ROVIBRATIONAL SPECTROSCOPY OF TRANS AND CIS CONFORMERS OF 2-FURFURAL FROM HIGH RESOLUTION FOURIER TRANSFORM AND QCL INFRARED MEASUREMENTS

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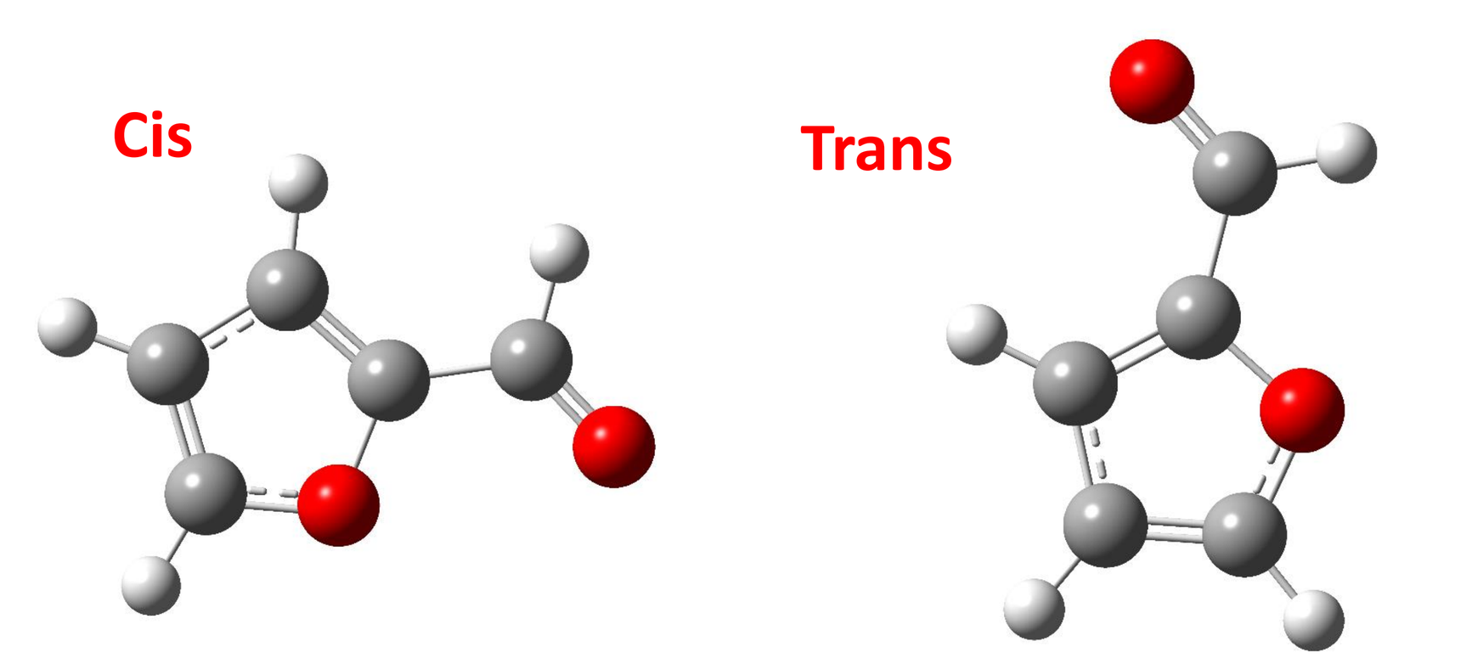
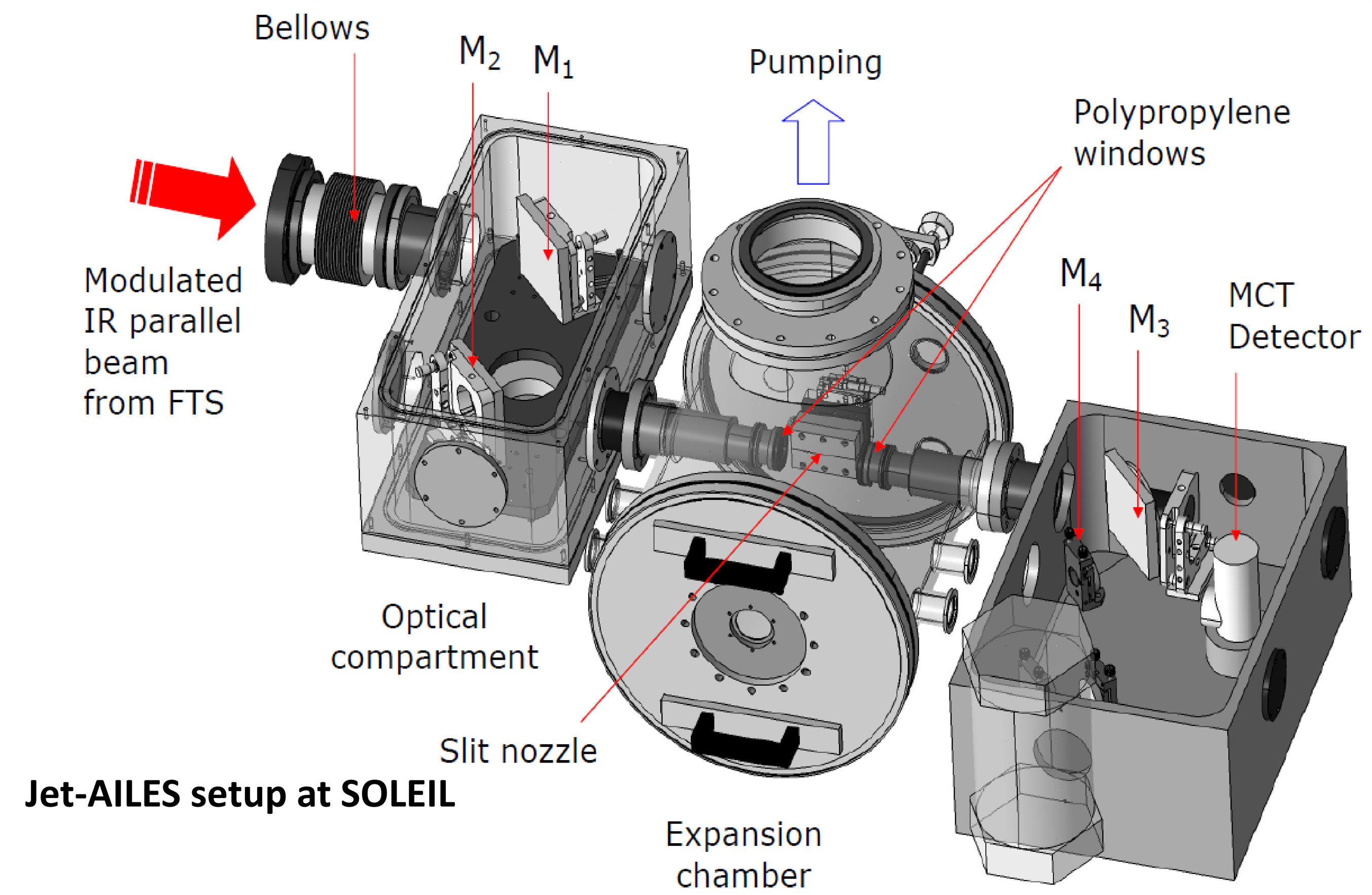
1. Introduction

The ortho-isomer **2-furfural** ($C_5H_4O_2$) is a primary atmospheric pollutant produces by the combustion of cellulose and hemicellulose contained in the biomass.
This molecule is involved in oxidation processes leading to the formation of **secondary organic aerosols**. Its contribution to the radiative forcing, poorly known, fully justifies to monitor 2-FF directly in the atmosphere or in atmospheric simulation chambers to characterize its reactivity.
This study presents **a jet-cooled rovibrational study** of **trans and cis conformers** of 2-FF in the Mid-IR.

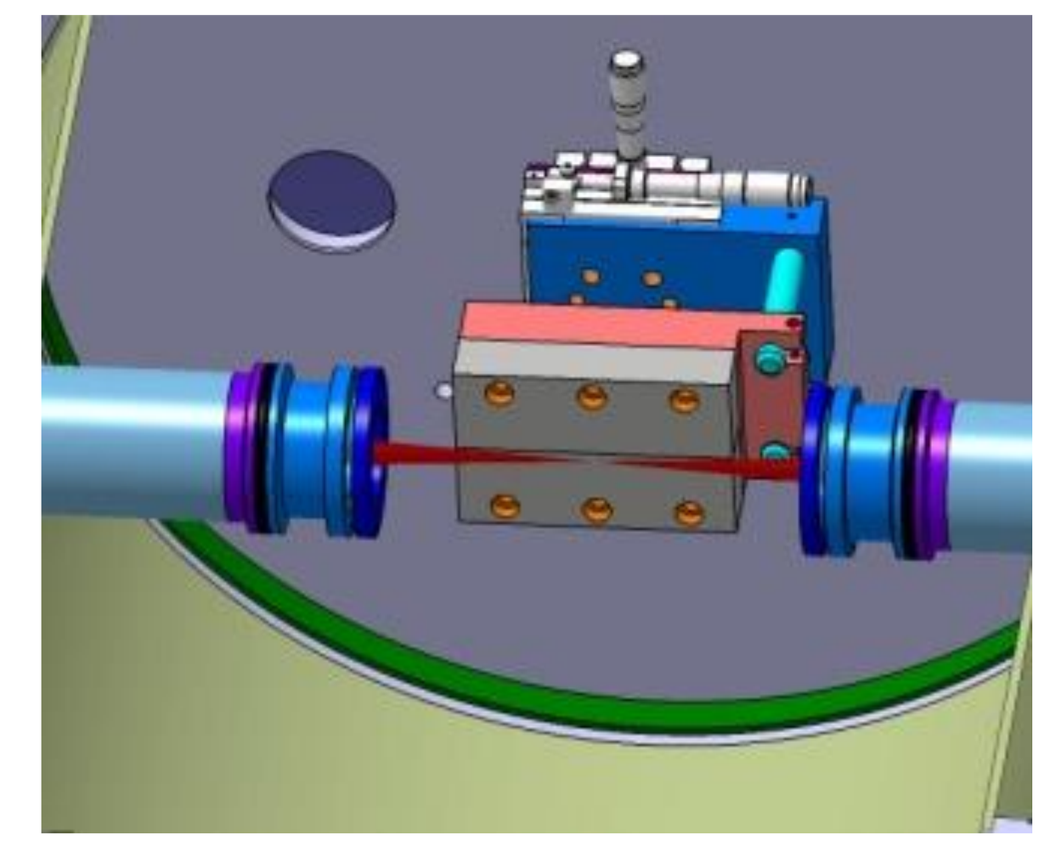


2. Experimental set-up

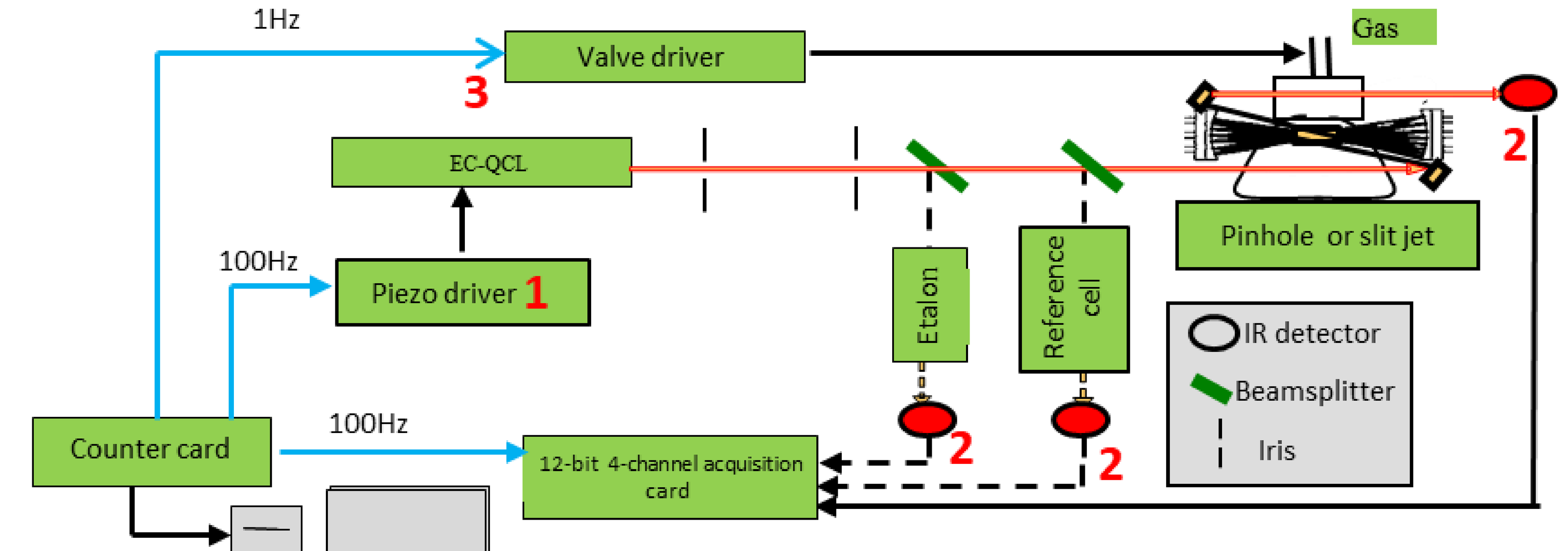
Jet-cooled spectra were **recorded at 20-50 K** using two setups.
- a supersonic jet coupled to a high-resolution Fourier transform spectrometer (JET-AILES)
- a pulsed jet coupled to a mid-IR tunable quantum cascade laser spectrometer (SPIRALES).

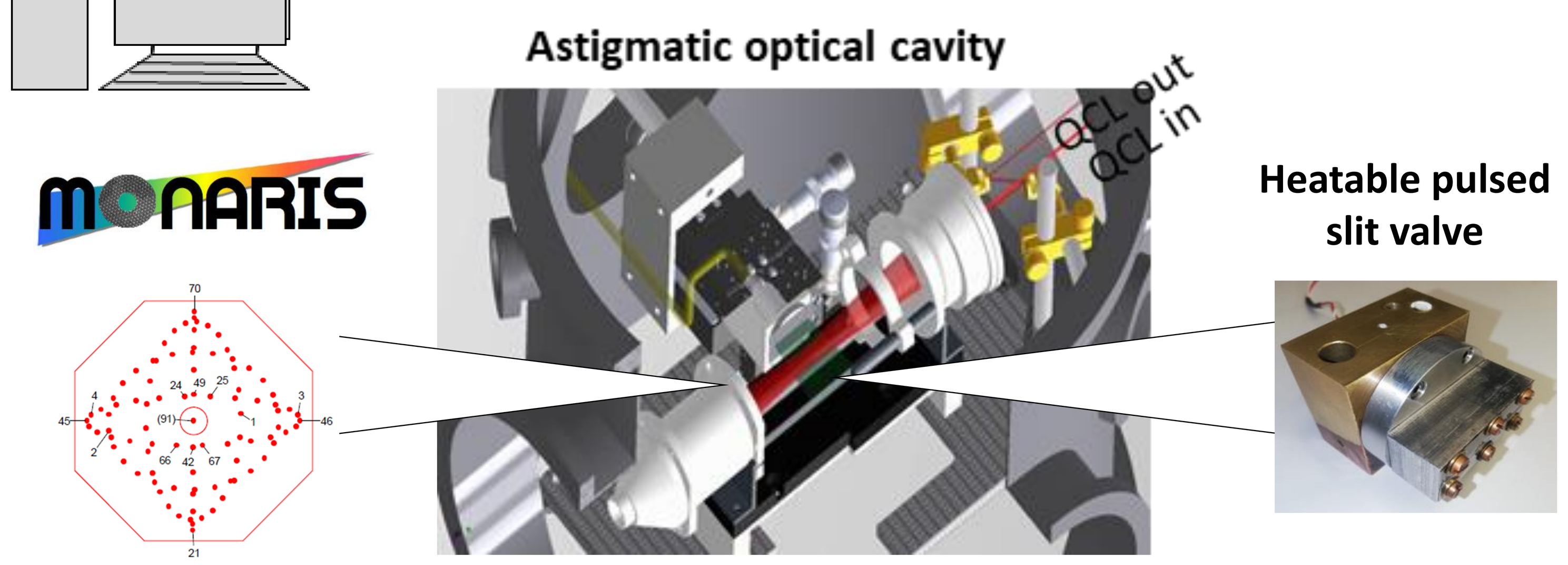


Jet-AILES setup at SOLEIL



Interaction IR-slit jet





3. State-of-the-art

Far-IR , Mid-IR and Raman studies [1,2] : relative stability trans/cis = 3 at 300 K (286(24) cm^{-1}) and a conformational barrier height 3252(20) cm^{-1}.
- no splitting due to internal rotation
- no relaxation expected in the jet

Microwave and mm-wave studies [3] : molecular parameters in the ground state and in low-frequency vibrational modes (< 300 cm^{-1}).

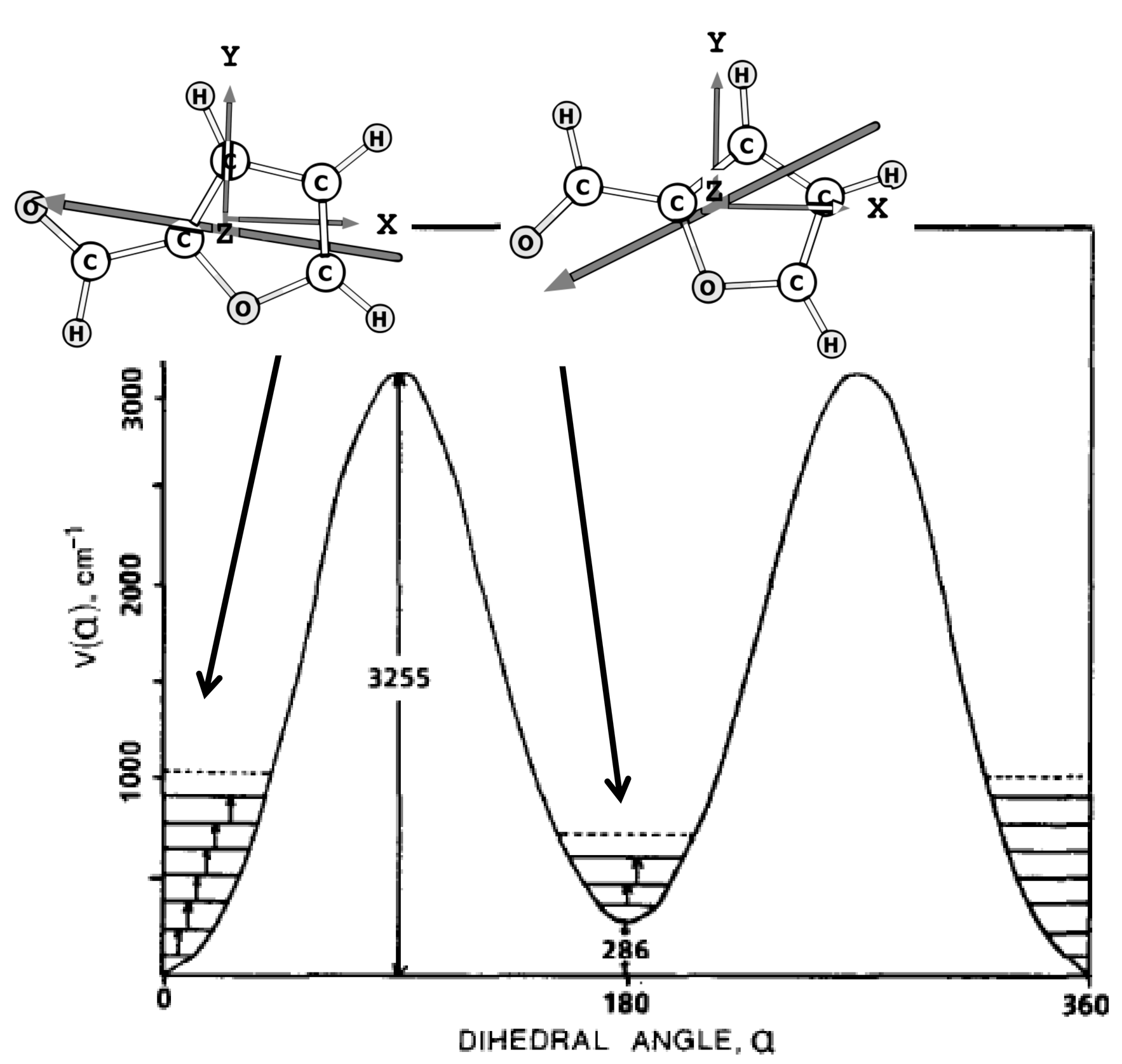
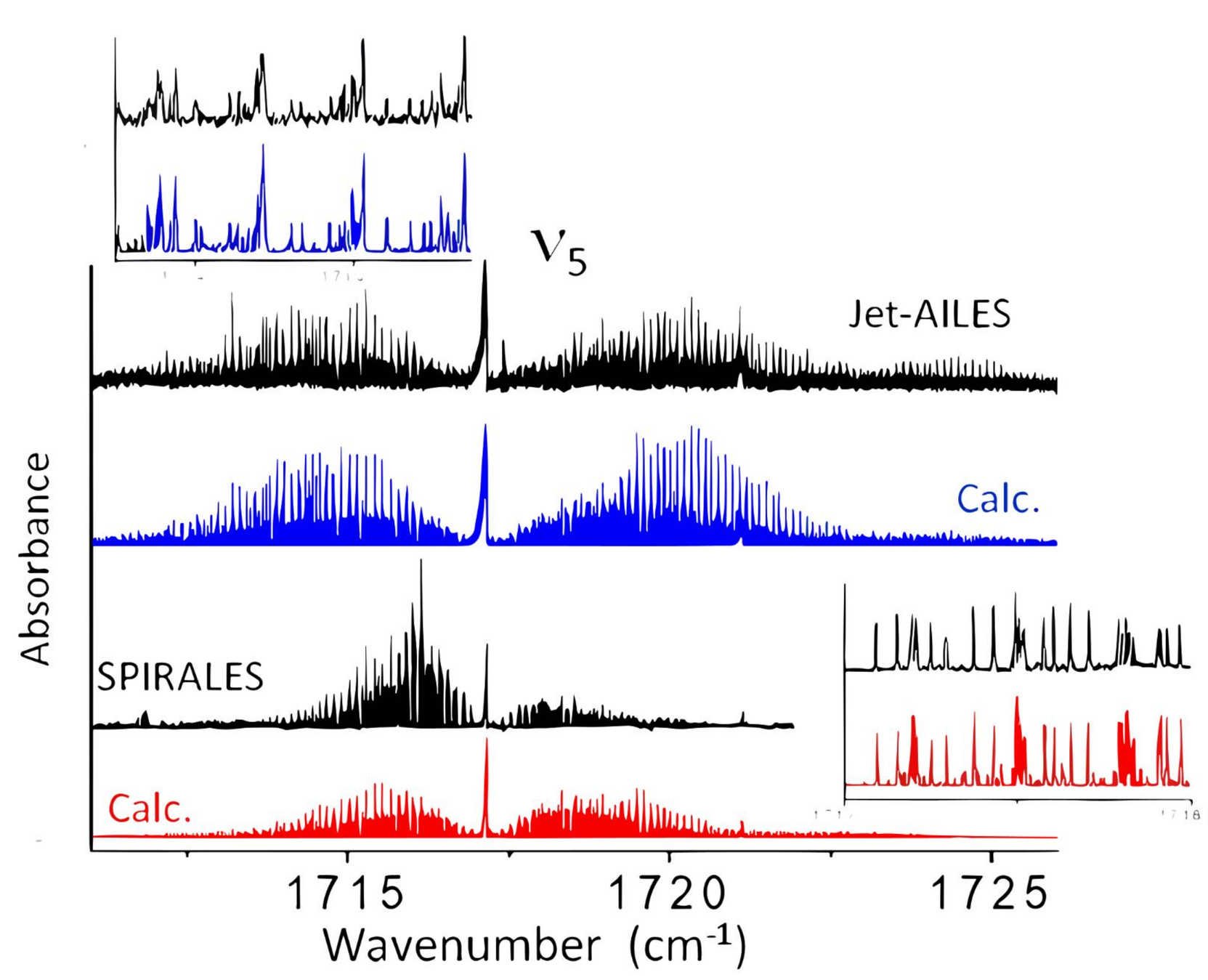


Fig 1 : torsional potential energy surface from FIR spectral data

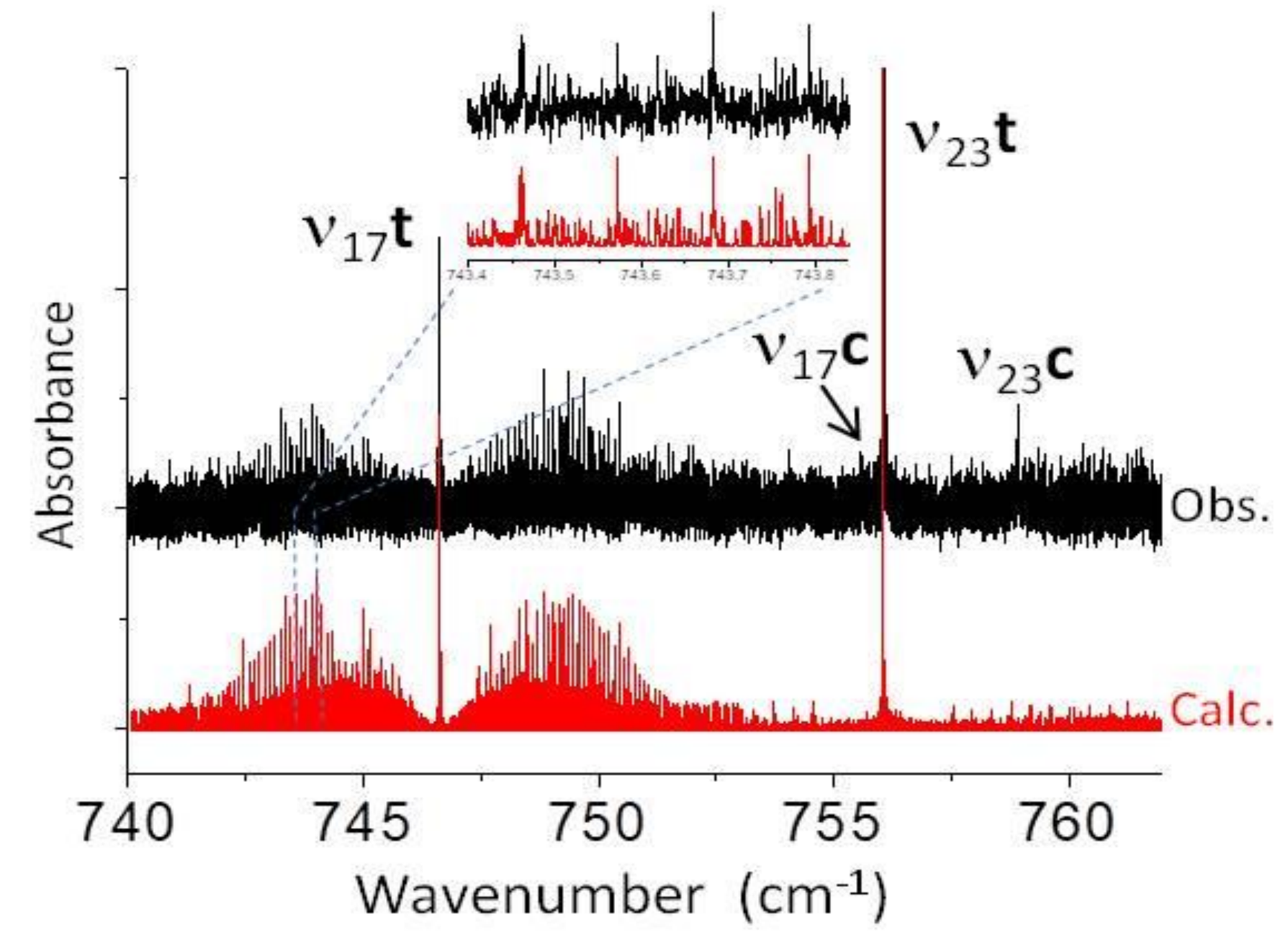
[1] Little, T. S., Qiu, *et al.* (1989). *Spectrochim. Acta A-M, 45*(8), 789-794.
[2] Adámek, P., *et al.* (1973). *J. Mol. Spectrosc.*, 47(2), 252-267.
[3] Motiyenko, R. A., *et al.*(2006). *J. Mol. Spectrosc.*, 240(1), 93-101.

4. Rovibrational spectral analysis

Reliable excited state molecular parameters for trans- and cis-2-FF vibrational bands were derived from fitting 11,376 and 3,355 lines distributed over 8 and 3 vibrational states with a root-mean-square of 12 MHz, respectively. Vibrational assignments were also performed based on anharmonic calculations.



Jet-AILES
650-1800 cm^{-1}
Accuracy : 0.001 cm^{-1},
10% FF/0.2 bar Ar, T_R = 50 K



SPIRALES
975-1035 cm^{-1} and 1620-1720 cm^{-1}
Accuracy : 0.0005 cm^{-1},
1% FF/2 bar Ar, T_R= 20 K

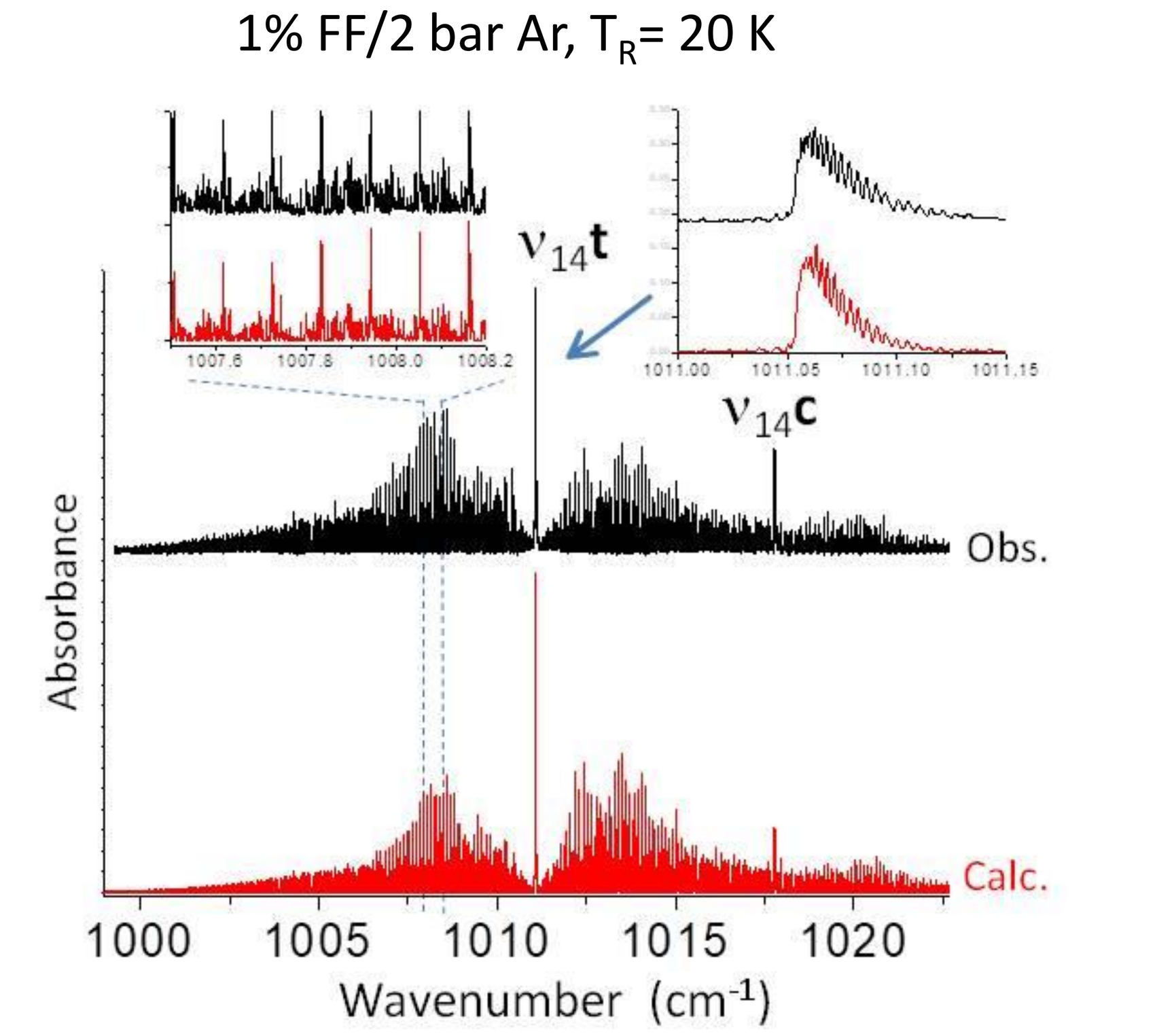


Table 1. 2-FF vibrational mid-IR assignments based on experimental measurements and anharmonic calculations at the hybrid/CBS level. All vibrational frequencies are given in cm^{-1} unit.

ν_{exp}	Mode	Symmetry	Conformer	ν_{harm}	ν_{anharm}	Description
1732.9	$\nu_{18}+\nu_{10}$	A′	trans	1779.6	1755.4	
1721.1	ν_5	A′	cis	1732.5	1705.3	C=O stretching
1717.1	ν_5	A′	trans	1726.4	1704.8	C=O stretching
1689.5	$\nu_{17}+\nu_{15}$	A′	trans	1719.4	1700.5	
1687.2	$\nu_{17}+\nu_{15}$	A′	cis	1722.2	1692.1	
1578.8	ν_6	A′	trans	1595.0	1566.1*	ring C=C asym stretching
1577.1	ν_6	A′	cis	1584.4	1554.2*	ring C=C asym stretching
1481.1	ν_7	A′	cis	1506.8	1479.2*	ring C=C sym stretching
1473.6	ν_7	A′	trans	1500.1	1475.8*	ring C=C sym stretching
1365.0	ν_9	A′	trans	1402.1	1368.8	C-H ip bending
1242.1	ν_{10}	A′	trans	1281.7	1259.0	ring C-H ip bending
1136.0	ν_{12}	A′	trans	1193.6	1173.3	ring C-H ip bending
1086.4	ν_{13}	A′	trans	1116.2	1101.8	ring C-H ip bending
1017.7	ν_{14}	A′	cis	1044.3	1022.7*	ring C-H ip bending
1011.0	ν_{14}	A′	trans	1038.6	1016.9*	ring C-H ip bending
948.6	ν_{15}	A′	trans	963.7	952.4	ring ip bending
886.9	ν_{16}	A′	trans	896.1	888.2	ring ip bending
755.6	ν_{17}	A′	cis	769.7	759.2	C-C-H scissoring
746.6	ν_{17}	A′	trans	755.7	750.6	C-C-H scissoring
996.4	ν_{20}	A″	trans	1010.5	996.7*	C-H oop bending
830.6	ν_{22}	A″	trans	840.9	814.6*	ring C-H oop bending
758.9	ν_{23}	A″	cis	775.5	757.9*	ring C-H oop bending
756.1	ν_{23}	A″	trans	769.2	755.2*	ring C-H oop bending

* no CBS convergence of anharmonic frequencies: hybrid values calculated using B98/aVQZ anhar-

Table 2. Molecular parameters (in MHz) of the ground state, v_{17} = 1, v_{23} = 1, v_{14} = 1, v_7 = 1, v_6 = 1, v_{17}, v_{15} = 1,1 and v_5 = 1 of *trans*-2-FF derived from the combined fit of eight states.

frequency (cm^{-1})	GS	ν_{17} 746.59621(2)	ν_{23} 756.05273(2)	ν_{14} 1011.05284(2)	ν_7 1473.58372(3)	ν_6 1578.77264(3)	$\nu_{17}+\nu_{15}$ 1689.52004(2)	ν_5 1717.14825(2)
A	8191.77383(13)	8196.9940(13)	8178.0125(220)	8196.3949(148)	8168.443(32)	8184.040(38)	8181.784(119)	8179.2141(305)
B	2045.929569(13)	2045.2823(58)	2045.3409(170)	2046.3469(48)	2041.9928(86)	2044.0863(87)	2043.6672(124)	2043.8979(101)
C	1637.183877(12)	1636.2156(47)	1637.5243(238)	1637.2606(37)	1636.8828(54)	1635.6319(25)	1635.0497(96)	1635.5041(61)
$\Delta_J(x10^3)$	0.1361873(39)	0.1342(20)	0.155(8)	0.1379(18)	0.1361873	0.1361873	0.110(8)	0.1269(41)
$\Delta_K(x10^3)$	1.7829(24)	1.7316(21)	2.114(111)	2.694(45)	1.7829[a]	1.7829[a]	-0.0456(26)	2.771(135)
$\Delta_{JK}(x10^3)$	0.706618(18)	0.9057(13)	0.808(57)	0.875(16)	0.706618[a]	0.706618[a]	3.59(32)	0.642(44)
$\delta_J(x10^3)$	0.0314688(12)	0.0306(14)	0.0418(122)	0.0283(12)	0.0314688[a]	0.0314688[a]	0.0314688[a]	0.0469(32)
$\delta_K(x10^3)$	0.82192(118)	0.544(82)	0.82192[a]	0.877(75)	0.82192[a]	0.82192[a]	0.82192[a]	0.82192[a]
$\Phi_J(x10^9)$	0.01758(44)							
$\Phi_{JK}(x10^9)$	0.6571(32)							
$\Phi_K(x10^9)$	5.097(13)							
IR RMS	0.0099	10.8	9.9	17.4	18.9	24.6	15.9	13.8
N lines	1844	2401	1224	3446	513	508	662	999
J''	1-99	1-56	1-39	1-56	2-33	4-52	4-52	1-52
K_a''	0-53	0-35	0-21	0-22	0-14	0-14	0-10	0-20

[a] Fixed to the GS value

Table 3. Molecular parameters (in MHz) of the ground state, v_{14} = 1 and v_5 = 1 of *cis*-2-FF derived from the combined fit of three states.

frequency (cm^{-1})	GS	ν_{14} 1017.76832(2)	ν_5 1721.12234(3)
A	8143.738729(71)	8149.490(40)	8135.273(67)
B	2098.724250(14)	2099.3461(62)	2096.7713(99)
C	1668.872904(14)	1668.9979(58)	1667.4017(61)
$\Delta_J(x10^3)$	0.1726591(62)	0.1625(37)	0.1779(38)
$\Delta_K(x10^3)$	1.81403(24)	1.894(173)	1.81403[a]
$\Delta_{JK}(x10^3)$	0.49995(32)	0.106(50)	0.49995[a]
$\delta_J(x10^3)$	0.0403044(13)	0.0403044[a]	0.0403044[a]
$\delta_K(x10^3)$	0.80893(11)	0.80893[a]	0.80893[a]
$\Phi_J(x10^9)$	0.02717(76)		
$\Phi_{JK}(x10^9)$	-0.3231(55)		
$\Phi_K(x10^9)$	-2.2598(265)		
IR RMS	0.0125	12.6	12.9
N lines	2488	624	244
J''	1-89	1-42	5-46
K_a''	0-38	0-18	0-12

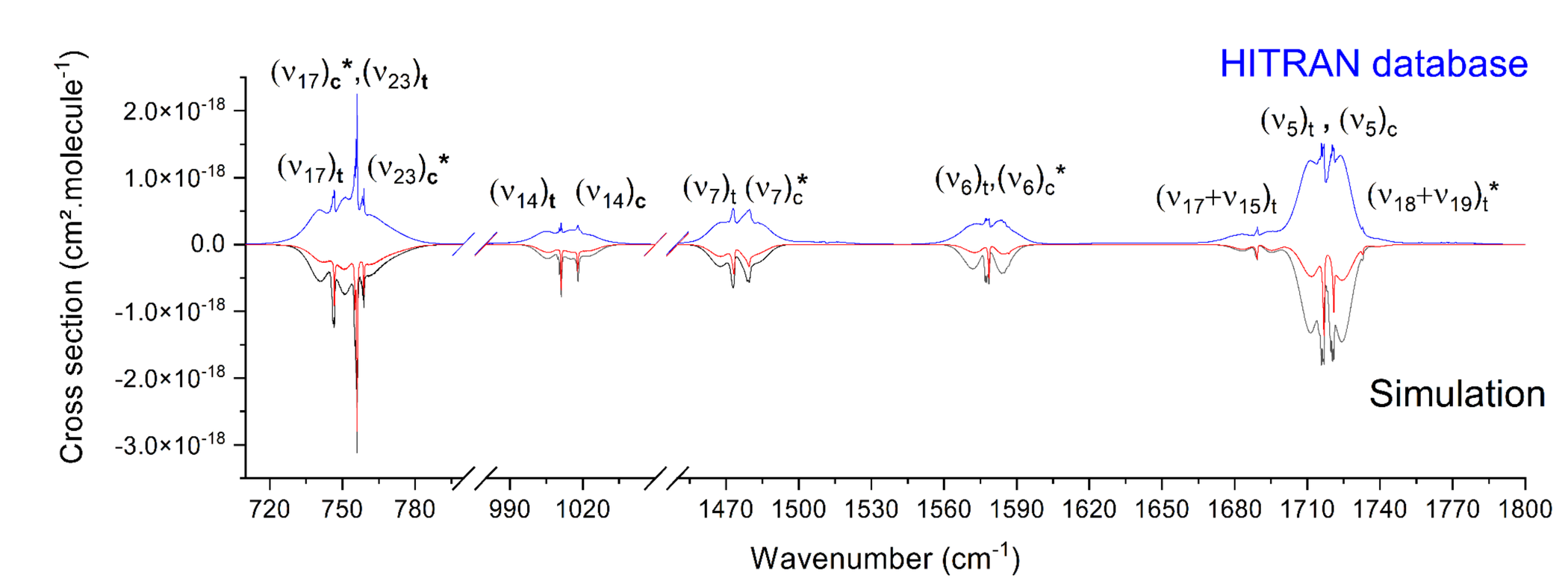
[a] Fixed to the GS value

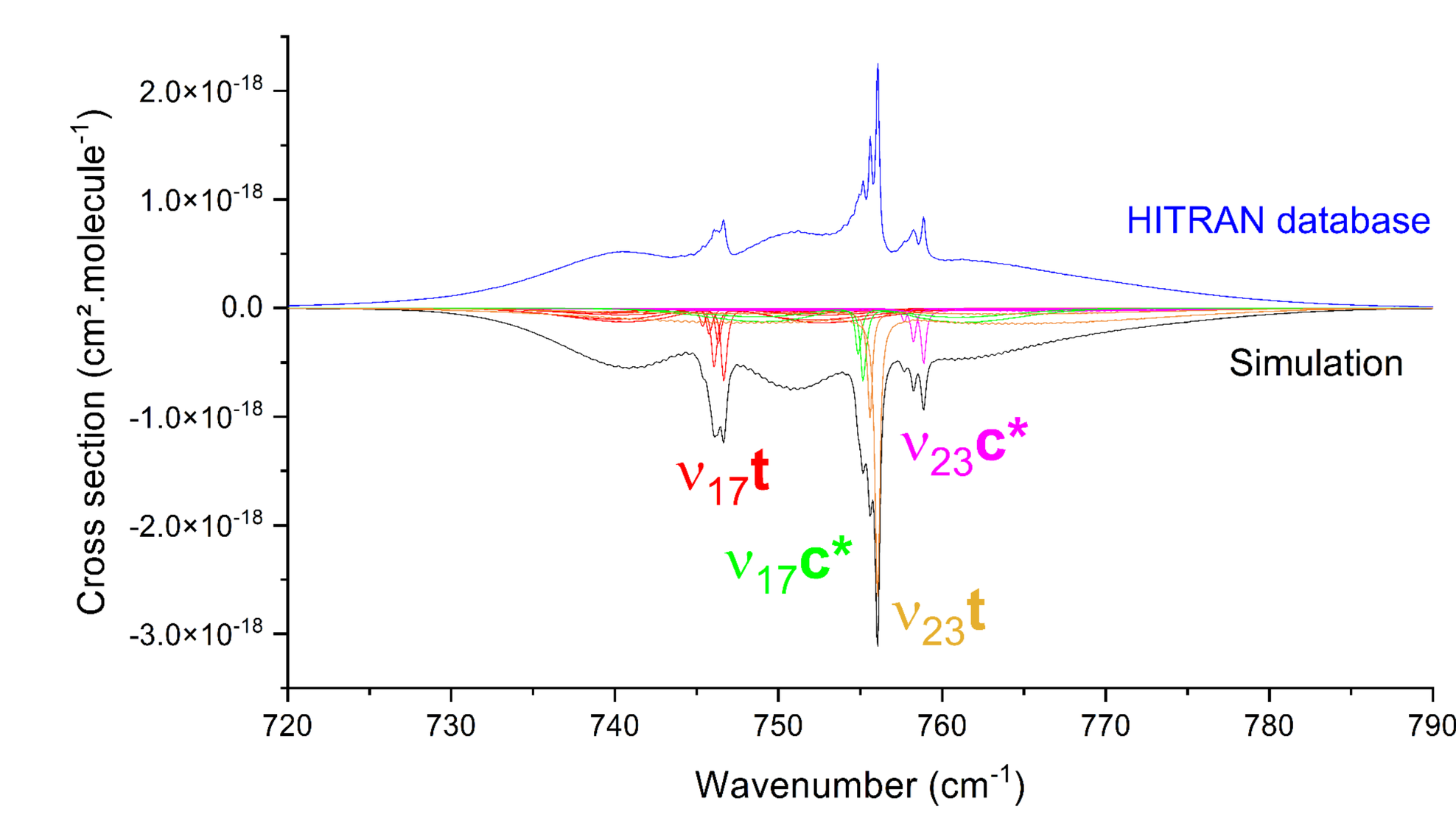
5. Cross sections

The room temperature middle resolution spectrum of 2-FF available in the HITRAN database [4] was reconstructed with a deviation <10% by extrapolating the high-resolution analyses and adding hot band in our simulation (40-63% of the fund. band).

Wavenumber	calculated from our simulations[a]		calculated from HITRAN[a]
	without hot bands	with hot bands	
cm^{-1}	$cm.molecule^{-1}$	$cm.molecule^{-1}$	$cm.molecule^{-1}$
700 – 795	1.26E-17	2.23E-17	2.22E-17
980 – 1050	3.19E-18	5.89E-18	6.15E-18
1450 – 1550	0.45E-17	0.87E-17	1.17E-17
1550 – 1610	2.55E-18	7.67E-18	8.53E-18
1660 – 1800	1.29E-17	3.48E-17	3.75E-17

[a] Results obtained from integration of the cross sections given in $cm^2.molecule^{-1}$





In terms of **perspectives,** a reliable anharmonic force field, capable of providing accurate anharmonic coefficients $\chi_{i,j}$, is necessary in order to assign hot band patterns and enhance the reconstruction of the room-temperature rovibrational spectrum for such medium-sized VOCs, where the rovibrational structure cannot be resolved at room temperature.

[4] Johnson, T. J., Profeta, L. T., Sams, *et al.* (2010). *Vib. Spectrosc.*, 53(1), 97-102.