



Molecular spectroscopy, an enrichment diagnostic.

Laurent Bruel, Pascal Lemaire, A. Pailloux

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**Proceedings of
the 15th International Workshop on
Separation Phenomena in
Liquids and Gases**

**第15届 “液体和气体中的分离现象”
国际会议论文集**

Edited by Shi Zeng and Mingsheng Zhou
曾实 周明胜 主编

SPLG

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内 容 简 介

“液体和气体中的分离现象”国际会议每两年召开一次,为同位素分离领域的高水平学术会议之一。本书为第15届“液体和气体中的分离现象”国际会议的科技报告文集。本书主题针对同位素分离的基础理论和技术,重点在同位素分离的离心法和激光法,也包括其他分离方法和技术、同位素的应用等,反映了同位素分离领域中的理论研究和应用研究的新思想、新进展。

本书可供从事同位素分离的科研技术人员和高等院校相关专业的教师以及研究生阅读参考。

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May 13-17, 2019

Wuxi, China

Edited by Shi Zeng and Mingsheng Zhou

Professor

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Tsinghua University

Beijing 100084

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The 15th International Workshop on Separation Phenomena in Liquids and Gases (SPLG 2019)

May 13-17, 2019, Wuxi, China



FOREWORD

Another SPLG Workshop (the 15th International Workshop on Separation Phenomena in Liquids and Gases, SPLG 2019) was held in China during May 13-17, 2019, 13 years after the 9th workshop (SPLG 2006) and 25 years after the 4th workshop (SPLG 1994). SPLG 2019 was jointly organized by Department of Engineering Physics and Wuxi Research Institute of Applied Technologies, Tsinghua University.

The SPLG workshop is a biannual event and has a history of 44 years, if taking the history of its predecessor into account. The predecessor of SPLG is GSR (Workshop on Gases in Strong Rotation), which was organized six times, respectively, in Stockholm, Sweden (1975), Cadarache, France (1977), Rome, Italy (1979), Oxford, UK (1981), Charlottesville, USA (1983), and Tokyo, Japan (1985). Then, The name of GSR was changed to SPLG after the 6th GSR. So far, fifteen SPLG workshops have been successfully held in Darmstadt, Germany (1987), Versailles, France (1989), Charlottesville, USA (1992), Beijing, China (1994), Iguacu, Brazil (1996), Nagoya, Japan (1998), Moscow, Russia (2000), Oak Ridge, USA (2003), Beijing, China (2006), Angra dos Reis, Brazil (2008), St. Petersburg, Russia (2010), Paris, France (2012), San Carlos de Bariloche, Argentina (2015), Stresa, Italy (2017), and now Wuxi, China (2019). The traditional topics of the workshop had been isotope separation, but were gradually extended to a wider range of fields to include other subjects of researches concerning various separation phenomena, separation methods and techniques, providing a platform of exchanging scientific ideas and information for the people of the separation society. A very good review of the SPLG history was given by Professor Wood in his talk "History of the SPLG Workshops" in SPLG 2017. The previous GSRs and SPLGs are summarized in the following table:

Year	Sites	Participants	Host	Countries	Papers	Sessions
1975	Stockholm	37	20	9	22	5
1977	Cadarache	44	16	9	20	4
1979	Rome	70	22	10	28	6
1981	Oxford	70	15	10	26	6
1983	Charlottesville	67	40	10	24	6
1985	Tokyo	90	66	8	22	5
1987	Darmstadt	65	24	13	26	7
1989	Versailles	72	27	15	32	6
1992	Charlottesville	38	13	8	22	6
1994	Beijing	39	20	8	22	6
1996	Iguacu	38	18	7	30	6
1998	Nagoya	90	62	9	48	6 + 3(para)
2000	Moscow	95	61	13	44	6 + 1(post)
2003	Oak Ridge	41	22	9	21	6
2006	Beijing	52	20	8	29(Oral)17(post)	8 + 1(post)
2008	Angra dos Reis	60	34	11	26	7
2010	St. Petersburg	102	66	16	53	5 + 1(post)
2012	Paris	107	40	16	37	9
2015	Bariloche	145	92	12	36	8 + 2(post)
2017	Stresa	63	18	13	35	7

The current workshop intended to cover seven topics:

1. Isotope Separation by Centrifugation;
2. Laser Isotope Separation;
3. Other Methods and Technologies of Isotope Separation;
4. New Methods and Applications of Isotopes and Their Acquisition;
5. Prospects and Economic Issues of Separation Methods and Technologies;
6. Nuclear Nonproliferation and Safeguards;
7. Purification Methods and Technologies.

It attracted 103 participants from nine countries. We were glad to see that there were many young researchers presenting their results, in addition to the older experienced participants with outstanding achievements. There were 30 oral presentations and 14 poster presentations, including seven plenary (special) talks given by, respectively, J. S. Tian, Z. H. Qiu, R. Snyder, V. D. Borisevich, T. Mashimo, A. Lamagna, and J. Jakutis Neto. Some excellent presentations given at the workshop are unable to be collected in the proceedings, unfortunately, because the authors were very strict about their results. We hope that they will bring their satisfactory results in the next SPLG workshop.

On behalf of the International Organizing Committee and the Local Organizing Committee, we would like to thank the strong support from Atomic Energy Industry Corporation, CNNC. We would also like to thank all participant for attending this workshop during their busy time. We are very grateful to Prof. N. N. Chen, academician of Chinese Academy of Engineering, Mr. J. S. Tian, deputy chief engineer and technique officer of CNNC, and Mr. Z. H. Qiu, chief technical officer of Atomic Energy Industry Corporation of CNNC, who spared their busy time to attend the workshop.

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September 30, 2019

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I . Laser Technology

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Molecular Spectroscopy, an Enrichment Diagnostic

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Abstract

In Molecular Laser Isotope Separation processes, high-resolution spectroscopy is commonly used to determine the rotational and vibrational temperatures.

In both versions of the MLIS processes (dissociation or SILEX version), the jet-cooled gas tends to form rapidly van der Waals complexes with the rare gas used as carrier gas. These phenomena are important for isotopic selection as they initiate the condensation phenomena.

In case of SF₆, small heteroclusters(SF₆-rare gas) are investigated with rovibrational laser jet-cooled spectroscopy in the ν_3 region (10 μm for SF₆), for some rare gas atom (RG). High-resolution spectra are measured for both the perpendicular and parallel bands for Ne, Ar, Kr and Xe heteroclusters. It is shown that the reduced vibrational red shifts are independent of the RG atom, leading us to a good understanding of their conformation.

In the case of UF₆, the unusual wavelength of the ν_3 band required the development of a specific DFB laser at 16 μm . This has been done at IES (CNRS/University of Montpellier) using the InAs/AlSb quantum cascade laser (QCL-DFB) technology that demonstrated room temperature operation in continuous regime for the first time above 16 μm with a linewidth of a few MHz.

Absorbance measurements with these lasers are now demonstrated on isolated NH₃ lines in the 16 μm range, at low pressure. Thermal induced frequency modulation ($2f/f$) is used to improve signal-to-noise ratio.

In the case of online isotopic ratios measurements, this laser could measure the UF₆ molecule number density of both isotopologues. For that purpose, it will be coupled to an integrated pulsed supersonic jet.

Keywords: SPLG 2019, UF₆, SF₆, Complex, Dimer, HTDS, Isotopy, Quantum Cascade Laser

1. Introduction

Several teams have studied the absorption spectrum of the ν_3 vibration of UF_6 . Takami et al.^[1] have even published very detailed spectral portions to isolate the Q branch of $^{235}\text{UF}_6$ between the R(5) and R(6) lines of $^{238}\text{UF}_6$ in a pulsed supersonic jet. To avoid hot bands (multi excited vibration with ν_3) and bring all the molecules into the ground state, the UF_6 plus buffer gas mixture should be cooled to below 50 K in an adiabatic expansion. At these temperatures van der Waals complexes appear. They are the product of homogeneous or heterogeneous aggregation of UF_6 , with the buffer gas, marking the beginning of condensation. The spectroscopy technic that we have implemented allows us to identify the different states of the gas in the expansion, either on a simulant of the molecular structure, the SF_6 , or on the UF_6 , according to the available Quantum Cascade Laser (QCL) diodes (10 μm or 16 μm). We report here the detailed spectroscopic results for SF_6 , conducted with a pulsed gas expansion, and also a continuous jet. The first paragraph focuses on aerodynamic results—temperature measurements—in continuous relaxation. The next identifies dimers and clusters bands versus the buffer gas type. The third will deal with QCL performance at 16 μm . The last paragraph will conclude the use of this diagnostic in isotopic separation.

2. High-resolution spectroscopy of UF_6 for aerodynamic

2.1 Theoretical calculations

To perform a sufficient spectral identification in the infrared region within a broad spectral range at very high speeds, only the absorption spectroscopy with QCL laser diode is possible. Now

that it is feasible, it was necessary to be able to compare the spectra with the theory to deduce very accurately the vibrational and rotational temperatures. Fortunately, the cold band of UF_6 can be calculated using Highly-spherical Top Data System (HTDS) software^[2].

Calculated temperature dependence of the spectra is very strong for UF_6 as shown on Figure 1 and on Figure 2, for respectively 20 K and 10 K; on Figure 3 is shown the superposition of $^{235}\text{UF}_6$ and $^{238}\text{UF}_6$ at 1 K. Even with an isotopic shift of 0.65 cm^{-1} , the two sets of rotational lines are not separated. Thanks to high-resolution spectroscopy, most of the rotational lines can be separated.

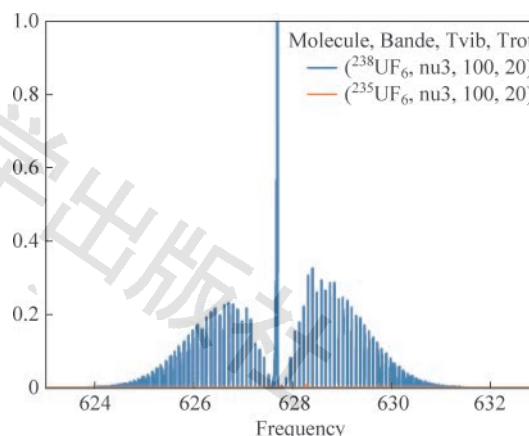


Figure 1: $^{235}\text{UF}_6$ and $^{238}\text{UF}_6$ cold bands at 20 K

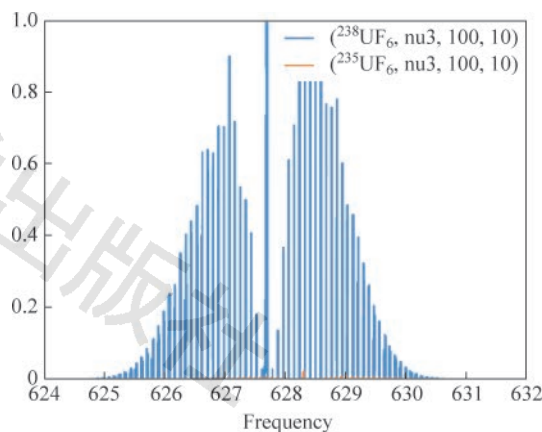


Figure 2: $^{235}\text{UF}_6$ and $^{238}\text{UF}_6$ cold bands at 10 K

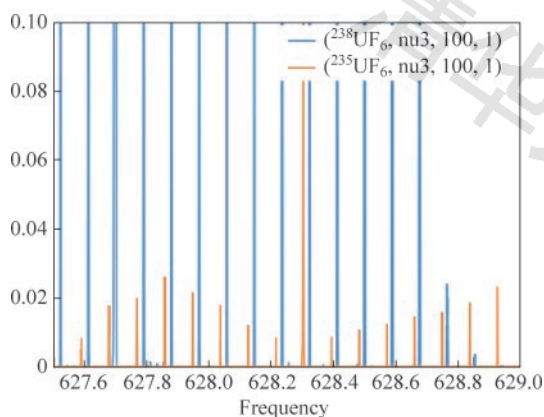


Figure 3: In orange, $^{235}\text{UF}_6$ rotational lines are inside the rotational structure of $^{238}\text{UF}_6$, in blue

2.2 Rotational temperature measurements

When we use SF_6 to simulate UF_6 we must be aware that the isotopic shifts are really different, as you can see on Figure 4 where all sulfur hexafluoride isotopologues are separated at all temperatures. Nevertheless, SF_6 is a validating tool to interpret phenomena relative to either aerodynamic or aggregation.

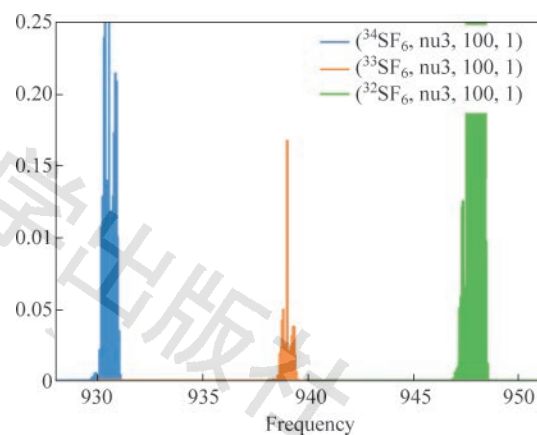


Figure 4: ν_3 vibration of the $^{34}\text{SF}_6$ $^{33}\text{SF}_6$ $^{32}\text{SF}_6$ isotopologues respectively

The way to get very good temperature measurements is as follows. A comparison theory/experiment is performed for all rotational transitions (Figure 5) and the best fit gives the rotational temperature. On this graph, realized with a laser resolution of 20 MHz, the calculated (HTDS) and measured spectra are in a very good agreement even at the line level. The rotational temperature can then be deduced with a precision of less than ± 5 K.

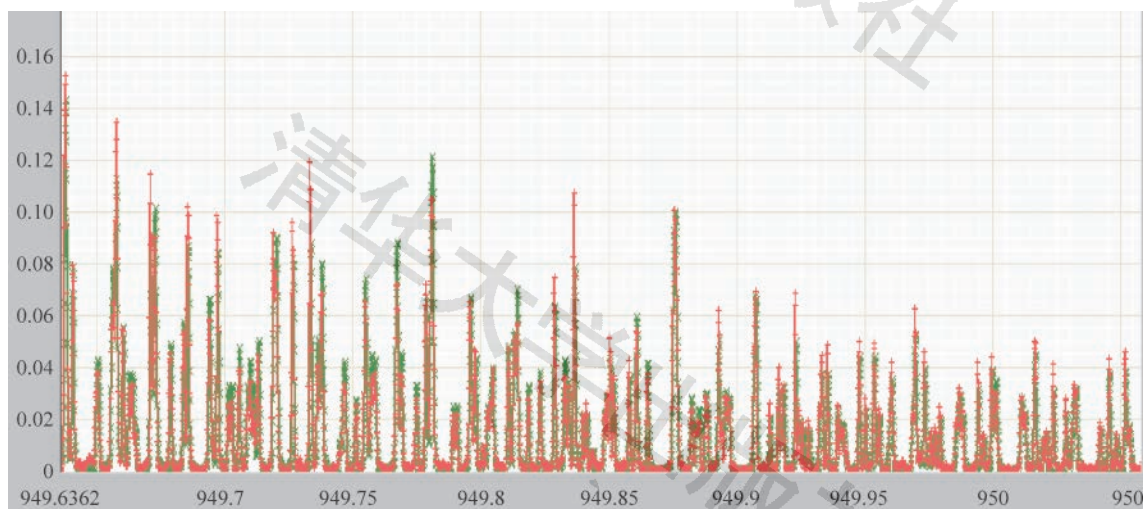


Figure 5: Theory and experiment agreement on the R side of the ν_3 vibration of SF_6 , at 20 MHz resolution

2.3 Vibrational temperature measurements

Hot bands involve other vibrational levels depending on vibrational temperature. Hot bands appear as the vibrational temperature increases. We use them to

measure that temperature, as hot bands population is linked to it. Assuming Boltzman distribution, the two Q branch surfaces can give an estimation of the expected temperature.

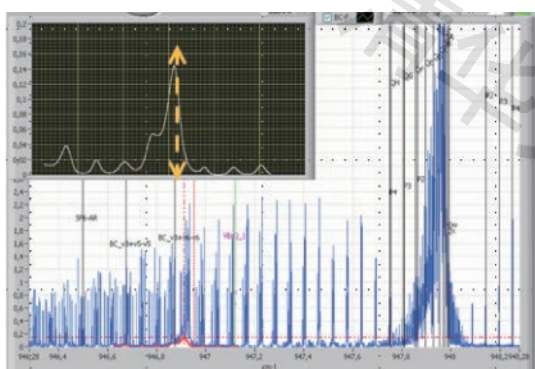


Figure 6: ν_3 bands at 100 K vibrational temperature and at 20 K rotational temperature, hot bands (in red) are visible (for instance here involving ν_5 bands vibration at 946.9 cm^{-1})

3. SF₆-Rg spectroscopy (clusterization)

The different configurations of aggregates (homoclusters, heteroclusters) in the different aerodynamic regimes, partial concentrations or gas laser interactions must be understood to choose the operating point of a laser isotopic separation process.

Aggregate high-resolution spectroscopy has been successfully investigated for the ν_3 vibration with the pulsed jet experiment of MONARIS in Jussieu

University^[3]. Experiments have been carried out with different rare gases (Rg).

3.1 SF₆-Rg heteroclusters

The parallel and perpendicular bands of SF₆-Rg heteroclusters have been identified. These bands arise from the degeneracy lifting of the triply degenerate state (ν_3) of the SF₆ monomer.

These experimental spectra are very weak compared to the strong monomer band. But, thanks to the accuracy of the calculated monomer band, the heteroclusters band is obtained by subtracting the theoretical spectrum from the measurement (in green on Figure 7).

These cluster spectra have been successfully computed and the experimental spectral shifts are in good agreement with the prediction based on a Buckingham-type potential. Some molecular parameters of this model (rotational constants, band centers and S-Rg distances) have been deduced from the measurements^[3].

3.2 (SF₆)₂-dimer

The first conformer of (SF₆)₂, (band #1), has been published in 1995 by Urban and Takami. A second conformer (band #2) has been identified recently^[3].

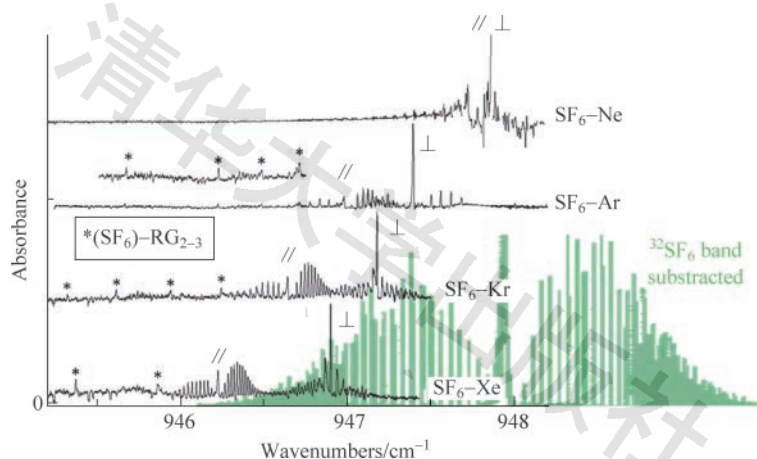


Figure 7: EC-QCL jet cooled pin hole spectra of both ν_3 parallel bands of SF₆-Rg heterodimers (Rg=Ne, Ar, Kr, Xe) with 0, 12% SF₆ and 1% Rg diluted in 8 bar helium at an axial distance $z=15 \text{ mm}$

Again, with the experimental data, they have been simulated by symmetric top transition, taking into account their symmetries D_{2d} and C_{2h} and their temperatures of 3 K and 8 K respectively (Figure 8).

Temperatures are distinct because # 2 is formed during early expansion at higher temperature. A collisional relaxation process leads to population conversion from dimer # 2 to dimer # 1.

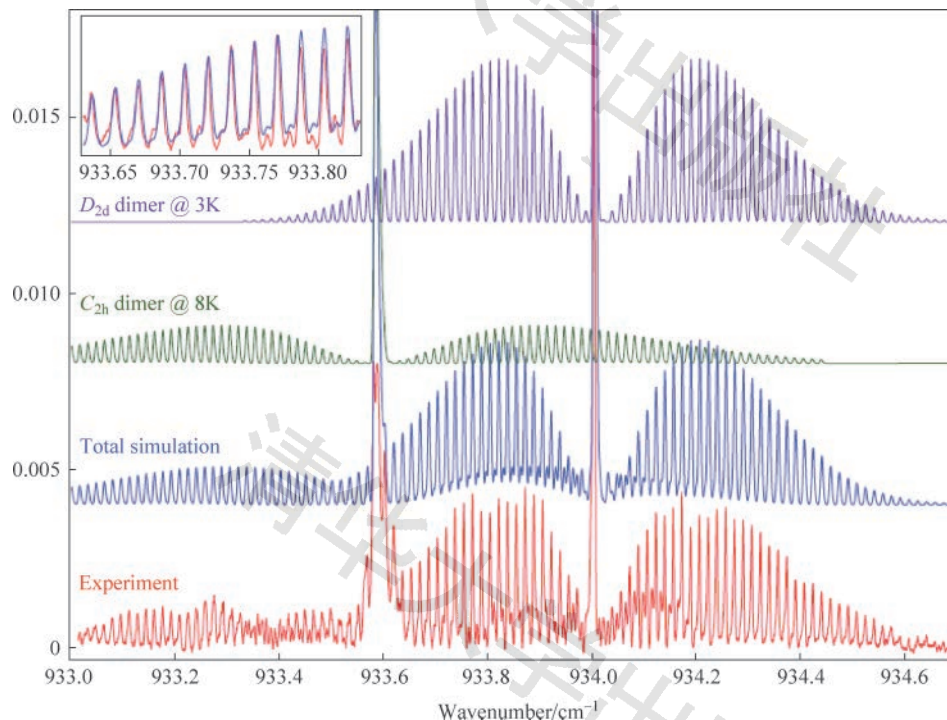


Figure 8: Parallel bands of the conformations # 1 and # 2 of the dimer $(SF_6)_2$, summation compared to experimental spectrum

3.3 $(SF_6)_2$ -Rg heteroclusters

When the structure of the homodimer SF_6 was well understood, the continuation of the heterogeneous aggregation in the mixture supersonic expansion was studied with several rare gases, for different geometries (slit or nozzle), SF_6 concentration, axial probe distance.

The #3 band (in red Figure 9) was easily assigned to the heterocluster $(SF_6)_2$ -Rg, because of linear dependence of the vibrational shift between # 2 and #3 bands with gas polarizability.

This linear dependence is showing that the trimer #3 configuration is the same as #2. This illustrates the lack of robustness of the #1 dimer, owing to external perturbations, like collisions or complexation with a He atom.

Finally, these results show that it is necessary to use sophisticated approaches to simulate these systems^[4].

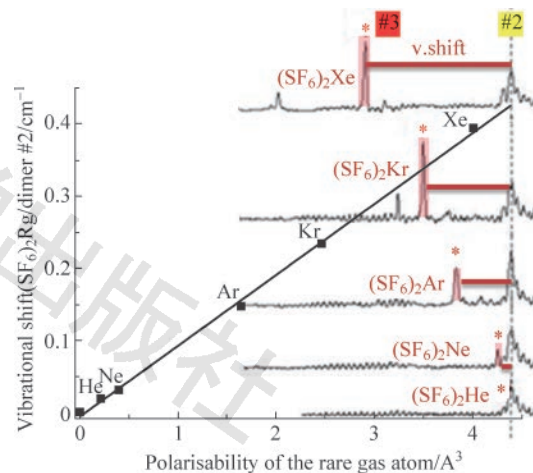


Figure 9: Spectra of different heteroclusters $(SF_6)_2$ -Rg for Rg=He to Xe, linear dependence of the vibrational shift with the polarizability of the rare gas atom is shown

4. QCL a tool for high-resolution spectroscopy

All these experiments have been done using the pulsed jet SPIRALES bench in Paris or on the continuous jet in our lab, with the same external cavity Quantum Cascade Laser at a wavelength of $10\mu\text{m}$ from a commercial supplier.

The energy domain of the vibrations and the isotopic differences are weaker for UF_6 , which will modify the behavior of the aggregates in the relaxation, the high-resolution spectroscopy will make it possible to understand the behavioral changes. To investigate the high-resolution spectroscopy of UF_6 , there is (in 2019) no commercial device available at the wavelength of $16\mu\text{m}$.

Thanks to a collaboration with the Institute of Electronics and Systems (IES, CNRS/University of Montpellier) in France, the the first world CW $16\mu\text{m}$ laser source^[5,6] operating up to ambient temperature has been developed in the University of Montpellier. We used one of these sources in this study. This laser can accept not only continuous regime, but it also tolerate room temperature regime at the same time. It can deliver 50 mW CW for approximately 7 W of electrical power.

QCLs are different from laser diode (Figure 10) as they use many current injectors in series connected by a quantum tunneling. Each injector provides one photon from the same electron. The gain can be high, depending on materials and design.

The wavelength is first obtained by adjusting the design of the gain structure which is an epitaxed multilayer, with a Bragg grating etched on top on the ridge to obtain a monomode emission linewidth of a few MHz.

InAs is advantageously used at higher wavelength, thanks to its electron's low effective mass, and it has been extended in the far IR (up to $25\mu\text{m}$). On the contrary InP is not suitable because the substrate is absorbing very near to $16\mu\text{m}$, due to a phonon resonance.

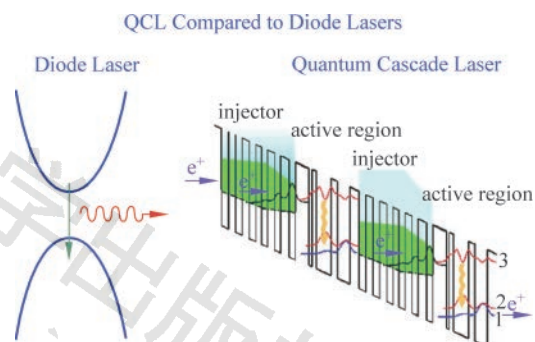


Figure 10: AlSb / InAs active zone (AlSb tunnel $\sim 1\text{ \AA}$ to $100\text{ \AA}$). One period = 20 MoCVD layers $N_p = 144$ periods ($7\mu\text{m}$ thick)

4.1 The use of QCL at $16\mu\text{m}$

Due to thermal effects, the emitted wavelength depends on both temperature and current. It is then possible to scan a 1.5 cm^{-1} range by varying the current, and scan a 6 cm^{-1} range by changing the operating temperature, as shown on Figure 11.

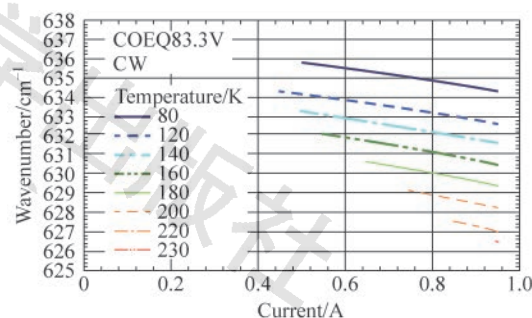


Figure 11: Example of current tunability at fixed temperature of our QCL ship

4.2 Laser test on NH_3 gas cell

A simple test on a low-pressure ammonia cell has been conducted to confirm that this laser source is usable for UF_6 spectroscopy.

Linewidth was found less than 30 MHz and the laser could effectively scan from 627 to 634 cm^{-1} by varying the temperature (Figure 12).

4.3 $2f/f$ detection from laser modulation

In addition to a small size, a large power at $16\mu\text{m}$, a very high spectral resolution..., the QCL can be modulated at a maximal frequency of 100 kHz. A synchronous demodulation with detection of the first and second orders permits us to increase signal to

noise ratio, using the so-called $2f/f$ technic.

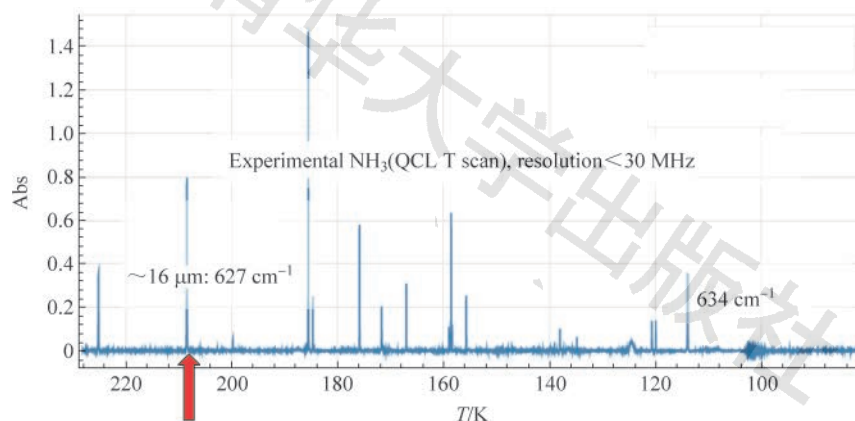


Figure 12: Experimental scan from 627 to 634 cm^{-1} with a 16 μm QC Laser. The red arrow indicates where the central position of the $^{235}\text{UF}_6$ lines is on the ammonia spectrum

Figure 13 is a numerical simulation with noisy signals coming from the $^{235}\text{UF}_6$ branch HTDS of the first and second orders is undertaken.

Compared to direct absorption, where the signals

are blurred, the demodulated signals are clean.

This technic is a necessary tool to obtain the high dynamic needed to acquire both isotopes at low assay.

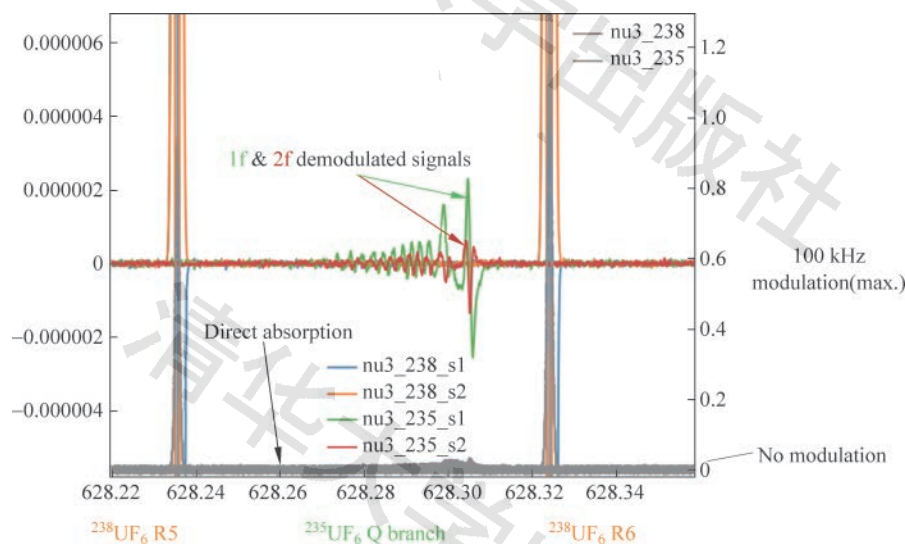


Figure 13: Simulation of noisy signals demodulated using the $2f/f$ scheme coming from the $^{235}\text{UF}_6$ branch (red and green) to be compared to direct absorption (in grey)

5. Conclusions

MLIS-type isotopic separation techniques are known to be potentially profitable, that is to say with high selectivity and with access to the entire UF_6

population, only involving isentropic expansion carrying the gas mixture at very low temperature. However, during the relaxation, a dimerization followed by homogeneous or heterogeneous aggregation arises according to the conditions of the process. To properly control the thermodynamic

state of the gas mixture, spectroscopy proves here to be the best tool. At high resolution it discriminates the types of aggregates, and for a process monitoring, it discriminates the isotopes, even if the rovibrational spectra are nested. For UF_6 , the wavelength of the characteristic vibration is in the far infrared and the only tool with this discriminant potential is the QCL laser diode that we used in this study.

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