0.76	2.38	0.2	2.0	2.3	247	314
GIIb	2122	662	576	-0.62	2.45	1.2	2.0	0.0	190	259
GIIc	2137	656	576	-0.02	1.50	1.4	2.7	1.5	175	235
GIId	2136	654	575	-0.01	1.57	0.5	1.6	0.8	192	223
GIIIa	2115	672	540	-3.98	2.01	3.6	1.7	0.2	596	432
GIIIb	2111	671	551	-4.46	2.41	1.0	2.0	1.3	852	554
GIIIc	2291	630	539	-3.00	0.93	1.3	1.8	0.5	811	584
GIIIId	2286	629	538	-3.16	1.09	2.7	2.7	0.6	902	670
AIa	2570	549	476	2.71	-1.59	1.2	1.1	0.0	532	384
AIb	2561	552	477	2.69	-0.93	0.8	3.1	0.8	546	405
AIc	2569	550	477	2.16	-2.80	1.0	1.2	0.4	526	276
AId	2592	546	475	2.17	-1.91	0.9	3.0	0.1	586	322
AIIa	2547	548	476	1.73	1.79	1.0	1.8	1.0	597	327
AIIb	2547	550	477	1.71	1.85	1.3	2.5	1.5	560	362

^a *A*, *B*, and *C* are the rotational constants (in MHz); χ_{aa} and χ_{bb} represent the diagonal elements of the ^{14}N nuclear quadrupole coupling tensor (in MHz) while $|\mu_a|$, $|\mu_b|$ and $|\mu_c|$ are the electric dipole moment components (in Debye). ^b Relative energies with respect to the global minimum, in cm^{-1} . ^c Gibbs energies calculated at 298 K at the MP2/6-311++G(d,p) level of theory, in cm^{-1} .

Table 3. Rotational parameters determined experimentally for the seven observed rotamers of dopamine.

	I (GIc)	II (GId)	III (GIa)	IV (GIb)	V (GIIc)	VI (GIId)	VII (GIIb)
<i>A</i> ^a	2192.70023(75) ^d	2195.1912(16)	2129.5962(13)	2136.1705(22)	2170.3939(12)	2168.0178(55)	2130.7139(17)
<i>B</i>	649.98068(10)	648.50802(20)	668.35393(19)	667.00988(18)	647.21814(11)	646.4331(12)	659.32824(12)
<i>C</i>	567.489911(85)	565.42383(23)	571.27207(19)	569.86122(38)	567.35500(16)	566.5753(12)	569.05166(24)
Δ_J	0.0627(10)	0.0543(27)	0.0594(27)	0.0486(43)	0.0647(18)	0.045(10)	0.0613(22)
χ_{aa}	0.702(17)	0.675(21)	1.652(27)	1.653(36)	-0.119(26)	[-0.01] ^e	-0.727(32)
χ_{bb}	-1.305(14)	-1.077(16)	-1.247(22)	-1.149(26)	1.636(19)	1.6196(28)	2.491(24)
σ ^b	1.4	1.8	2.1	2.1	1.7	2.0	1.7
<i>N</i> ^c	37	27	39	28	33	17	22

^a *A*, *B* and *C* are the rotational constants (in MHz); Δ_J is a quartic centrifugal distortion constant (in kHz); χ_{aa} and χ_{bb} are the diagonal elements of the ^{14}N nuclear quadrupole coupling tensor (in MHz). ^b rms deviation of the fit (in kHz). ^c Number of measured transitions. ^d Standard error in parentheses in units of the last digit. ^e Fixed to the theoretical value.

The findings presented in this study regarding dopamine provide an initial insight into the conformational behavior of this neurotransmitter in the gas-phase, which appears to be quite diverse given the seven distinct conformations found during these experiments.

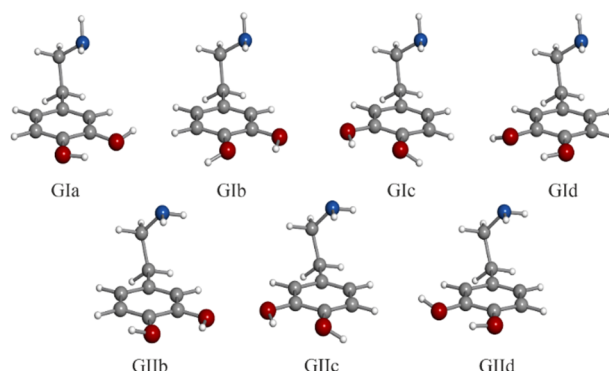


Figure 2. The molecular structure of the seven conformers identified for neurotransmitter dopamine.

3.2. The Structure of the Elusive Simplest Dipeptide GlyGly

The arrangement of proteins relies on a delicate interplay of noncovalent interactions, both inter- and intramolecular, present in the polypeptide chains. The examination of the structural characteristics and folding processes of polypeptides and proteins can initially be approached by exploring the conformational properties of isolated short peptides, with the latter as a prelude to the former. Given that specific intramolecular interactions have been demonstrated to be crucial for the folding of dipeptides, analyzing these smaller molecular models can provide essential insights regarding both structure and interactions. In this regard, the analysis of the rotational spectroscopic study of the glycylglycine (HGlyGlyOH or GlyGly) dipeptide [80] is intended to exemplify the intramolecular interactions and the conformational landscape associated with the simplest homodipeptide.

GlyGly, formed through two glycine amino acid units, represents the simplest dipeptide. This compound is characterized by its solid state, exhibiting a high melting temperature of approximately 263 °C and a low vapor pressure that complicates the accurate measurement of its gas-phase spectrum. Consequently, its conformational properties are not yet well understood. The combination of laser ablation methods with Fourier transform microwave spectroscopy has enabled the observation of the rotational spectrum of the GlyGly dipeptide for the first time. A LA-MB-FTMW spectrometer was employed for this study at the University of Valladolid [67]. The observed rotational spectrum of GlyGly, depicted in Figure 3, primarily featured lines displaying distinctly resolved hyperfine structures, with multiple components extending across several MHz. This phenomenon can be explained through the ^{14}N nuclear quadrupole coupling interaction of two nuclei. Numerous sets of both *a*-type and *b*-type R-branch rotational transitions were attributed to three distinct rotamers of GlyGly, designated as X, Y, and Z. Table 4 presents the experimentally determined molecular constants for the three GlyGly conformers characterized through FTMW spectroscopy, alongside those derived from quantum chemical calculations. The conformational identification of X, Y, and Z rotamers as conformers pI, pII and npI, respectively, is founded on the strong accordance between the experimental and theoretical values of the molecular constants, as demonstrated by the data in Table 4.

Table 4. Experimental and theoretical spectroscopic parameters for the three observed conformers of GlyGly.

	Rotamer X	pI	Rotamer Y	pII	Rotamer Z	npII
<i>A</i> ^a	3124.81219 (66) ^d	3074	5056.1357 (11)	4966	3380.9980 (11)	3300
<i>B</i>	846.30680 (17)	858	668.787909 (17)	670	912.71335 (35)	922
<i>C</i>	675.17061 (12)	685	597.87466 (15)	598	798.10977 (29)	807
χ_{aa} ($^{14}\text{N}_t$)	−3.6379 (24)	−3.20	0.106 (17)	0.23	−1.6209 (25)	−0.86
χ_{bb} ($^{14}\text{N}_t$)	2.6732 (36)	2.75	−1.474 (19)	−1.62	0.6953 (82)	0.61
χ_{aa} ($^{14}\text{N}_c$)	2.4907 (25)	2.55	2.301 (20)	2.38	1.6781 (52)	1.78
χ_{bb} ($^{14}\text{N}_c$)	1.2924 (32)	1.28	1.959 (20)	2.07	1.1034 (84)	1.18
σ ^b	2.3		2.3		2.7	
<i>N</i> ^c	51		29		34	

^a *A*, *B* and *C* are the rotational constants (in MHz); Δ_I is a quartic centrifugal distortion constant (in kHz); χ_{aa} and χ_{bb} are the diagonal elements of the ^{14}N nuclear quadrupole coupling tensor (in MHz). N_t and N_c represent the terminal and central ^{14}N nuclei, respectively ^b rms deviation of the fit (in kHz). ^c Number of measured transitions. ^d Standard error in parentheses in units of the last digit.

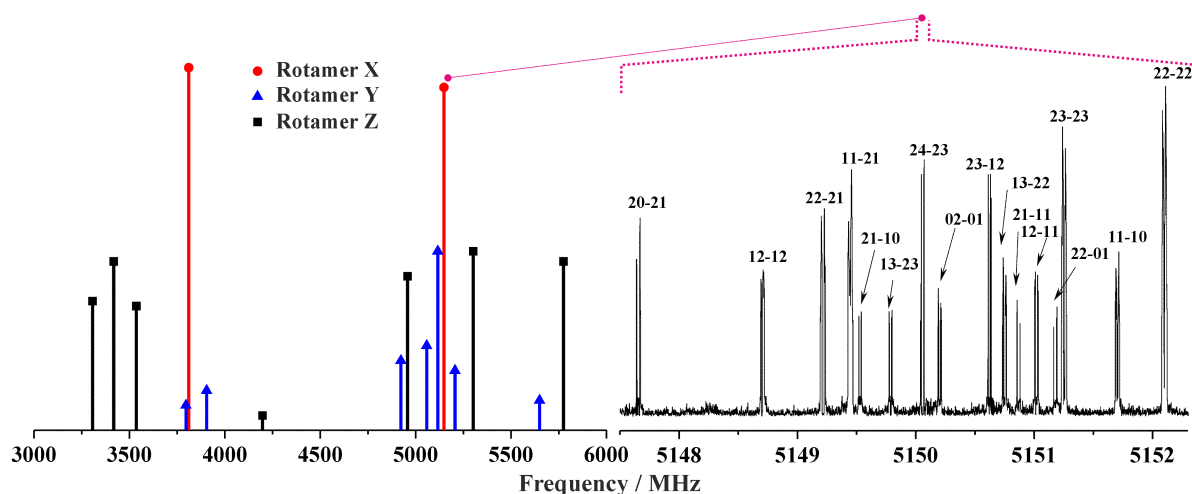


Figure 3. (Left) The stick representation of the recorded spectra of GlyGly within the frequency range of 3 to 6 GHz illustrates the rotational transitions corresponding to the X, Y, and Z rotamers. (Right) The $2_{12} \leftarrow 1_{01}$ rotational transition of rotamer X showing the nuclear quadrupole hyperfine structure. Each hyperfine component is labeled with the corresponding values of I' , $F' \leftarrow I''$, F'' quantum numbers.

The molecular structures for the conformers of GlyGly are shown in Figure 4. The structure for the conformer pI is stabilized by two five-membered rings featuring $\text{N-H} \cdots \text{O}=\text{C}$ and the $\text{N-H} \cdots \text{NH}_2$ interactions, whereas pII conformer is reinforced by the same $\text{N-H} \cdots \text{NH}_2$ interaction closing a five members ring and a bifurcated $\text{NH}_2 \cdots \text{O}=\text{C}$ interaction. In respect to the third conformer npII, it incorporates a seven-membered ring with an $\text{O-H} \cdots \text{O}=\text{C}$ interaction, alongside five-membered $\text{N-H} \cdots \text{NH}_2$ interactions. Additional low-energy conformers of GlyGly were not detected during the experiment, despite being anticipated as observable species through theoretical simulations. This fact can be explained considering that some conformers, which are thermally populated under pre-expansion conditions, might collisionally relax to lower energy conformers, thereby becoming “missing” after the jet expansion. This phenomenon has been observed in biomolecules, including α -amino acids [81,82]. Ruoff et al. [83] concluded that the collisional elimination of a higher energy conformer remains feasible when the isomerization energy barrier is less than 400 cm^{-1} .

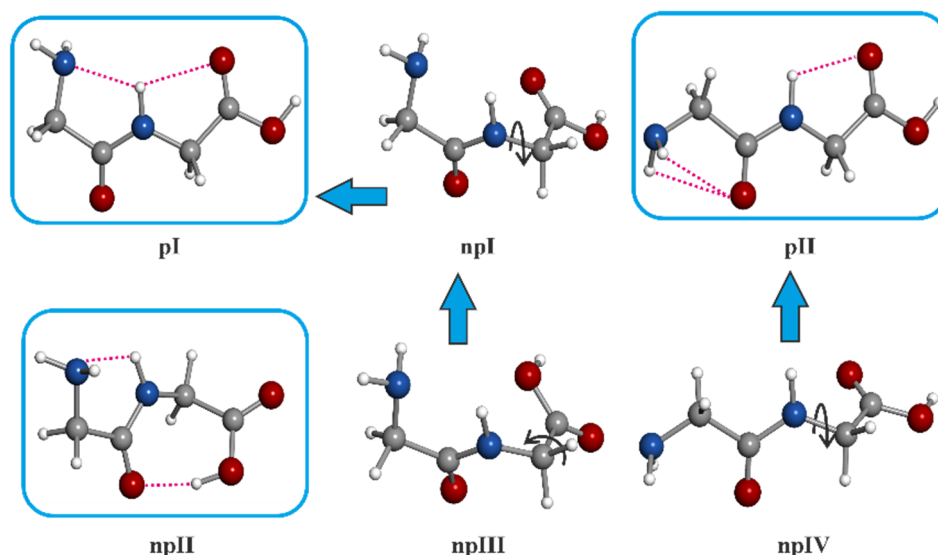


Figure 4. The GlyGly lowest energy conformers. The three observed species are highlighted. Pink lines denote the internal interactions that reinforce the stability of the molecular configurations. The blue arrows represent the pathways for conformational interconversion (refer to Figure 5 for additional details).

Quantum chemical calculations, at the M06-2x/aug-cc-pVTZ level of theory, on the plausible relaxation profiles of the non observed GlyGly conformers (see Figure 4) were carried out. The calculated interconversion energy profile between the npI and pI conformers is depicted in Figure 5. The finding of a very low barrier of 36 cm^{-1} elucidates

the absence of the npI conformer in the supersonic expansion. The same explanation applies to the lack of detection for conformers npIII and npIV. The relaxation pathway from conformer npIV to pII (see Figure 5) reveals an interconversion barrier of 45 cm^{-1} which further explains the non-detection of npIV species. A two-stage relaxation mechanism could clarify the non-observance of conformer npIII in the supersonic expansion. Conformer npIII is capable of initially transitioning to npI, through a 240 cm^{-1} barrier for the $\text{N}_\text{c}\text{CC}=\text{O}$ angle, which then relaxes to the pI conformer as indicated in the energy profile in Figure 5. All these aspects underscore the idea that the conformational behavior of the GlyGly dipeptide is, to some extent, dynamic.

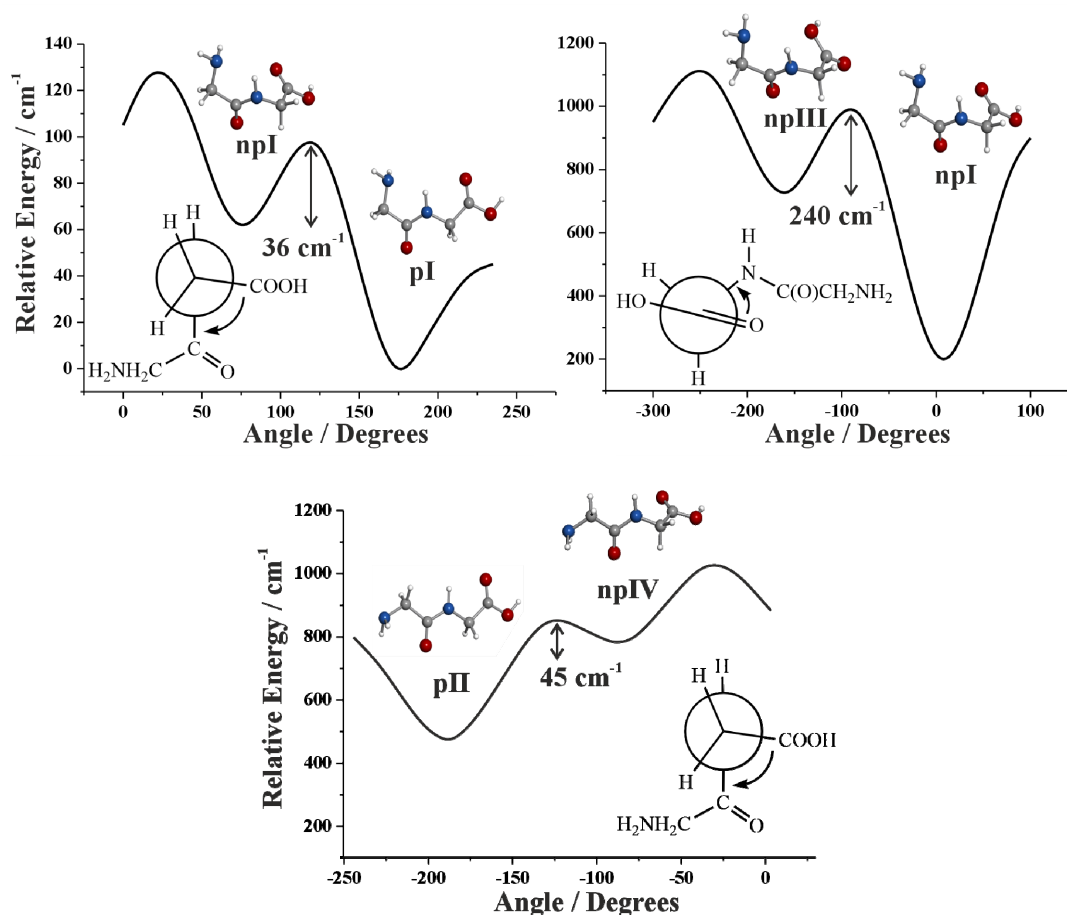


Figure 5. Potential energy profiles between the lowest energy conformers of GlyGly calculated at the M06-2x/aug-cc-pVTZ level of theory.

4. Rotational Spectroscopy of Atmospheric Species

Carbonyl oxides are reaction intermediates in the ozonolysis process of alkenes in the troposphere [84]. This type of reaction occurs in two separate stages; the initial stage involves a 1,3-cycloaddition of ozone to the alkene's double bond resulting in the formation of a primary ozonide, which is subsequently decomposed to yield a carbonyl compound and a carbonyl oxide. Since Rudolph Criegee proposed this mechanism in 1949 [85,86], these carbonyl oxides have been widely recognized as Criegee intermediates (CIs).

The atmospheric relevance of CIs has been a subject of discussion for many years, and it is now acknowledged that they significantly impact atmospheric chemistry and climate change due to their notable reactivity. Although the mechanism for CIs formation has been known since 1949, their characterization in laboratories has been hindered for a long time due to the short lifespan of CIs and the absence of appropriate precursors for their generation. Nevertheless, the advent of a new method for producing gas-phase CIs has facilitated direct kinetic and spectroscopic investigations of Criegee intermediates, making this topic one of considerable interest in last two decades. In 2008, Taatjes et al. [87] reported the first gas-phase laboratory detection of the simplest CI, CH_2OO . Various laboratory techniques have since been utilized to examine these molecular species, including rotational spectroscopy. A comprehensive overview of the majority of studies involving CIs can be found in several reviews [88–95]. A few rotational spectroscopy studies concerning the structure and reactivity of CIs are outlined below.

4.1. Conformational Investigation of Alkyl Derivatives of CIs: Propionaldehyde Oxide, C_2H_5CHOO

As substitutional groups replace a hydrogen atom of the simplest CI, various conformers might exist. This is the case of the ethyl CI derivative, C_2H_5CHOO , which exhibits a broader range of conformations than that for the methyl CI, CH_3CHOO [96,97], attributable to the enhanced flexibility of the ethyl group. The methyl derivative, CH_3CHOO , is present in two distinct conformers, namely *syn* and *anti*, with the *syn* conformer demonstrating greater stability over the *anti* conformer by 15.50 kJ/mol. On the other hand, the ethyl group's flexibility allows C_2H_5CHOO to adopt additional conformations in the gas phase; specifically, it can exist in two *syn* and two *anti* forms (refer to Figure 6). The conformers labeled as “1”, *syn1* and *anti1*, possess C_s symmetry, characterized by a planar arrangement of the heavy atom skeleton, whereas the conformers labeled “2” exhibit C_1 symmetry.

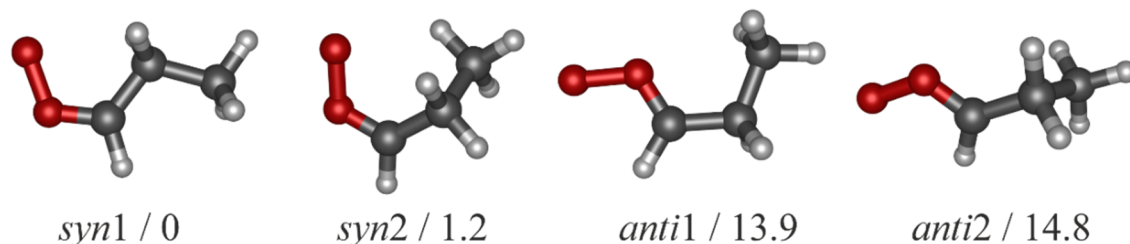


Figure 6. The four plausible conformers of C_2H_5CHOO . Relative energies in kJ/mol are shown.

The different conformations of CIs show distinct reactivity towards various reactions as shown by Lin & Chao [92], Kuwata [98] and Chung et al. [99]. This is the reason why it is of utmost importance to characterize the gas-phase molecular structures of these species and understand their conformational behavior. The first investigations of C_2H_5CHOO molecule were carried out using UV spectroscopy [100,101]. In these works it was found that *syn1* and *syn2* species presented different unimolecular decay rates. Nevertheless, the authors did not identify any spectral characteristics for the *anti* isomers, likely due to the challenge of detecting each conformer with full selectivity using that particular spectroscopic method. First rotational spectroscopy experiments for C_2H_5CHOO were done using the PNFTMW spectrometer at Prof. Endo's lab at the National Yang Ming Chiao Tung University in Taiwan [68,69]. The transient C_2H_5CHOO intermediate was produced in the electric discharge of a gas mixture of 1,1-diiodopropane and O_2 diluted in argon gas [102]. A few mL of 1,1-diiodopropane was introduced into a reservoir, and a gas blend comprising 2% oxygen and 98% argon at an overall pressure of 1.5 atm was passed through the liquid container. This methodology is used to ensure the precursor molecules attain an adequate partial pressure. The gas mixture was directed through a pulsed-solenoid valve, with a voltage of 800 V applied at the nozzle's outlet to initiate an electric discharge that activated the chemical reaction among the precursors. The resultant products were analyzed using Fourier-transform microwave spectroscopy in the frequency range of 4–40 GHz.

Three distinct conformers, namely *syn1*, *syn2* and *anti1*, were unambiguously identified by comparing the molecular constants derived from experimental data (see Table 5) with those derived from quantum chemical calculations (refer to Table 6). Nonetheless, comprehensive searches aimed at detecting any spectral signatures of the conformer *anti2* yielded no lines attributed to this species. The absence of conformer *anti2* in the experiment was ascribed to a collisional relaxation process to the conformer *anti1* via a low-energy interconversion barrier (illustrated in Figure 7).

Table 5. Rotational constants for the three observed conformers of C_2H_5CHOO .

	<i>syn1</i>	<i>syn2</i>	<i>anti1</i>	<i>anti2</i>
<i>A</i> /MHz	15,827.30797 (92) ^a	9165.3125 (17)	14,783.5573 (16)	20,416.5767 (28)
<i>B</i> /MHz	2831.2119 (12)	3931.5104 (62)	2870.62137 (69)	2335.53358 (77)
<i>C</i> /MHz	2474.3361 (12)	3178.4222 (61)	2477.44947 (53)	2262.51748 (94)
Δ_J /kHz	0.5664 (39)	3.680 (30)	0.8680 (79)	1.3392 (90)
Δ_{JK} /kHz	−1.747 (27)	−10.337 (96)	−4.172 (56)	−50.60 (25)
δ_J /kHz	0.1012 (27)	1.095 (26)	0.1857 (89)	−0.056 (10)
<i>N</i>	54 ^b	32 ^b	24 ^c	14
σ /kHz	2.7	4.0	3.7	3.0

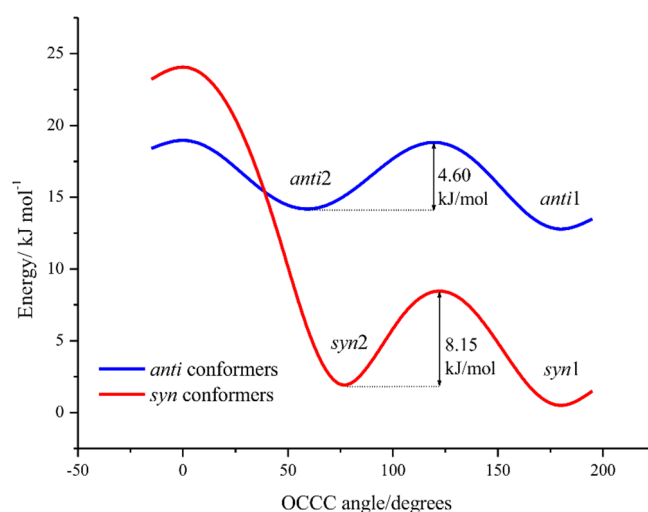
^a Values in parentheses denote 1 σ errors, applied to the last digit. ^b Number of *A/E* components included in the fit. ^c Number of pure rotational transitions included in the fit.

Table 6. Theoretical spectroscopic constants for the four conformers of C₂H₅CHOO calculated at CCSD(T)/aug-cc-pVTZ level.

	<i>syn1</i>	<i>syn2</i>	<i>anti1</i>	<i>anti2</i>
<i>A</i> /MHz	15,796	9130	14750	20,216
<i>B</i> /MHz	2830	3944	2874	2331
<i>C</i> /MHz	2472	3190	2479	2261
μ_a]/D	4.25	3.12	4.96	5.39
μ_b]/D	1.67	3.05	2.08	0.55
μ_c]/D	0.00	0.25	0.00	0.95
$\Delta E/\text{cm}^{-1}$	0 ^a	103	1158	1237

^a Relative energy to that of *syn1*.

The process of interconversion occurs during the initial stages of the supersonic expansion, facilitated by interactions between various conformers and buffer gas molecules. The isomerization barrier values, which indicate the conditions under which a higher energy conformer can be collisional removed, have been derived experimentally [83]. These barrier heights are influenced by the characteristics of the carrier gas, and research has demonstrated that heavier inert gases exhibit improved cooling efficiency in supersonic expansions, attributed to the greater collision energies they generate [83,102]. Consequently, an Ar-seeded expansion is anticipated to promote the transformation of higher energy conformers to their lower energy counterparts, whereas higher energy species are likely to persist in a Ne-seeded expansion. This elucidates the presence of *syn1*, *syn2*, and *anti1* conformers, and the non observation of *anti2*. Although the interconversion barrier height between *anti2* and *anti1* is sufficiently low to facilitate the relaxation of conformer *anti2*, the barrier for *syn2/syn1* conformers is high enough to inhibit interconversion between those species even in the presence of an Ar expansion. To validate this hypothesis, further experiments utilizing Ne as the carrier gas were performed. The spectral lines corresponding to the conformers *syn1*, *syn2*, and *anti1*, were detected, along with new lines for a conformer designated as *anti2* (refer to Tables 5 and 6). Thus, four distinct species comprising two *syn* and two *anti* conformers were characterized for the ethyl-substituted CI through FTMW spectroscopy [103,104].

**Figure 7.** Potential energy profile of C₂H₅CHOO calculated at CCSD(T)/aug-cc-pVTZ level of theory. The interconversion barrier heights between *syn* and *anti* conformers are indicated. Note: Reprinted from Cabezas et al. [103] with permission from AIP Publishing.

4.2. Reaction of CH₂OO and CH₃CHOO with HCOOH

The reactions of CIs with organic acids can be regarded as a significant elimination route for these intermediates, as they can rival the reaction with water [105]. Such reactions yield chemical species that have larger molecular weights and lower vapor pressures compared to the initial reactants, thus playing a role in the generation of secondary organic aerosols (SOAs) [106]. The rate coefficients for the reactions involving CH₂OO and CH₃CHOO intermediates with formic and acetic acids have been reported [106–108]. However, details concerning the mechanisms of these reactions and their products are limited to theoretical predictions [109–111].

FTMW spectroscopy is used to examine the reaction between the simplest Criegee intermediate, CH₂OO, and formic acid. Quantum chemical calculations indicate that the CH₂OO + HCOOH reaction reveals two primary

pathways that produce hydroxylated ozonide (HSOZ, cyclic-HOCHOOCH₂O) and hydroperoxymethyl formate (HPMF, HC(O)OCH₂OOH), refer to Figure 8.

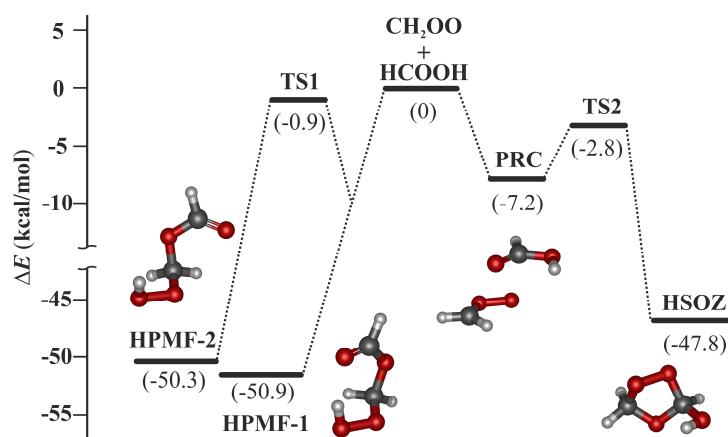


Figure 8. Energy profile for the reaction between CH₂OO and formic acid calculated at the CCSD/aug-cc-pVTZ level of theory. Total energies relative to that of separated molecules are given in parentheses (in kcal mol⁻¹). Note: Reprinted from Cabezas and Endo [112] with permission from the Royal Society of Chemistry.

The spectroscopic experiments are done using the PNFTMW spectrometer at Prof. Endo's lab at the National Yang Ming Chiao Tung University in Taiwan [68,69]. In these experiments, electric discharges of a gas mixture of 0.3% formic acid, 2% O₂ and 97.7% Ar mixed with 1,1-diiodomethane are used to produce the short-lived species. Two different conformers of HPMF, HPMF-1 and HPMF-2 (see Figure 8), are detected through their rotational transitions. These conformers of HPMF are predicted to be formed by a reaction mechanisms that imply 1,4- and 1,2-insertions of HCOOH over the CH₂OO molecule, respectively. Formic acid anhydride (FAA) is detected in the rotational spectrum, and it is identified as the main decomposition byproduct of HPMF in the gas phase. The rotational spectra, both with and without deuterated compounds (DCOOH and HCOOD), illustrate the formation of FAA under our experimental circumstances from the dehydration of HPMF. This process occurs via a mechanism that entails the transfer of hydrogen from the -CH₂- group to the -OH group, which is ultimately released as a water molecule, leading to the production of FAA. These findings are entirely consistent with the generation of FAA from HPMF following the reaction of CH₂OO with formic acid (refer to Figure 9). Measurements of the relative intensities of the rotational transitions for HPMF and FAA reveal that FAA is nearly 15 times less abundant than HPMF. This supports the notion that HPMF is not as ephemeral as previously thought, and the conversion process to FAA is not exceedingly rapid.

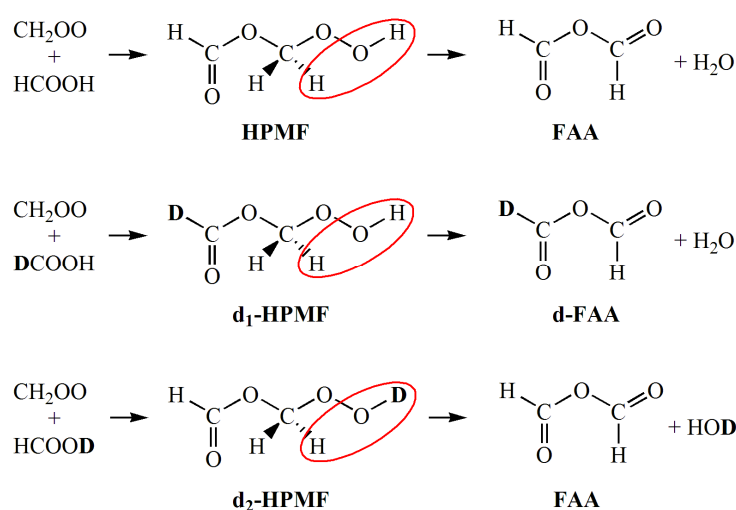


Figure 9. The mechanism for the formation of formic anhydride (FAA) starting with the Criegee intermediate and involving interactions with formic acid molecules, progressing through HPMF. The three reactions vary based on the isotopic forms of formic acid used; one version lacks deuterium, while the other two incorporate it at distinct positions. The red circle highlights the atoms responsible for generating the water molecule that is released during the dehydration process. Note: Reprinted from Cabezas and Endo [112] with permission from the Royal Society of Chemistry.

In an independent study, Porterfield et al. [113] observed also HPMF by FTMW spectroscopy simulating the ozonolysis of ethylene in a reactor. The authors detected only one conformer of HPMF, which is the most stable form resulting from the 1,4-insertion mechanism. This observation can be explained by the low production rate of CH_2OO in their experimental setup in contrast to the synthetic method employing CH_2I_2 and O_2 . Additionally, they discovered secondary products resulting from the ozonolysis reaction, including glycolaldehyde, formaldehyde, formic anhydride, and ethylene oxide. Recently, Chung et al. [114] studied the same reaction utilizing step-scan temporally resolved Fourier-transform absorption spectroscopy. These authors [114] reproduce the experimental results relative to both HPMF conformers obtained by Cabezas & Endo [112] and confirm the formation of FAA in the dehydration of HPMF.

The reaction addition between formic acid (HCOOH) and acetaldehyde oxide (CH_3CHOO), whether in *syn* or *anti* configurations, produces the hydroperoxyethyl formate HPEF as the insertion product. Theoretical calculations suggest that this reaction can follow multiple pathways, resulting in the formation of two distinct conformers of HPEF from *syn*- and *anti*- CH_3CHOO , respectively. As illustrated in Figure 10, CH_3CHOO can be subjected to nucleophilic attack by the O-H group of HCOOH in a 1,2-insertion reaction, leading to the generation of products *syn*-HPEF-I and *anti*-HPEF-II. Conversely, a 1,4-insertion pathway occurs when the $\text{O}=\text{C}-\text{OH}$ group engages with CH_3CHOO , producing *syn*-HPEF-II and *anti*-HPEF-I species in a process that encounters no energetic barrier. Kumar et al. [115] and Liu et al. [116] have also examined through quantum chemical calculations the formation of vinyl hydroperoxide (VHP) resulting from the reaction between *syn*- CH_3CHOO and HCOOH in an exothermic mechanism that promotes hydrogen transfer via a double hydrogen migration.

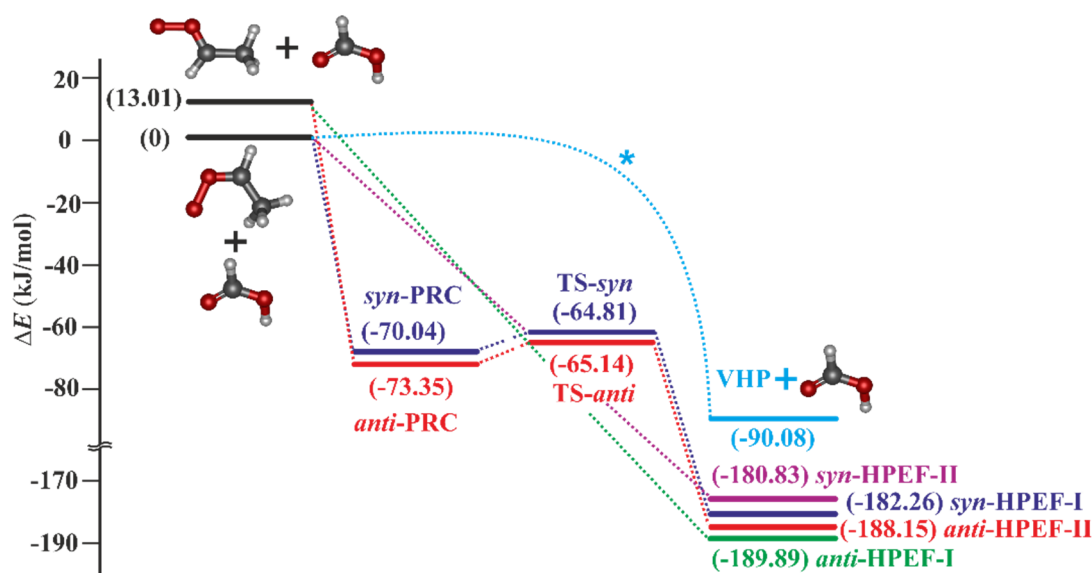


Figure 10. Energy profile for the $\text{CH}_3\text{CHOO}+\text{HCOOH}$ reaction. The CCSD/aug-cc-pVTZ level of theory was used for all the calculations. Total energies relative to that of separated molecules are given in parentheses (in kJ mol^{-1}). The reaction route indicated with an asterisk pertains to the tautomerization of *syn*- CH_3CHOO catalyzed by formic acid, resulting in the formation of vinyl hydroperoxide (VHP). Note: Reprinted from Cabezas and Endo [117] with permission from the Royal Society of Chemistry.

The FTMW investigation of the $\text{CH}_3\text{CHOO} + \text{HCOOH}$ reaction system [117] reveal the formation of two conformers of HPEF. These are identified as the *anti*-HPEF-I and *syn*-HPEF-I species, with their assignment corroborated by isotopic substitution experiments. Despite *syn*-HPEF-I and *anti*-HPEF-I being the most energetically favorable products in their respective reaction pathways, the energy disparity between the HPEF-I and HPEF-II products is minimal (1.42 and 1.72 kJ/mol , respectively), in relation to the overall exothermic nature of the reaction. Therefore, it can be inferred that thermodynamic considerations alone are insufficient to account for the spectral observations, indicating that a combination of both kinetic and thermodynamic factors are responsible for the formation of specific HPEF conformers within the $\text{CH}_3\text{CHOO} + \text{HCOOH}$ reaction.

Liu et al. [116] used VUV photoionization experiments to investigate the reaction between CH_3CHOO and HCOOH . While the experimental settings utilized by the aforementioned authors display certain resemblances to those employed in the FTMW studies, the outcomes diverge significantly. Liu and colleagues detected VHP generated through the tautomerization of *syn*- CH_3CHOO facilitated by formic acid (refer to Figure 10) and find no spectral evidence supporting the existence of HPEF. This stands in stark contrast to the findings from the

rotational experiments, which indicates HPEF as the sole product resulting from the reaction between CH_3CHOO and HCOOH . Furthermore, variations in the method for generating CIs are evident between the two studies, with Liu's research using UV photolysis and Cabezas' study implementing electric discharges, potentially influencing the detection of distinct species.

5. Rotational Spectroscopy of Interstellar and Circumstellar Molecules

The intricate chemical diversity of the interstellar and circumstellar media has been proved by the discovery of approximately 340 distinct chemical species to date [13–15]. The catalog of detected molecules encompasses very simple molecules such as CH, CN, and CH^+ , which were among the earliest compounds discovered in the ISM [118–120], as well as more complex structures like PAHs [20,22]. The advent of radio astronomy in the mid-twentieth century facilitated the discovery of numerous new molecules, and this momentum has persisted almost linearly over time, owing to advancements in sensitivity and angular resolution. Most of these 340 molecular discoveries have been done through a combination of rotational spectroscopy and radio astronomy, where the emission frequencies observed in the interstellar medium and circumstellar medium have been matched against laboratory spectroscopic data of established compounds. Around 90% of the molecules detected in the ISM are transient species that cannot be synthesized through conventional chemical methods and stored in the laboratory. In this way, their astronomical identifications would not have been possible, in most cases, without laboratory experiments that allowed in situ generation. The studies described below are relevant in this context.

5.1. Mg- and Na-Bearing Species Studied by LA-MB-FTMW

The first metal-bearing molecules, NaCl, AlCl, KCl, and AlF, were detected in 1987 in the circumstellar envelope of the carbon-rich star envelope IRC+10216 by Cernicharo & Guélin [121]. Later in the 90s, the first magnesium molecules, MgCN and MgNC, were discovered in the envelopes of the evolved stellar objects IRC+10216 and CRL 2688 [122,123]. Theoretical investigations concerning the formation of magnesium-bearing molecules in IRC+10216 indicate that the radiative combination of magnesium cation with hydrogen cyanide occurs, which is then followed by the dissociative recombination of HMgCN^+ with an electron. Consequently, the hydrogenated species HMgNC appears to be a highly promising candidate for detection in the IRC+10216 object.

In order to obtain reliable spectral predictions to undertake an astronomical search of such species, precise laboratory rotational frequencies are necessary. With this purpose, a rotational investigation of HMgNC was done at the University of Valladolid [124]. The spectrum of HMgNC is obtained utilizing a laser ablation molecular beam Fourier transform microwave spectrometer operating within the frequency range of 4 to 26 GHz [65]. HMgNC molecules are generated through the laser ablation of pure magnesium rods within the throat of a pulsed supersonic expansion of a highly diluted ethylcyanide ($\text{CH}_3\text{CH}_2\text{CN}$, 0.2%) in neon, maintaining a stagnation pressure of 15 bar. A pulsed Nd:YAG-laser ($\lambda = 355$ nm, ~ 20 mJ/pulse) focused on the rod is used to produce the vaporization of the solid magnesium and to trigger the chemical reaction in the gas precursor mixture [125]. In order to optimize the experimental conditions for detecting the rotational transitions of HMgNC, the formation of the radical MgNC is investigated since both species require analogous experimental settings within the LA-MB-FTMW setup. Frequency scans are performed to identify the $J = 1-0$ transition predicted around 11 GHz, as indicated by previous quantum chemical calculations from Gronowski and Kołos [126]. A group of three lines (Figure 11) is identified near 10.962 MHz. The observed frequency splittings closely matched the predicted values, taking into account the electric nuclear quadrupole coupling constant associated with the nitrogen nucleus. No additional fine or hyperfine structures resulting from spin-rotation or spin-spin interactions are detected, suggesting that the spectrum being analyzed is characteristic of a closed-shell molecule. A further rotational transition in the 21.9 GHz region is then measured, resulting in the unambiguous identification of HMgNC. A Hamiltonian of the following form is used to analyze all the observed frequencies: $\mathbf{H} = \mathbf{H}_R + \mathbf{H}_Q$, where $\mathbf{H}_R$ contains rotational and centrifugal distortion parameters while $\mathbf{H}_Q$ the quadrupole coupling interactions. The experimental molecular constants derived for HMgNC were; $B_0 = 5481.4333(6)$ MHz, $D_0 = 2.90(8)$ KHz, and $eQq(\text{N}) = -2.200(2)$ MHz. The standard deviation of the rotational fit was 1.6 kHz.

Employing the molecular parameters obtained from the laboratory study and utilizing a dipole moment value of 3.49 D, as predicted by the *ab initio* calculations of Gronowski & Kołos [126], an astronomical investigation was performed in IRC+10216. Four harmonic transitions were identified and attributed to the rotational transitions $J = 8-7$, $10-9$, $12-11$, and $13-12$ associated with HMgNC. By fitting the recorded frequencies, values of $B_0 = 5481.49(3)$ MHz and $D_0 = 3.2(1)$ kHz were obtained, i.e., nearly identical to the rotational constants obtained in the laboratory. This provided a basis for confirming the identification of a new magnesium-containing species, constituting the third discovery of a magnesium-bearing molecule in the CSM [124].

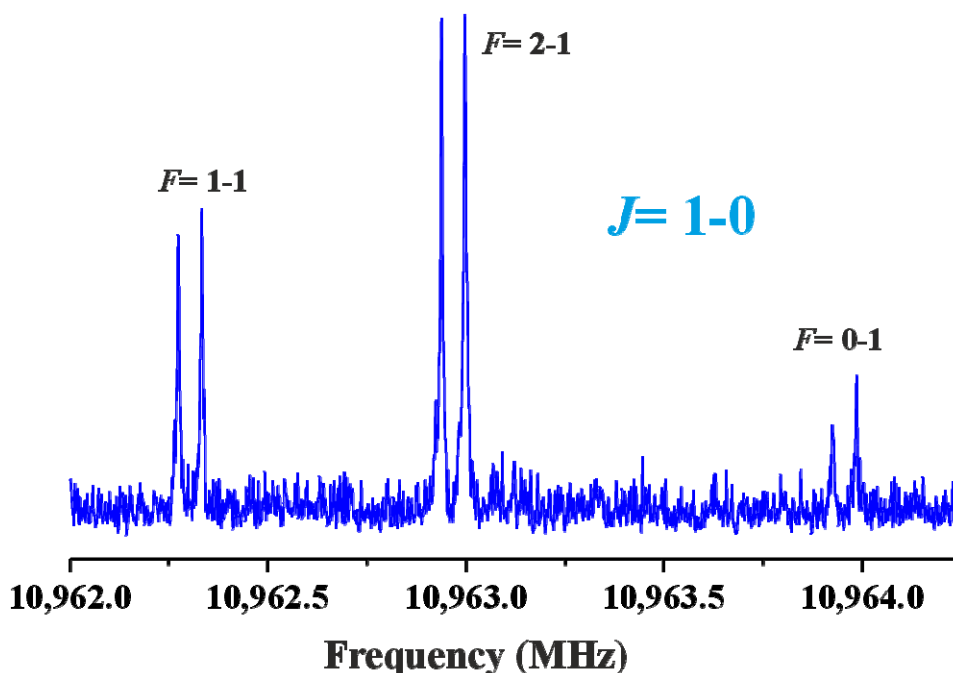


Figure 11. The rotational transition $J = 1-0$ of HMgNC detected around 11 GHz. The hyperfine structure resulting from nuclear quadrupole coupling interaction is clearly discerned. The spectrum was achieved by 200 shots and a step scan of 0.3 MHz.

The detections of a considerable diversity of cyanides and isocyanides in space implies that longer carbon chains featuring metals similar to those found in the cyanopolyynes group- HC_3N , HC_5N , HC_7N , etc.—can be detected in space as well. However, until 2019, none of these metal-bearing species had been detected in any astronomical source. The first refractory species with a $-\text{C}_3\text{N}$ moiety was MgC_3N , detected in IRC+10216 in 2019 by Cernicharo *et al.* [127]. Then, other metallic species with carbon chains have been detected, but only Mg-bearing molecules; MgC_2 , MgC_4H , MgC_6H , MgC_5N , MgC_4H^+ , MgC_6H^+ , MgC_3N^+ and MgC_5N^+ [127–130]. As Mg there are other metals that can be abundant as well in the same sources where MgC_xN and MgC_yH species have been detected. This is the case of Na, and therefore, its cyanoacetylide is a promising candidate to be detected in IRC+10216.

NaCCCN was investigated in the laboratory, at the University of Valladolid, using a FTMW spectrometer coupled to a laser ablation that works within the frequency spectrum of 2–18 GHz. The transient species NaCCCN was generated by the chemical reaction between Na vapor metal, vaporized by picosecond Nd:YAG-laser pulses ($\lambda = 355$ nm and 10 mJ/pulse), and BrCCCN which was vaporized by heating at ca. 65 °C. The molecules resulting from this reaction were expanded as a supersonic jet and rapidly cooled to a rotational temperature of ~ 2 K between the two mirrors of the Fabry–Pérot resonator. Then, they were probed by Fourier transform microwave spectroscopy.

With the help of the predicted molecular parameters obtained from quantum chemical calculations from the same work [131] the rotational spectrum lines of NaCCCN was analyzed. A group of lines with several hyperfine components was detected centered in 5284 MHz (see Figure 12). Then other five group of lines at 2.6, 7.9, 10.5, 13.2 and 15.8 GHz were measured. They correspond to the $J = 1-0$, $J = 3-2$, $J = 4-3$, $J = 5-4$ and $J = 6-5$ rotational transitions, respectively. NaCCCN possesses two nuclei with quadrupole moment, ^{14}N ($I = 1$) and ^{23}Na ($I = 3/2$), and therefore each rotational transition of NaCCCN presents a very complex hyperfine pattern as shown in Figure 11 for the $J = 2-1$ rotational transition. A $^1\Sigma$ Hamiltonian with this form: $\mathbf{H} = \mathbf{H}_r + \mathbf{H}_Q(\text{Na}) + \mathbf{H}_Q(\text{N})$ was used to fit all the observed hyperfine components, a total of 122. The analysis provided the rotational parameters B and D and the electric nuclear quadrupole coupling constants for the ^{23}Na and ^{14}N nuclei, which are listed in Table 7. The good accordance between the experimental and predicted values confirms the detection of NaCCCN molecule.

In 2023, NaCCCN was discovered in IRC+10216 [132] through the observation of seven lines in the Q-band line survey data gathered with the Yebes 40 m radiotelescope [133]. The observed frequencies were in very good agreement with those predicted from the laboratory measurements. A new set of molecular constants for NaCCCN was derived from the merged fit of the lines observed in IRC+10216 and those measured in the laboratory [131] (see Table 7). They perfectly agree with the previous values, both theoretical and experimental. The rotational temperature and column density derived for NaCCCN in IRC+10216, assuming a dipole moment value of 12.9 D, are 13.5 ± 1.7 K and $(1.2 \pm 0.2) \times 10^{11} \text{ cm}^{-2}$, respectively.

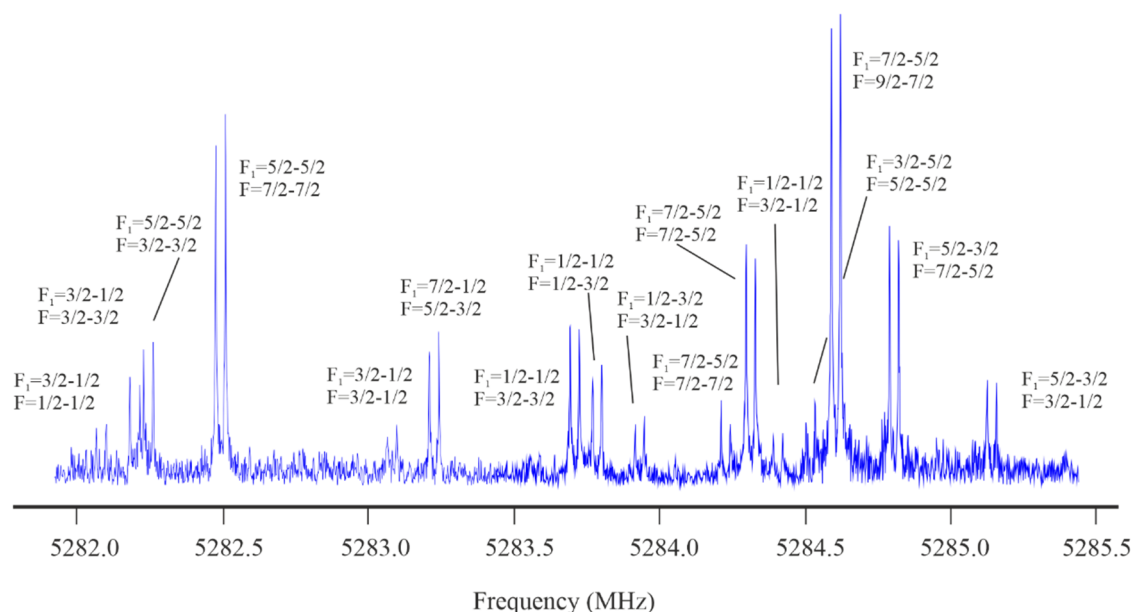


Figure 12. Section of the rotational transition $J = 2-1$ of NaCCCN. The nuclear quadrupole coupling hyperfine structure arising from both from both ^{23}Na ($I = 3/2$) and ^{14}N ($I = 1$) nuclei is resolved. Each hyperfine component is labeled with the corresponding values of F_I' , $F' \leftarrow F_I''$, F'' quantum numbers. The spectra were achieved by accumulating 200 pulses in each frequency step.

Table 7. Theoretical and experimental spectroscopic constants for the NaCCCN.

	Theoretical	Laboratory	Lab + IRC+10216
B/MHz	1343.3 ^a	1321.094334 (28) ^f	1321.094464 (27) ^f
D/kHz	0.0922 ^b	0.1011 (7)	0.10483 (56)
$eQq(\text{Na})/\text{MHz}$	-6.808 ^c	-7.0497 (7)	-7.0497 (7)
$eQq(\text{N})/\text{MHz}$	-3.9748 ^c	-3.8761 (5)	-3.8761 (5)
rms ^d /kHz		0.9	15.9
N ^e		122	129

^a Composite method including vibration-rotation interaction at MP2/aug-cc-pVTZ level. ^b MP2/aug-cc-pVTZ level. ^c CCSD/aug-cc-pVTZ level. ^d Root mean square of the fit. ^e Number of hyperfine components included in the fit. ^f Values in parentheses denote 1σ errors, applied to the last digit.

5.2. Transient CN-Bearing Species Formed by Electric Discharges

Investigations of cyanide compounds derived from prevalent interstellar molecules can yield valuable information regarding the chemical mechanisms that contribute to the chemical complexity in astronomical objects, such as the Taurus Molecular Cloud TMC-1. This source is a starless core with a kinetic temperature of approximately 9 K and it has been recognized for exhibiting a highly diverse chemical composition associated with cyanopolynes (HC_{2n+1}N) and the radical species of the type C_nN . Through the use of the sensitive QUIJOTE line survey [134], more than 60 new molecules have been identified over the last four years. A majority of these identified molecules are hydrocarbons, along with their derivatives containing cyano (CN) and ethynyl (CCH) groups, in addition to protonated forms of commonly occurring molecules [135–138]. Furthermore, it is noteworthy that around ten of these molecular species contain sulphur [18,139–143]. Apparently, sulphur exhibit peculiar chemistry in this cloud, enabling the formation of considerable quantities of sulphur-containing molecular species.

In this context, the cyano derivative of thioketene (H_2CCS) can be considered a promising candidate to be observed in TMC-1, taking into account the abundance of the latter. Its cyano derivative, called cyanothioketene (NCCHCS; see Figure 13), was then investigated in the laboratory to allow the radioastronomical search using the QUIJOTE survey. The rotational spectrum of NCCHCS was recorded employing a Balle-Flygare type Fourier-transform microwave (FTMW) spectrometer at the National Yang Ming Chiao Tung University in Taiwan [69,71]. As NCCHCS is a short-lived species, it was generated in the gas-phase by pulsed electric discharge of 2000 V with a duration of 450 μs over a mixture of vinyl cyanide (CH_2CHCN , 0.3%) and carbon disulfide (CS_2 , 0.3%), both diluted in argon. The NCCHCS molecules produced in the discharge were then probed by FTMW spectroscopy capable of resolving small hyperfine splittings (see Figure 13).

Before conducting the experiments, the theoretical spectroscopic parameters (rotational constants and the electric dipole moment components) for NCCHCS were derived through quantum chemical computations employing the coupled cluster method CCSD(T)-F12/cc-pCVTZ-F12. On the other hand, the ^{14}N hyperfine constants were calculated at the MP2/cc-pVTZ level of theory, and the vibration-rotation interaction constants were estimated at the B3LYP/cc-pVTZ level of theory. The results are shown in Table 8.

Using the frequencies predicted from the laboratory data an astronomical search in TMC-1 for NCCHCS was carried out. Twenty three transitions lines were easily detected in the QUIJOTE line survey, with $J = 9$ up to 14, including $K_a = 0, 1$ and 2, providing an unambiguous detection of this species in space [144]. The intensity lines vary between 0.4 mK and 1.1 mK. Frequencies observed in TMC-1 were analyzed employing a standard Watson Hamiltonian in the S -representation. The obtained rotational and distortion constants are presented in Table 8. These values show a high degree of consistency with those obtained from fit using the laboratory data. A combined analysis of the laboratory and TMC-1 data yields enhanced values for these parameters. These constants are suggested for the calculation of the rotational spectrum of NCCHCS.

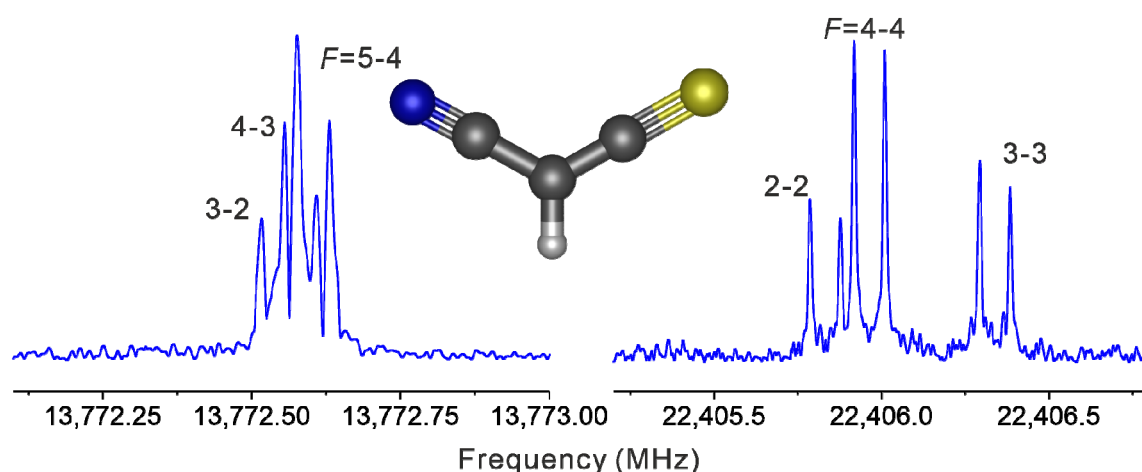


Figure 13. FTMW hyperfine spectrum of the $4_{04}-3_{03}$ (left) and $3_{12}-3_{03}$ (right) rotational transition for NCCHCS (molecular structure shown in the center of the figure). Each hyperfine component is split into two Doppler components due to the fact that the orientation of the supersonic jet expansion aligns with the stationary wave present in the Fabry-Pérot cavity of the spectrometer. The spectra were achieved by 300 shots of accumulation and a step scan of 1.0 MHz with a repetition rate of 10 Hz.

Table 8. Molecular constants (all in MHz) of NCCHCS.

	Theoretical	Laboratory	TMC-1	Lab+TMC-1
A	23,613	23,743.58026 (105) ^a	23,744.47 (74)	23,743.58064 (90)
B	1790	1785.880959 (232)	1785.88036 (96)	1785.880880 (115)
C	1661	1658.684211 (190)	1658.6848 (10)	1658.684441 (98)
$10^4 D_J$	5.7	6.5243 (142)	6.544 (11)	6.5385 (37)
$10^2 D_{JK}$	-6.39	-6.4936 (52)	-6.59052 (75)	-6.4959 (34)
$10^4 d_1$	1.13	1.3199 (127)	1.301 (15)	1.3088 (42)
χ_{aa}	-1.87	-1.9970 (100)	-	-1.9970 (98)
χ_{bb}	0.29	0.3827 (72)	-	0.3827 (70)
rms ^b /kHz		2.4	8.4	4.5
N ^c		65	23	88

^a Values in parentheses denote 1σ errors, in units of the last significant digits. ^b Root mean square of the fit. ^c Number of hyperfine components included in the fit.

Another molecular species with CN moiety that could be observed in TMC-1 is the 1-cyano propargyl (HC_3HCN) radical. This is an isomer of the interstellar species 3-cyano propargyl ($\text{CH}_2\text{C}_3\text{N}$) radical, detected in TMC-1 in 2021 [145]. Molecular structures of both radicals are shown in Figure 14. One of the routes to form $\text{CH}_2\text{C}_3\text{N}$ in space is the reaction $\text{C} + \text{CH}_2\text{CHCN} \rightarrow \text{CH}_2\text{C}_3\text{N} + \text{H}$. This reaction, studied using crossed molecular beam experiments and theoretical calculations [146,147], suggest that HC_3HCN radical is also formed in the same reaction at least twice more efficiently than $\text{CH}_2\text{C}_3\text{N}$. To carry out an astronomical search of the HC_3HCN radical, its rotational spectrum was investigated in the laboratory. As in the case of NCCHCS species, a Balle-Flygare

narrowband-type Fourier transform microwave (FTMW) spectrometer at the National Yang Ming Chiao Tung University of Taiwan [69,71] was used to this purpose. In this case, HC₃HCN was produced in a supersonic expansion by a pulsed electric discharge of a gas mixture of CH₂CHCN (0.2%) and C₂H₂ (0.4%) diluted in Ar. Since HC₃HCN is an open-shell species, its rotational spectrum will be composed of paramagnetic lines, because of the Earth's magnetic field. To cancel this phenomenon, three sets of Helmholtz coils placed perpendicularly to one another were used. The spectral resolution of the measurements is 5 kHz, and the frequency measurements have an estimated accuracy better than 3 kHz.

The predicted *a*-type dipole moment for the HC₃HCN radical is 3.70 D, and thus, the *a*-type rotational transitions are expected to be fairly strong. Hence, the 2₀₂–1₀₁, 3₀₃–2₀₂, 4₀₄–3₀₃ and 5₀₅–4₀₄ were observed around 10.7, 16.1, 21.5, and 26.8 GHz. Figure 15 displays two spectra corresponding to two *a*-type *K_a* = 0 rotational transitions. The HC₃HCN radical was readily confirmed as the spectral carrier based on the following arguments. (i) The frequencies of the transitions observed closely align with the calculated frequencies, (ii) each transition showcases a hyperfine spectral structure that is similar to what is expected for an open-shell molecule with three coupling nuclei; and (iii) the lines show paramagnetic behavior. The final dataset comprises 193 hyperfine components that originated from 12 rotational transitions with *a*- and *b*-type transitions.

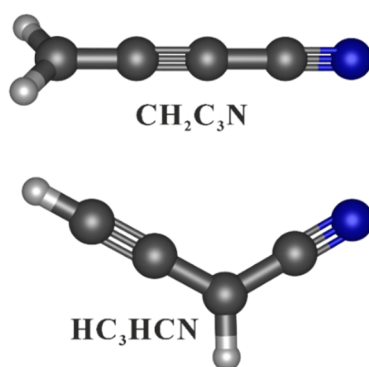


Figure 14. Molecular structures and relative energies of the CH₂C₃N and HC₃HCN radicals.

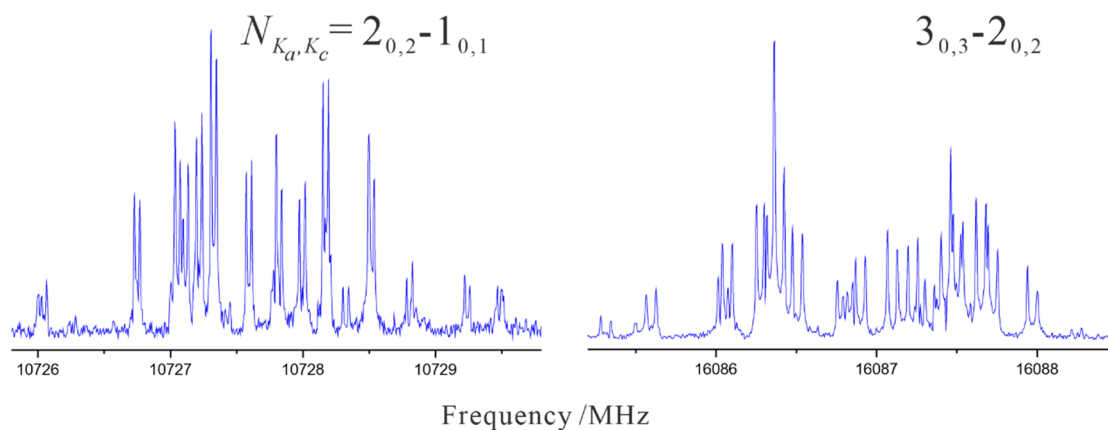


Figure 15. The 2₀₂–1₀₁ and 3₀₃–2₀₂ rotational transitions for the HC₃HCN radical. Further hyperfine lines, not depicted in this figure, were likewise detected. The spectra were obtained through the accumulation of 100 shots and a scanning step of 0.5 MHz at a repetition frequency of 10 Hz. The coaxial configuration of the adiabatic expansion alongside the resonator axis results in instrumental Doppler doubling. The resonance frequencies are determined by averaging the two Doppler components.

All the hyperfine lines were analyzed using an appropriate Hamiltonian for an asymmetric top molecule with a doublet electronic state (²A'') and the centrifugal distortion expressed in Watson's A-reduced form. [148] The employed Hamiltonian has the following form:

$$\mathbf{H} = \mathbf{H}_{\text{rot}} + \mathbf{H}_{\text{sr}} + \mathbf{H}_{\text{mhf}} + \mathbf{H}_{\text{Q}}$$

where $\mathbf{H}_{\text{rot}}$ contains rotational and centrifugal distortion parameters, $\mathbf{H}_{\text{sr}}$ denotes the spin-rotation term, $\mathbf{H}_{\text{mhf}}$ is the term related to magnetic hyperfine coupling interactions resulting from hydrogen and nitrogen nuclei, while $\mathbf{H}_{\text{Q}}$

encompasses the nuclear electric quadrupole interaction attributed to the nitrogen nucleus. A comprehensive explanation of these terms is available in Hirota 1985 [149]. Through least-squares analysis of all recorded transition frequencies, the values for twenty-two molecular constants were derived. The standard deviation of the fit is 2.0 kHz, which is marginally less than the precision of the experimental measurements, suggesting that the intricate hyperfine structures produced by the three nuclei are accurately described by the utilized Hamiltonian. The molecular constants obtained are presented in Table 9 alongside those estimated from ab initio computations.

The spectroscopic parameters displayed Table 9 were employed to yield reliable frequency predictions to assist the astronomical searches for HC₃HCN within TMC-1. The frequency predictions show an accuracy better than 10 kHz in the Q band (30–50 GHz) and approximately 10–20 kHz in the W band (72–116 GHz). A first attempt to search for this species using the QUIJOTE survey was reported in 2022 [150]. The molecule could not be detected in TMC-1 and only the 3 σ upper limit to its column density was derived. The upper limit found for HC₃HCN was $<6.0 \times 10^{11} \text{ cm}^{-2}$, which implies an abundance ratio HC₃HCN/CH₂C₃N < 3.8 . However, a deeper integration in TMC-1 done from 2022 to June 2024 provides a more sensitive QUIJOTE survey than what was used in 2022 [150]. As a result, the HC₃HCN molecule was detected in TMC-1 in the year 2025 by Cabezas et al. [151]. The most intense hyperfine features of a total of eight rotational transitions, with N quantum number from 6 to 8, were detected in the line survey providing an unambiguous detection of this species in space. An analysis of the observed intensities using a line profile fitting method provided rotational temperature of $7 \pm 1 \text{ K}$, while the observed intensities are reproduced with a column density of $(2.2 \pm 0.2) \times 10^{11} \text{ cm}^{-2}$. The derived column density for HC₃HCN is about three times lower than the upper limit estimated in the previous astronomical search [150]. Given the column density of CH₂C₃N in TMC-1, $1.6 \times 10^{11} \text{ cm}^{-2}$ [145], the column density ratio between the two isomers, HC₃HCN/CH₂C₃N, is 1.4.

Table 9. Spectroscopic parameters of HC₃HCN (all in MHz).

	Experimental	Theory ^d
A	29,173.01440 (72) ^a	27909
B	2807.94534 (25)	2835
C	2556.92917 (25)	2574
Δ_N	0.0014120 (19)	0.0014
Δ_{NK}	−0.109826 (50)	−0.091
δ_N	0.0003574 (45)	0.000345
ϵ_{aa}	−60.5224 (30)	−51.35
ϵ_{bb}	−5.3817 (12)	−6.385
ϵ_{cc}	−0.5405 (13)	−1.60
ϵ_{ab}	∓ 1.214 (73) ^b	−1.64
$a_F^{(\text{H}\alpha)}$	−32.2969 (32)	−31.70
$T_{aa}^{(\text{H}\alpha)}$	8.7599 (36)	9.14
$T_{bb}^{(\text{H}\alpha)}$	−7.9786 (61)	−8.43
$T_{ab}^{(\text{H}\alpha)}$	± 12.58 (20) ^d	13.55
$a_F^{(\text{H}\beta)}$	−51.3475 (46)	−55.10
$T_{aa}^{(\text{H}\beta)}$	−25.3318 (27)	−29.31
$T_{bb}^{(\text{H}\beta)}$	24.5181 (48)	28.42
$T_{ab}^{(\text{H}\beta)}$	$[\pm 0.79]$ ^c	0.79
$a_F^{(\text{N})}$	6.6999 (27)	1.18
$T_{aa}^{(\text{N})}$	−10.3977 (22)	−11.33
$T_{bb}^{(\text{N})}$	−9.1827 (48)	−9.51
$T_{ab}^{(\text{N})}$	$[\pm 1.72]$ ^c	1.72
$\chi_{aa}^{(\text{N})}$	−2.7743 (22)	−2.82
$\chi_{bb}^{(\text{N})}$	0.6098 (42)	0.57
$\chi_{ab}^{(\text{N})}$	$[\pm 2.70]$ ^c	2.70

^a Values in parentheses denote 1 σ errors, applied to the last digit. ^b Only the relative signs are determined. ^c Values in brackets have been kept fixed to those obtained theoretically. ^d RCCSD(T)-F12/cc-pCVTZ-F12.

6. Outlook

High-resolution rotational spectroscopy is recognized as one of the most effective methods for distinguish between minor changes in the gas-phase molecular. Due to its versatility, it is presently applied to various physico-chemical studies, including investigations into the most essential characteristics of the electronic wavefunction as well as serving as a highly appropriate method for gathering data for astronomical searches for molecules. This

paper provides an overview of some of the latest applications of this spectroscopy, along with a discussion of some of the experimental methods used in these studies.

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Data Availability Statement

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Conflicts of Interest

The author declares no conflict of interest.

Use of AI and AI-Assisted Technologies

No AI tools were utilized for this paper.

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