

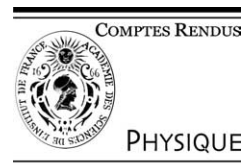


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Gas phase molecular spectroscopy/Spectroscopie moléculaire en phase gazeuse

Microwave Fourier transform spectrometers: a powerful tool for the spectroscopy in the XXIst century

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Presented by Guy Laval

Abstract

We present some recent applications of microwave Fourier transform spectroscopy for the study of various molecular systems: weakly bonded complexes, carbon chains for their importance in interstellar medium or molecules of biological interest. The recent developments are presented and some perspectives are discussed. *To cite this article: D. Petitprez, G. Wlodarczak, C. R. Physique 5 (2004).*

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Résumé

Spectrométrie micro-ondes à transformée de Fourier : un outil puissant pour la spectroscopie au XXI^{ème} siècle.

Nous présentons quelques applications de la spectroscopie micro-ondes à transformée de Fourier à l'étude de systèmes moléculaires variés : complexes faiblement liés (de type van der Waals ou liaison hydrogène), chaînes carbonées (pour leur intérêt astrophysique) ou molécules d'intérêt biologique. Les derniers développements sont décrits et quelques perspectives discutées. *Pour citer cet article : D. Petitprez, G. Wlodarczak, C. R. Physique 5 (2004).*

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Keywords: Microwave spectroscopy; Molecular complexes; Carbon chains; Biomolecules

Mots-clés : Spectroscopie micro-ondes ; Complexes faiblement liés ; Chaînes carbonées ; Biomolécules

1. Introduction

Microwave spectroscopy, after a rapid development after the Second World War, has become a classical tool for the analysis of rotational spectra and the determination of geometrical structures. From a technical point of view, various forms of modulation have been used in conventional spectrometers (Stark modulation, amplitude or frequency modulation of the radiation) [1]. The achieved sensitivity was high ($\alpha_{\max} = 10^{-9}$ – 10^{-10} cm⁻¹ at 20 GHz) but the resolution mostly Doppler limited.

Twenty-five years ago a new technique was introduced by Flygare and co-workers [2–4] using microwave pulses to polarize a gas sample and then a Fourier transform to invert the polarization decay signal emitted by the sample. Rapidly this technique was coupled to a Fabry–Perot resonator and a supersonic expansion. The low rotational temperature (1–3 K) in the supersonic expansion has allowed an increase of the sensitivity by populating only the low-lying rotational energy levels. Finally an improvement in the spectral resolution was obtained by arranging the molecular beam coaxially to the resonator axis giving a spectral resolution of 1 to 3 kHz [5,6].

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2. Description of the experimental set up

Most of the MicroWave Fourier Transform (MWFT) spectrometers in use all around the world (there are about 20 spectroscopy groups using this type of device) are based on a similar scheme. A pulsed microwave source (adjustable power: $10\ \mu\text{W}$ – $20\ \text{mW}$), in the frequency range 5–20 GHz, sometimes extended to 40 GHz, polarizes a gas sample. This sample is generally diluted in a carrier gas, argon or neon for most of the applications, at concentrations of about 0.1–1%, at a backing pressure of 1–3 bars in most cases (in several applications this pressure can reach 40 bars). The gas sample is expanded in the cavity at supersonic velocities. In the case of weakly bound complexes they are formed directly in the expansion. More sophisticated nozzles which allow a simultaneous injection of two different species are also available: in case of reactive species the conditions in the supersonic expansion avoid their chemical reaction and an intermediate species can be observed, giving some details on the reaction pathway [7]. As will be discussed later in the paper, electrical discharges can be applied to the

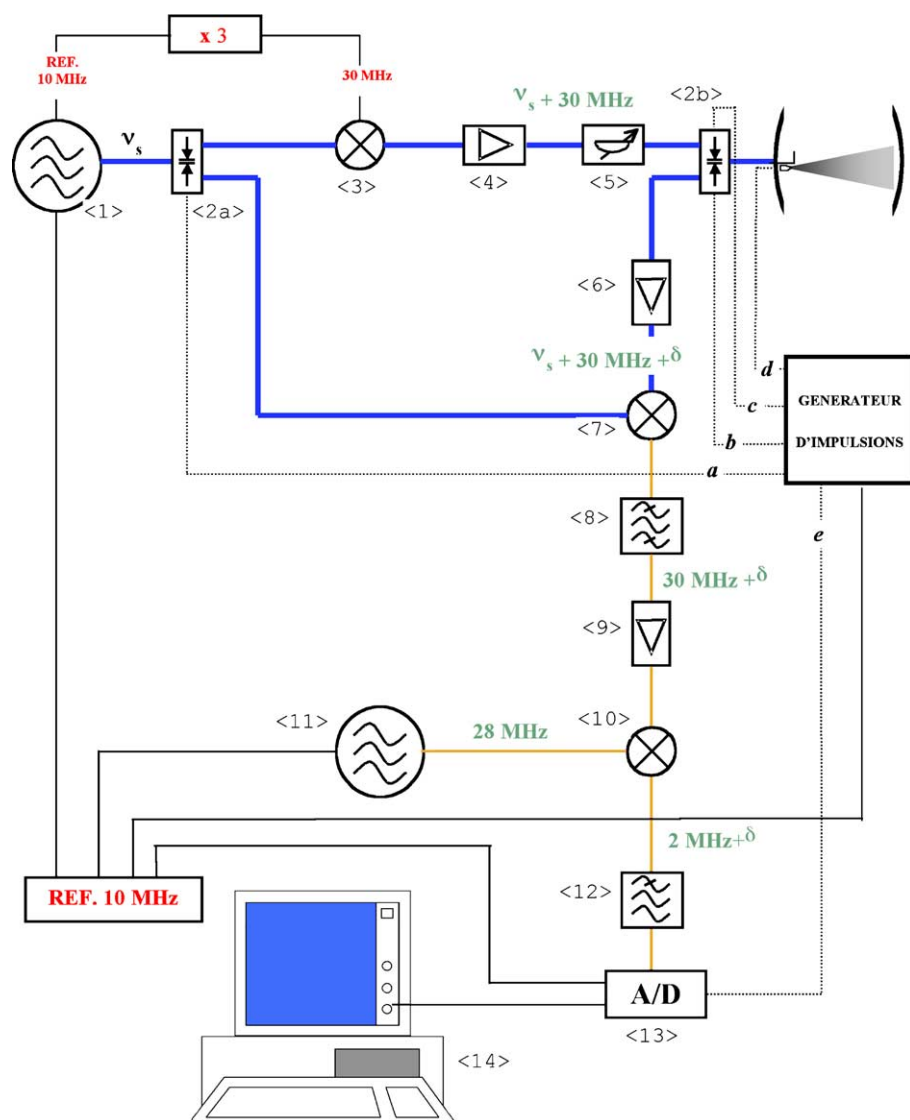


Fig. 1. Diagram of the MWFT spectrometer in use in our group: (1) MW synthesizer (2–20 GHz); (2a), (2b) SPDT switches; (3) single sideband modulator; (4) power amplifier; (5) attenuator; (6) low noise MW amplifier (band: 2–18 GHz, gain: 50 dB; noise figure: 2 dB); (7) image rejection mixer; (8) band pass filter; (9) amplifier; (10) mixer; (11) MW synthesizer (1–100 MHz); (12) low pass filter; (13) A/D converter, (14) computer.

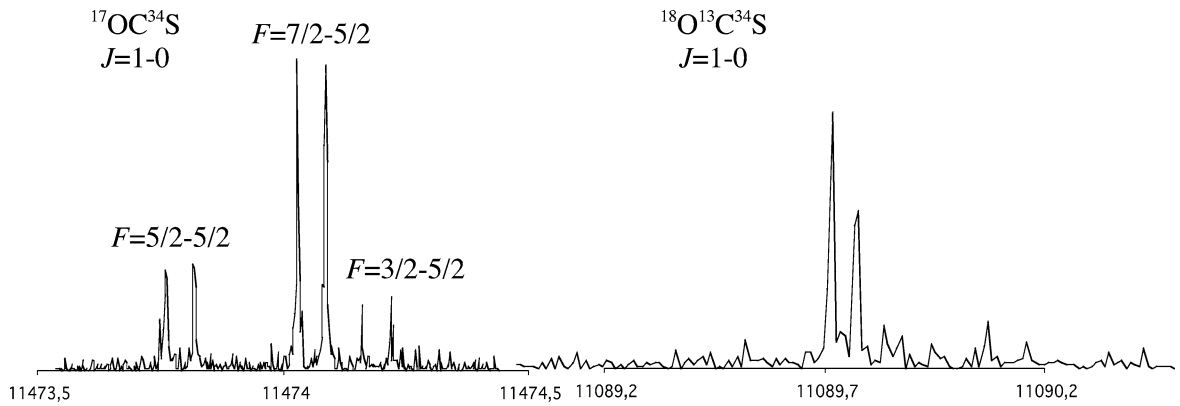


Fig. 2. Recording of the $J = 1-0$ transition for two isotopic species of OCS in natural abundance. For the $^{17}\text{O}^{13}\text{C}^{34}\text{S}$ species, the hyperfine structure due ^{17}O (nuclear spin $I = 5/2$) is fully resolved; intensity scale in arbitrary units, frequency scale in MHz.

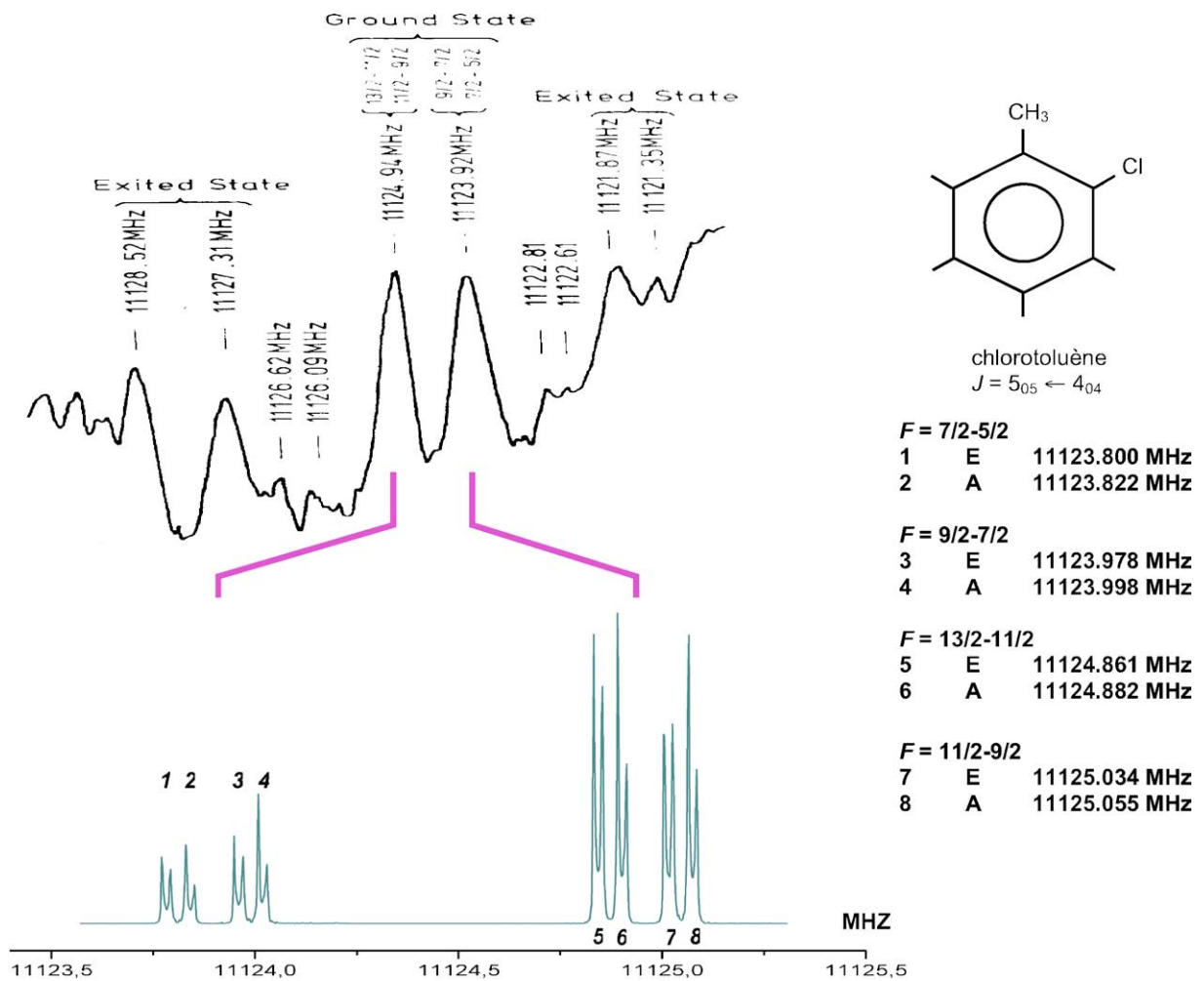


Fig. 3. Comparison of rotational spectra of chlorotoluene recorded with a Stark spectrometer (upper trace; taken from [45]) and with our MWFT spectrometer (lower trace [46]).

nozzle, but to produce reactive species, laser ablation [8] or laser photolysis [9] can also be coupled to this type of spectrometer. A schematic diagram of the spectrometer built in our group, [10–12], is given in Fig. 1.

A classical molecule used to appreciate the sensitivity of a microwave spectrometer is OCS, a linear molecule with a large variety of isotopic species. In Fig. 2 are presented two spectra belonging to $^{17}\text{O}^{34}\text{S}$ (natural abundance: 16 ppm; 100 spectra co-added) and $^{18}\text{O}^{13}\text{C}^{34}\text{S}$ (natural abundance: 0.4 ppm; 1000 spectra co-added). The lines appear as doublets due to Doppler effect.

An example of the gain in spectral resolution is given in Fig. 3, where the Stark and MWFT spectra of chlorotoluene are reported. The hyperfine structure due to the chlorine nucleus (labeled by the quantum number F) is mixed with the fine structure due to the internal rotation of the methyl group (labeled by the symmetry A or E).

Many advances have been achieved during these last twenty years that would not have been possible without this technique. We shall briefly discuss here some examples, without any aim of exhaustivity.

3. Van der Waals (vdW) and hydrogen bonded complexes

The coupling of the supersonic expansion to the MWFT spectrometer has induced the emergence of a new field, the spectroscopy of weakly bound complexes. These complexes are formed in the cold expansion and are not destroyed by collisions. Many of the studied complexes are formed between the expanded species and the atoms of the carrier gas, usually argon or neon. The properties of such complexes, geometrical structure or dissociation energy for instance, can be deduced from their rotational spectra and when available from their vibrational spectra. The evolution of the properties of the complexes when going from helium to xenon has not often been explored, because the complexes with helium are very weakly bound and the heavier rare gases (like Kr or Xe) have many isotopes, which induces crowded spectra. When going from Xe to He, the floppiness of the molecular complex increases, which can be observed by additional splitting occurring in the rotational spectra [11]: an example is given in Fig. 4, showing the splitting induced by the large amplitude motion of the neon atom around the thiirane molecule within the thiirane-neon complex. The VdW complexes containing two or three rare gas atoms have also been investigated. A complete list of the complexes studied by MWFT or theoretical calculations is regularly upgraded by Novick [13].

More recently $\text{He}_N\text{-OCS}$ [14] and $\text{He}_N\text{-N}_2\text{O}$ [15] clusters with $N = 3$ to 12 were studied by high resolution microwave and infrared techniques, bridging a gap between complexes containing one or two helium atom and clusters containing tens of thousands of helium atoms as studied by HENDI spectroscopy (helium nanodroplet isolation spectroscopy). In the microwave experiment a backing pressure up to 50 bars was used. Both experiments on OCS and N_2O showed that for a critical value of N (5 for OCS and 6 for N_2O) the rotational constant reaches a limit, implying that the additional helium atoms are decoupled from the rotational motion of the OCS or N_2O molecule. These experimental results have been recently confirmed by theoretical

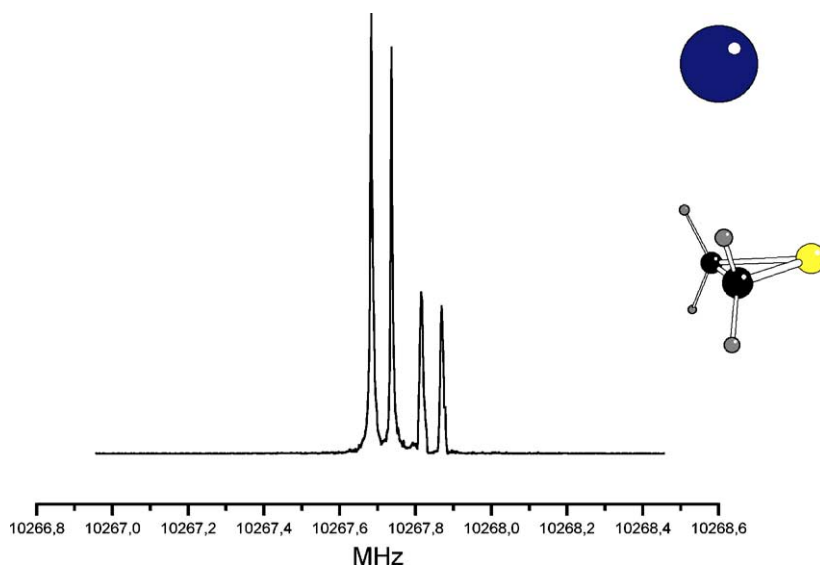


Fig. 4. Splitting of the $J = 1_{11} - 0_{00}$ transition of the thiirane–neon complex ($\text{C}_2\text{H}_4\text{S}-^{22}\text{Ne}$); the observed splitting is 133 kHz between the two lines.

calculations. This example shows the ability of microwave spectroscopy to give remarkable information on solvation processes in helium clusters, complementary to experiments carried in the rapidly growing field of HENDI spectroscopy. It has to be noticed that the assignment of the spectra to the different clusters present at the same time in the expansion has been made on the basis of the analysis hyperfine structure due to the ^{14}N nucleus.

Hydrogen bonded complexes have also been extensively studied during these last twenty years and a lot of documented literature is regularly published on this subject [13]. Among the significant results obtained recently, we can quote the work on water dimer $(\text{H}_2\text{O})_2$, for which a coupling with far infrared spectroscopy and high level quantum chemical calculations has brought a significant progress in the knowledge of its potential surface [16]. Water complexes with formic acid have extensively studied, leading to a lot of structural information on three types of complexes [17]. For atmospheric chemistry the $\text{H}_2\text{O}-\text{SO}_3$ complex is relevant to explain the formation of sulfuric acid in atmosphere, and has been investigated by the group of Leopold (Minneapolis) [18]. This group has also explored many donor-acceptor complexes and has brought new insights on the proton transfer.

Finally a last surprising result has been obtained recently by Gerry and coworkers (Vancouver) by vaporizing metals reacting with a second precursor entrained by a noble gas. They observed complexes of the type $\text{Ar}-\text{AuCl}$ [19] which are very strongly bound, a sign of a chemical bond between the metal and the noble gas.

4. Carbon chains

Carbon chains are molecules of great importance in the interstellar medium and some series have been so far detected in giant molecular clouds. We can quote as an example the cyanopolyine series HC_nN , where n is an odd integer lying between 1 and 11, but also the C_nH series, with $n = 1 - 6$ or the C_nN series with $n = 1 - 6$. The reader interested by the complete list of the interstellar molecules can have a look on Wootten's website [20]. Most of these carbon chains are unstable in laboratory conditions but can be rather abundant in the cold and quiet environment of some molecular clouds like TMC1 [21]. Their interstellar identification can only be sure after a spectroscopic study (see the story of the detection of HC_{11}N [22]). Most of the recent works on carbon chains has been carried out by the group of Thaddeus at Harvard, with the use of a MWFT spectrometer [23]. A high voltage (1000–2000 V), pulsed or continuous, is applied to the nozzle. For the cyanopolyines series a mixture of cyanoacetylene (0.5%) and diacetylene (0.5%) in neon at a total pressure of 2–2.5 bars has been used and the larger species detected was HC_{21}N . The sensitivity of the spectrometer has been increased by one order of magnitude by cooling the mirrors

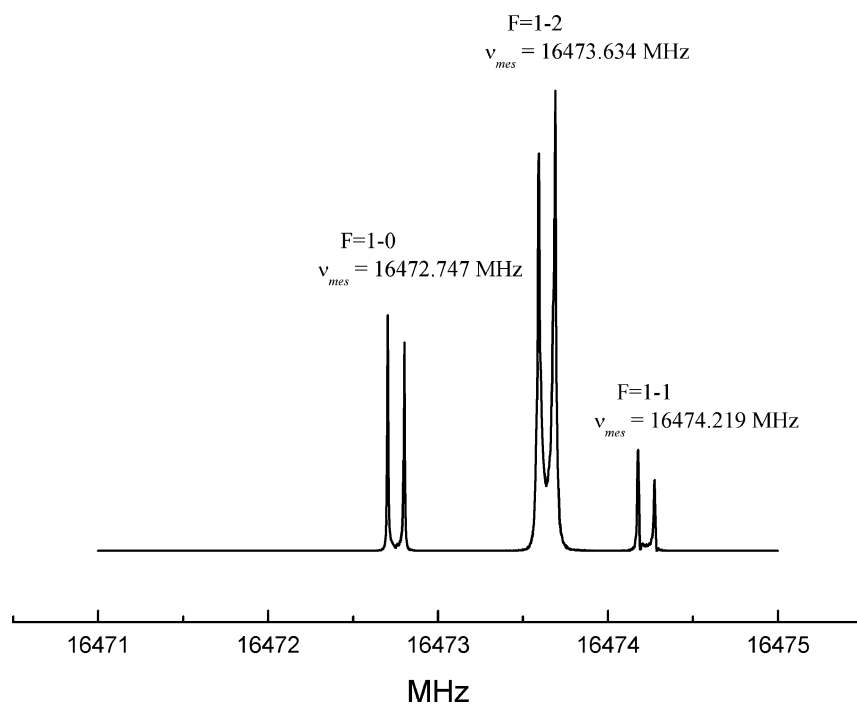


Fig. 5. Hyperfine structure of the $J = 111-000$ transition of $^{15}\text{NH}_2^{14}\text{NH}_2=\text{CO}$ (urea) observed in natural abundance (0.8%); Experimental conditions: nozzle temperature: 130°C , carrier gas: neon at a total pressure of 1 bar; 300 co-added scans.

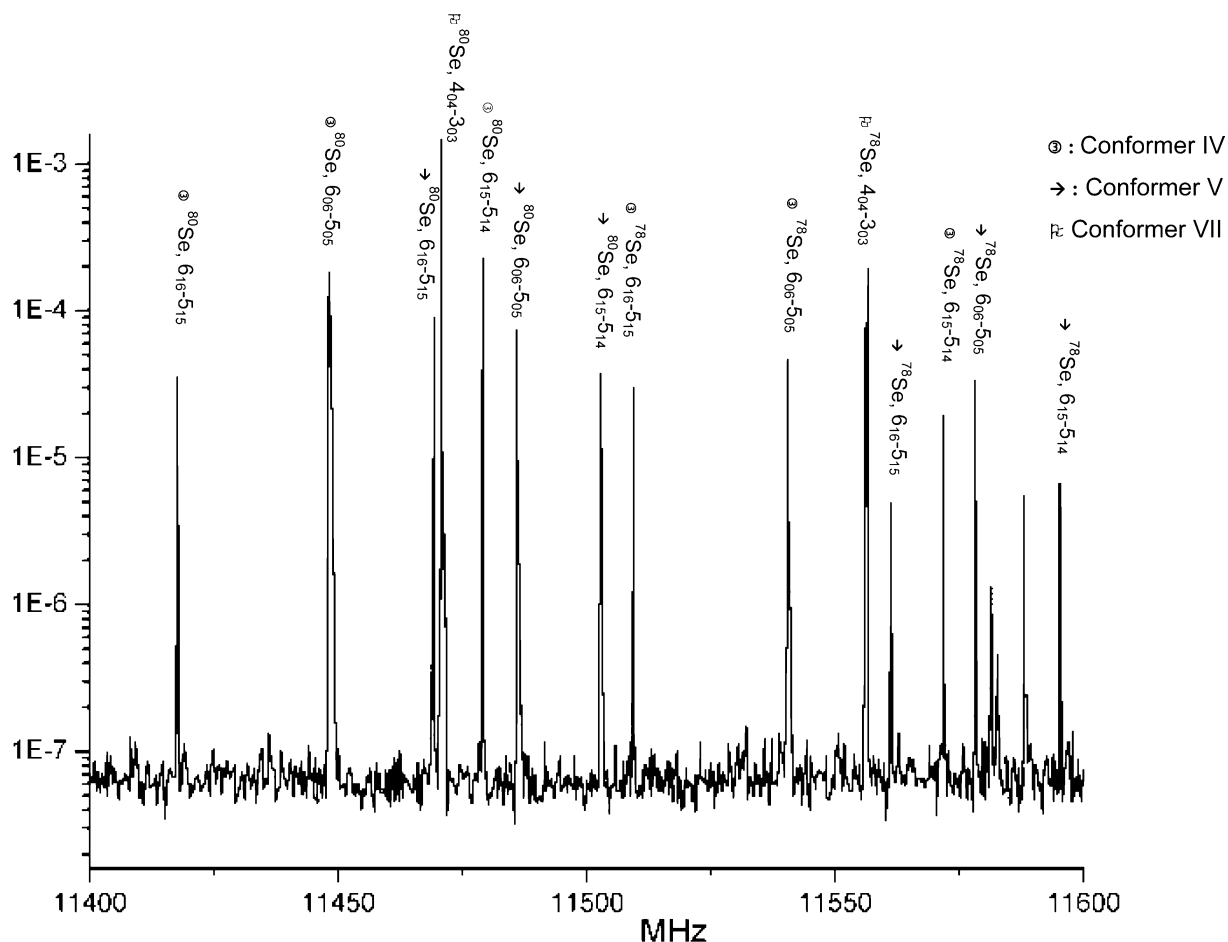


Fig. 6. Recording of a part of the microwave spectrum of buteneselenol $\text{H}_2\text{C}=\text{CHCH}_2\text{CH}_2\text{SeH}$, showing the evidence for three different conformers.

of the Fabry–Perot cavity and the electronic devices at the temperature of liquid nitrogen. Many other carbon chains have been studied: C_nH (up to $n = 14$), carbenes H_2C_n (up to $n = 10$, including ring chain compounds), silicon carbon chains SiC_n (up to $n = 8$), sulfur carbon chains HC_nS ($n = 5\text{--}8$) and $\text{H}_2\text{C}_n\text{S}$ ($n = 4\text{--}7$) [24]. Some significant results have also been obtained in the groups of Endo [25] and Yamamoto [26] in Tokyo. This new laboratory work has allowed the detection of new carbon chains either in TMC1 or IRC + 10216 and also produced a new insight on the formation of carbon bearing molecules in the interstellar medium [27]. The optical transitions of some of these new species could be linked to the old problem of the diffuse interstellar bands [23].

5. Biomolecules

The rotational spectroscopy of molecules of biological interest is not a new subject but it has received more attention in the last decade. One motivation of this type of work is the potential detection in interstellar medium: for instance glycine, the simplest amino acid, has been extensively searched but not yet securely detected, even if a recent paper claims its detection [28]. Since the discovery of extra-solar planetary systems exobiology has received an increasing interest. Prebiotic species or molecules considered as building blocks of life are now receiving more attention in the spectroscopy groups [29]. The difficulty lies in the production of the species in the gas phase. Two ways are currently used: heating of the sample, which is the simplest method (see the spectrum of urea given in Fig. 5), but cannot be used for the species which decompose before their vaporization, or laser desorption which is more convenient for a larger class of molecules. In their pioneering work on glycine, Suenram and coworkers [30–34] have noticed that the thermal method produced more stable results than laser desorption. More recently another amino acid, proline, has been investigated by MWFT in Valladolid with the laser technique [35]. The complexes of such

molecules with water are also of interest: the formamide-water complex has been studied at NIST [36] while the corresponding complex of urea has been searched without success in our group. When the number of atoms of the molecule increases, the number of conformations of the molecule also increases but MWFT spectroscopy is able to resolve the spectra belonging to different conformers (see Fig. 6). The supersonic expansion limits the number of observable conformers to the most stable ones. Similar techniques are also used in the infrared domain, where conformational information can also be obtained. A recent work on the conformational structure of tryptophan, another amino acid, in the 330–1500 cm^{-1} region with the use of the free electron laser 'FELIX' shows the promises of this infrared source for the study of larger biomolecules [37].

Among the other applications of MWFT spectroscopy, the detection of atmospheric pollutants has been considered, by introducing directly a sample of polluted atmosphere through the nozzle. An increase of the sensitivity can be obtained by mixing the sample with neon: if air is used as the carrier gas, the sensitivity is reduced by a factor of 50, due to the fact that oxygen and nitrogen are not monoatomic gases [11,38]. Small cavities have been developed in our laboratory and in other places (Kiel, NIST-Gaithersburg) to bring the spectrometer in polluted areas or to study the emission of motor vehicles in near real time in order to quantify their content in oxygenated hydrocarbons [39,40]. These portable spectrometers have also allowed the study of hazardous gases, such as sarin [41].

6. Conclusion

Twenty five years after its first introduction, MWFT spectroscopy has produced an incredible amount of results on various molecular systems in the gas phase. In the field of weakly bound complexes, a lot of information has been brought which allows the determination of several rules concerning their geometry. Reliable theoretical calculations are rather difficult to achieve for these complexes and the available experimental data provide useful benchmarks for the development of theoretical models. The field is evolving towards clusters containing many rare gas atoms or hydrogen bonded complexes between a biomolecule and water or two biomolecules. In the field of molecular recognition, it is important to know what regions of biomolecules show the greatest propensity to form hydrogen bonds. The search for chemical complexity in the interstellar medium will also need more laboratory work on exotic species. The spectroscopy of larger species or complex mixtures is under development and the coupling of MWFT spectrometers with mass spectrometers will allow the control of the targeted species. Finally we have to keep in mind that the information obtained in the microwave region is complementary to information which can be obtained in other frequency ranges: millimeter or submillimeter wave domain for rotational spectroscopy; infrared or far infrared domain for ro-vibrational spectroscopy. Some promising studies involve double irradiation methods: microwave–optical [42], microwave–microwave [43], microwave–submillimeter [44] double resonance spectroscopy may bring valuable information either on higher energy levels or on intra-molecular dynamics.

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