

# MM-WAVE AND AB INITIO STUDIES OF THE CONFORMATIONAL LANDSCAPE OF METHOXYPHENOLS IDENTIFIED AS SOA PRECURSORS

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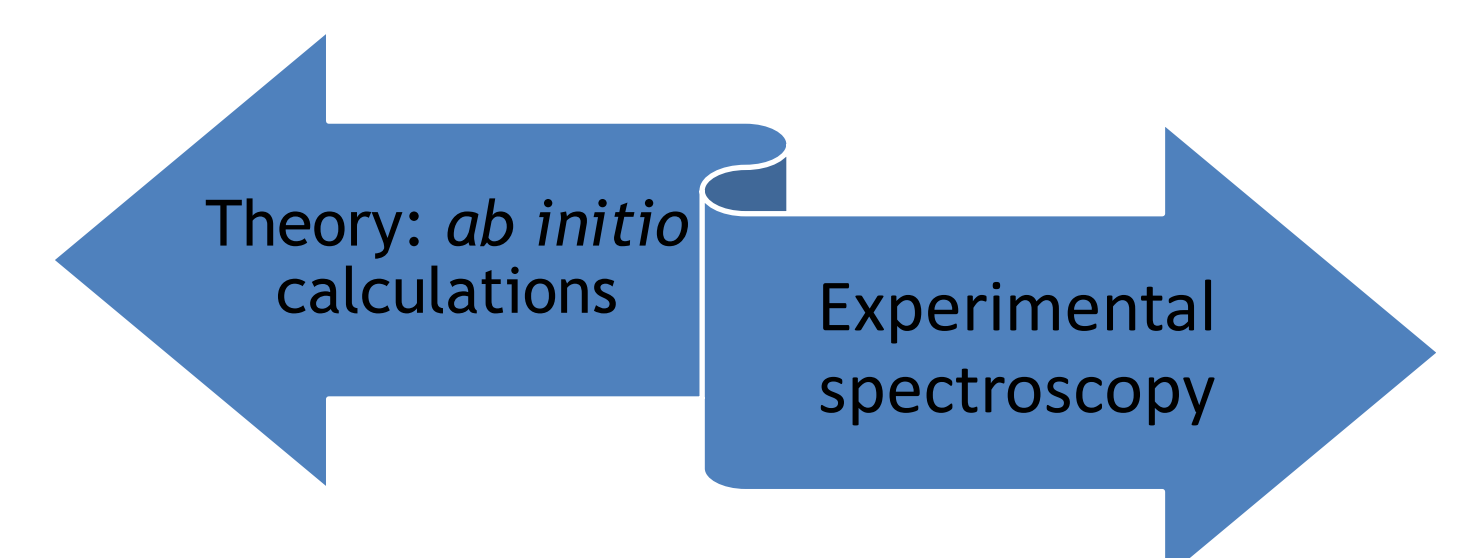
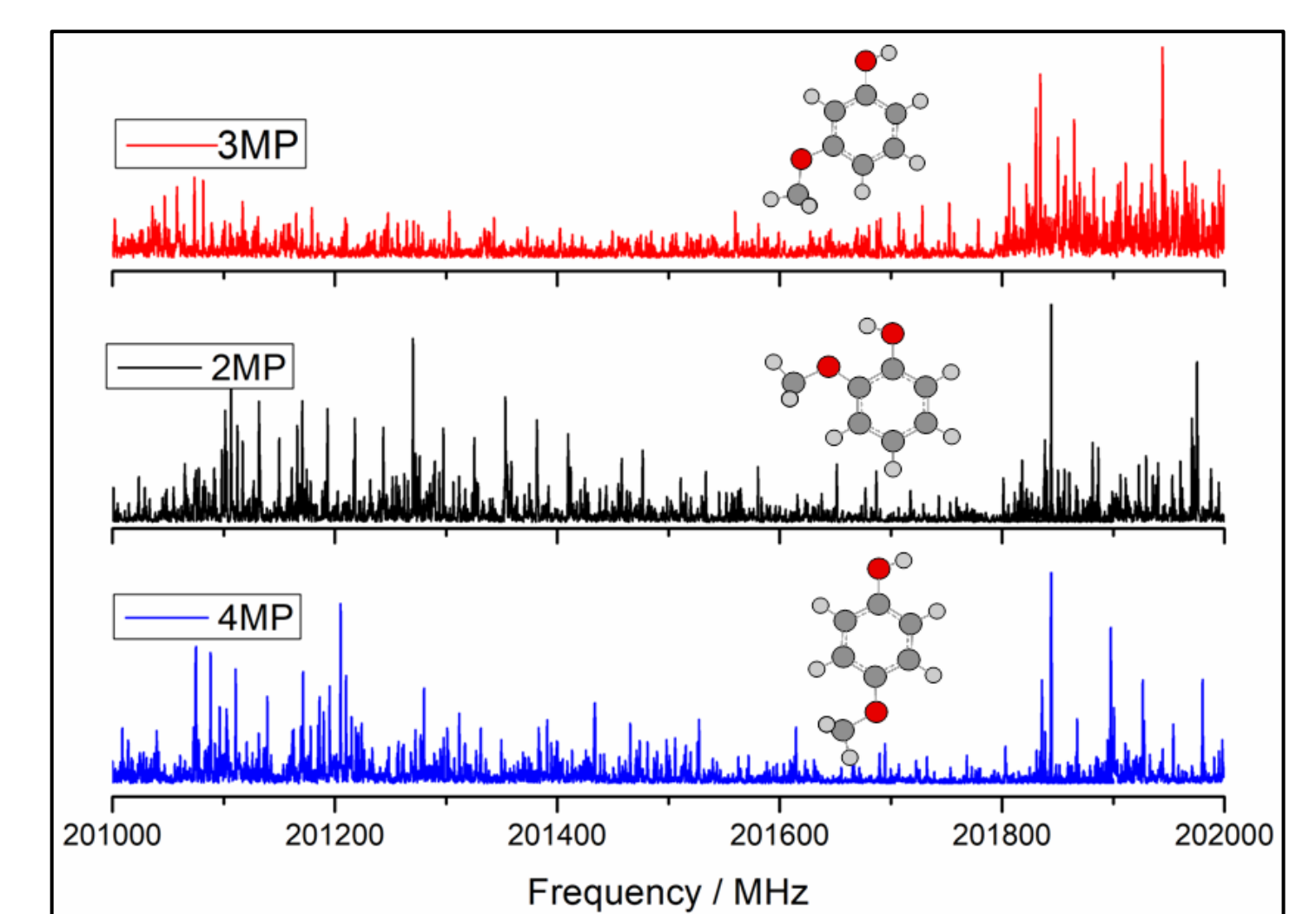
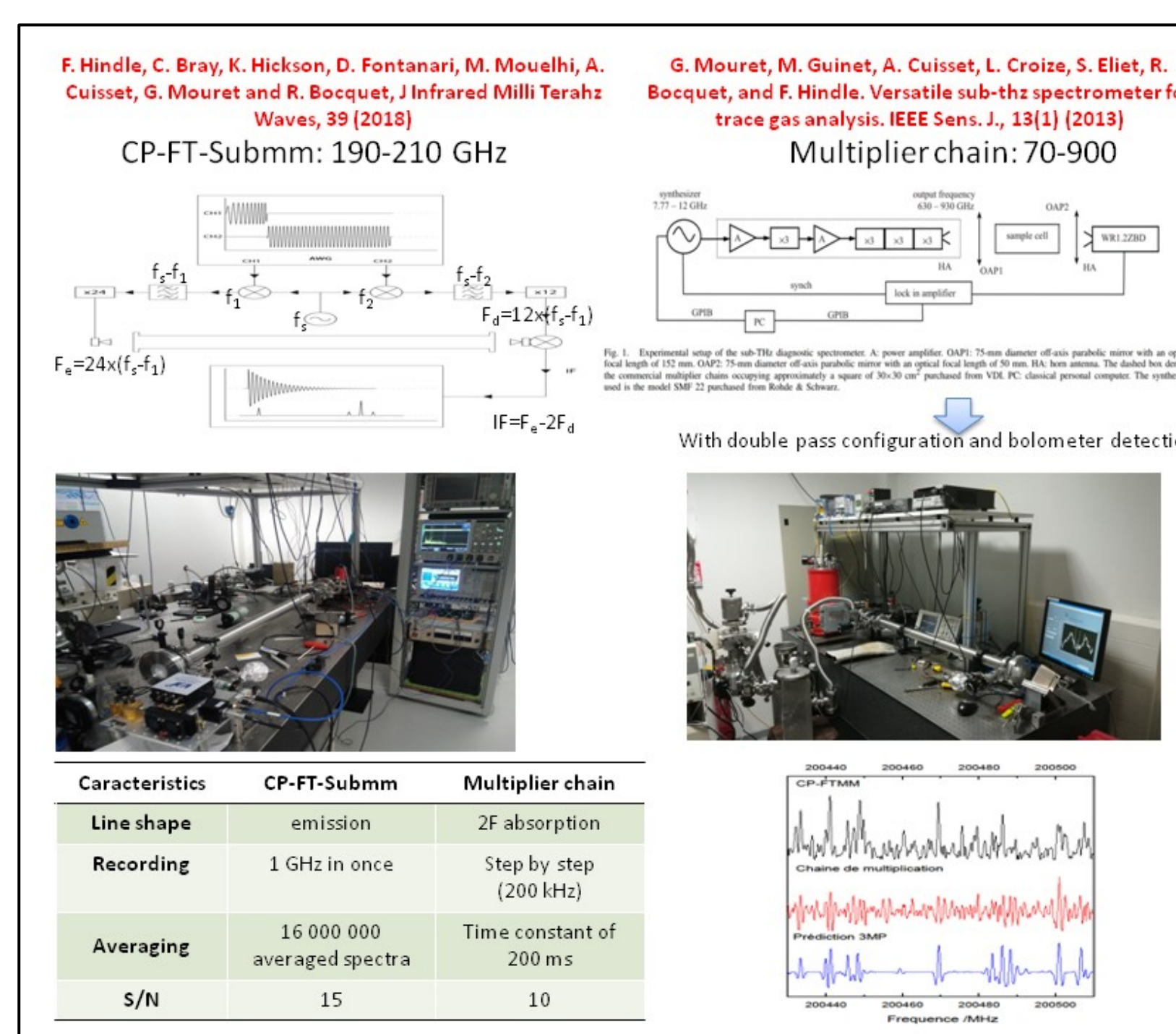
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## Introduction



- Methoxyphenols (MP) are semi-volatile organic compounds produced in abundance during biomass burning episodes. They are issued from the pyrolysis of wood lignin and their oxidation in the atmosphere contributes to SOA formation.
- The survey in gaseous phase of these tracers of biomass fires requires a complete high resolution spectroscopic study in order to obtain line lists (positions, intensities, cross section, ...) for an improved satellite data mining.
- The conformational study of the different isomers of MP (2-MP, 3-MP, 4-MP) is performed. The results of the analysis of the rotation spectra in the millimeter wave domain are presented. A combination of theoretical quantum chemical calculations and high resolution millimeter wave experimental spectroscopy was necessary in order to obtain a complete conformational landscape.

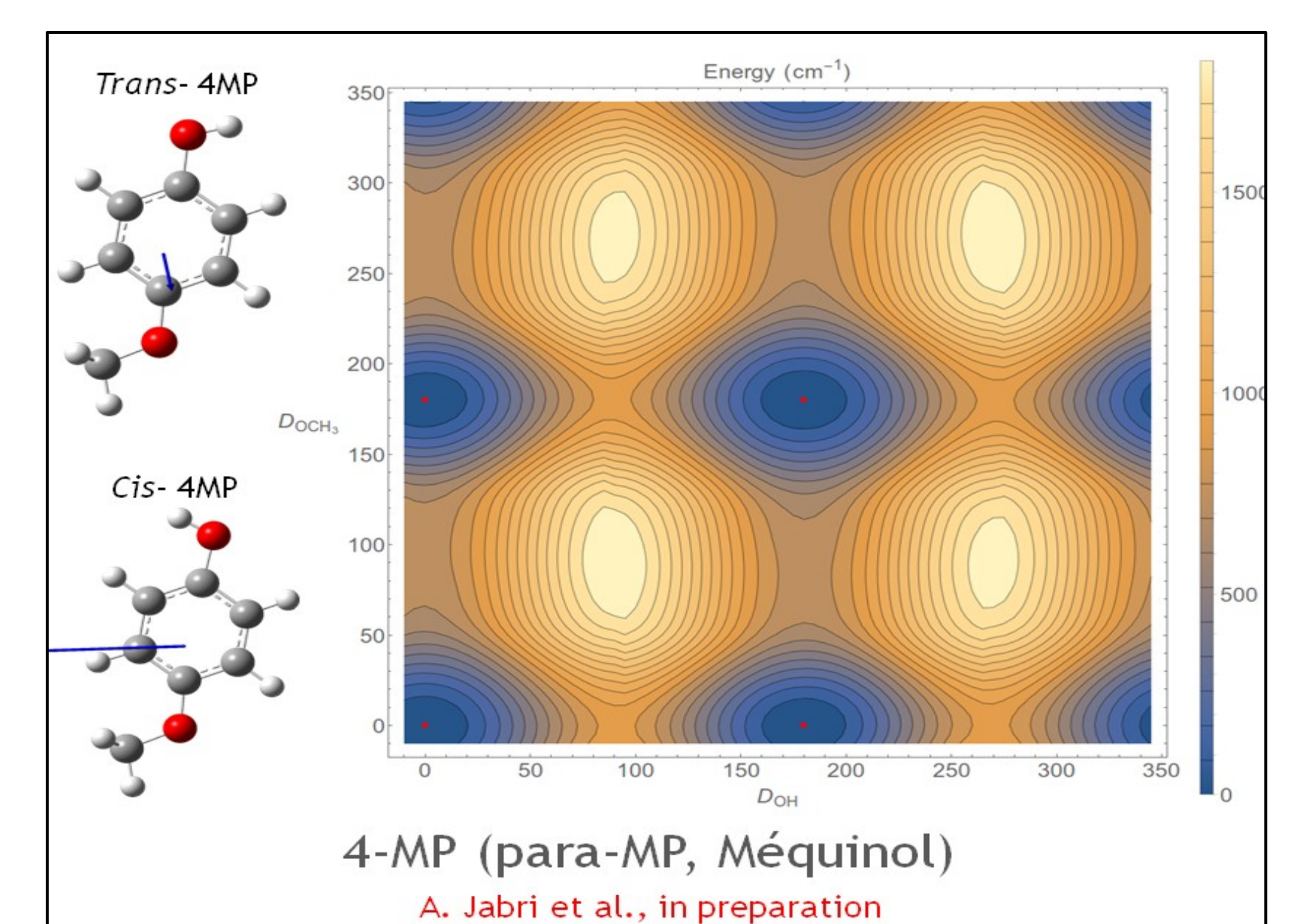
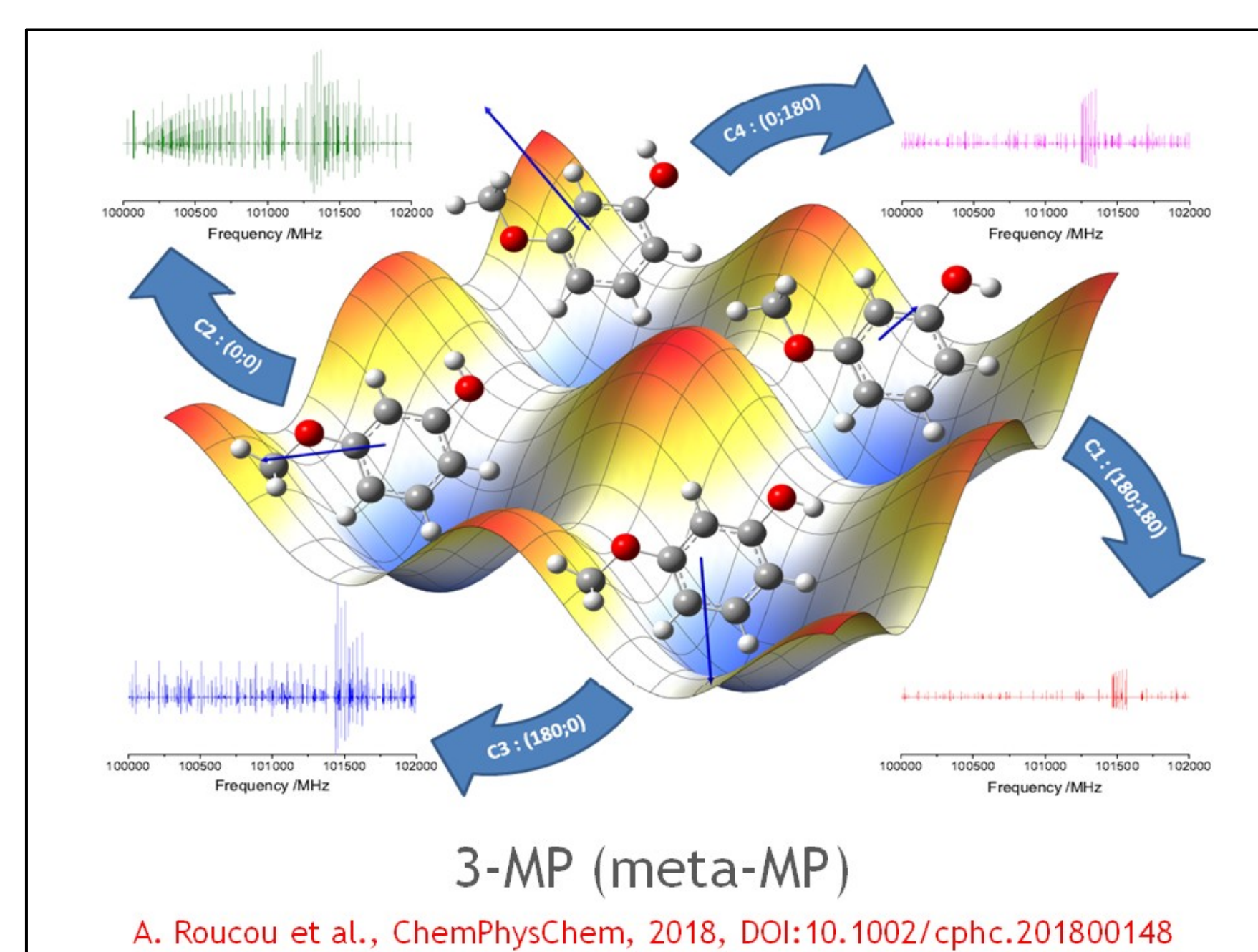
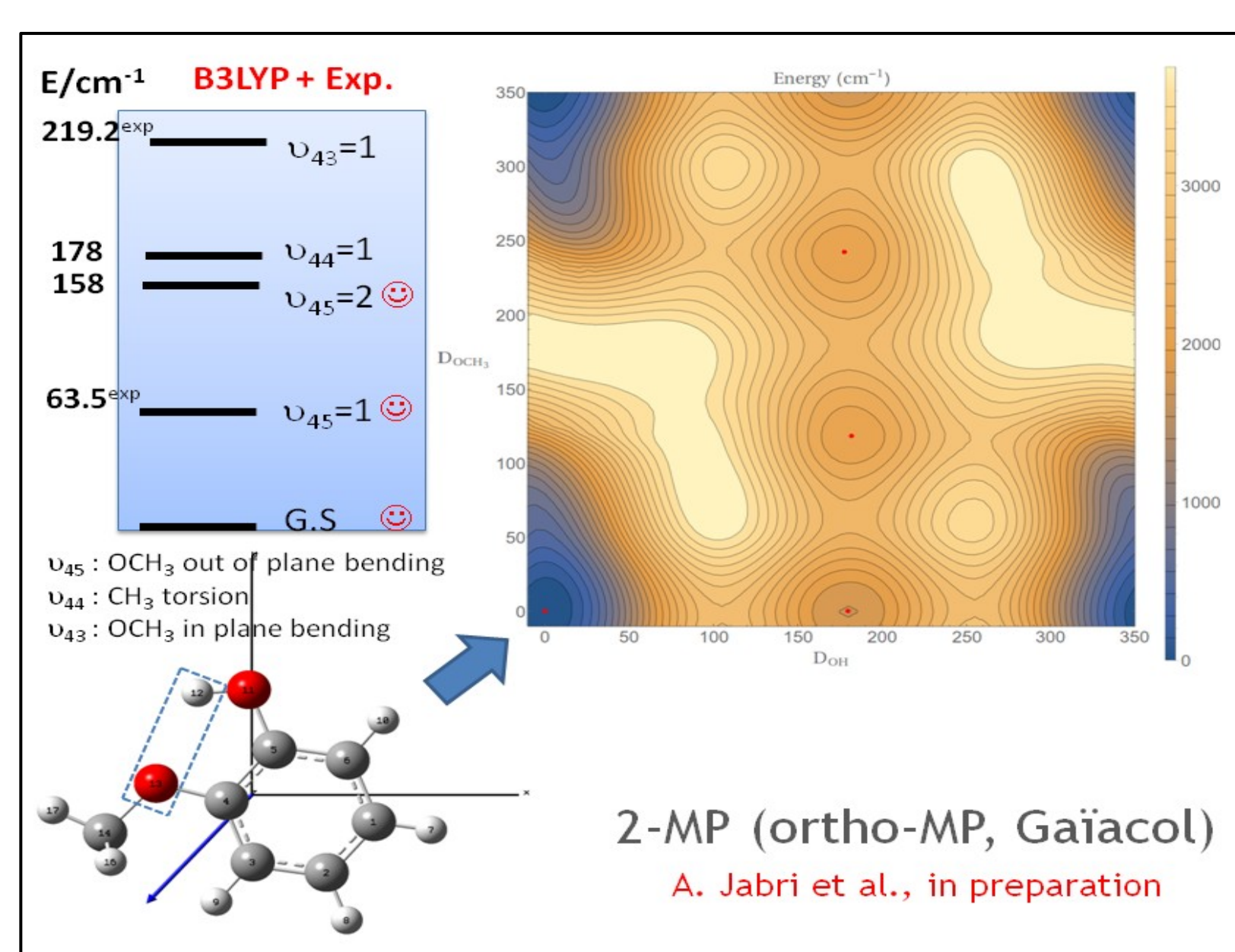
## Materials and Methods



## Objectives

- Understand for each isomer the effect of the variation of the geometric structure on the spectroscopic properties.
- Perform a high resolution spectroscopic study in the ground state but in the excited low frequency modes too, which will help the study of the rovibration in the infrared region.

## Results and Discussions



Isomer	2-MP (Guaiacol) (70-330 GHz)			3-MP (70-330 GHz)				4-MP (Mequinol) (CP: 190-210 GHz)				
	C1			C1	C2	C3	C4	C1 (-cis)				
Nbre. $v_t$	G.s	$v_{45}=1$	$v_{45}=2$	Gs	Gs	$v_{45}=1$	$v_{45}=2$	Gs	Gs	$v_{45}=1$	$v_{44}=1$	
A / MHz	2607.06212(176)	2605.45300(193)	2604.0688(34)	2840.8815(55)	3628.74476(136)	3615.98914(157)	3603.19449(189)	3625.235359(91)	2847.05497(54)	4879.84802(39)	4864.77217(62)	4872.0367(43)
B / MHz	1560.79653(62)	1560.52488(101)	1560.1783(36)	1303.52742(143)	1129.694225(50)	1130.478542(55)	1131.283069(70)	1131.967582(42)	1298.127597(128)	990.884783(100)	991.03929(33)	990.6002(64)
C / MHz	982.871808(233)	984.254361(239)	985.68133(36)	898.982164(103)	866.618684(49)	867.650530(47)	868.692281(56)	867.7652716(288)	897.065116(38)	828.439462(96)	829.410369(252)	828.85992(81)
$\Delta I''$ exp. / amu. Å <sup>2</sup>	-3.45949(28)	-4.35784(46)	-5.2762(16)	-3.42823(83)	-3.46823(10)	-4.34266(11)	-5.21953(14)	-3.475145(40)	-3.453841(96)	-3.555179(22)	-4.51072(40)	-4.1772(56)
$\Delta I''$ calc. / amu. Å <sup>2</sup>	-3.20	-4.32	-5.20	-3.20	-3.20	-4.284	-5.192	-3.20	-3.20	-3.20	-4.43	-4.09
Pop. %				45.6		25.3		21.5		7.6	50.58	
$\mu$ ( a / b ) / D		2.74 (2.05/1.82)		0.77 (0.63/0.45)		1.74 (1.74/0)		2.01 (0/2.01)	2.41 (1.41/1.95)		2.50 (-0.86/2.35)	
$J_{max} / K_{max}$		167 / 63		130 / 22		175 / 63		159 / 50	149 / 31		148 / 27	
N. lines(a/b)	6478/5095	5214/4068	2887/2942	934/842	6570/0	4861/0	3117/0	0/4623	1850/2063	0/979	0/762	82/112
Rms / kHz		94.6		72.4		74.8		75.8	75.9		72.2	

- While guaiacol only have one conformer stabilized by an intramolecular hydrogen bond, its millimeter wave spectrum recorded at ambient temperature contains several rotational structures corresponding to the vibrational modes under 500 cm<sup>-1</sup>. We have identified these structures by comparison with the values of the inertial defects  $\Delta I''$ .
- The 3-methoxyphenol is the isomer presenting the most complex conformational landscape. We managed to identify for the first time the four stable conformations.
- The 4-methoxyphenol exists in two different conformers (*cis* and *trans*) according to the orientation of the methoxy (-OCH<sub>3</sub>) group with respect to the hydroxy (-OH) group. Until now, we analyzed the rotational spectrum of the *-cis* ground state, and the rotational spectra of the  $v_{45}$  and  $v_{44}$  modes. The spectral analysis of the *-trans* conformer is a work in progress.

## Conclusion and perspectives

- Analysis of the rotational structures in the vibrational ground state and in the excited states of low frequency modes.
- Determination of spectroscopic constants ( $A$ ,  $B$ ,  $C$ ,  $D_J$ ,  $D_{JK}$ ,  $D_K$ , ...) at very high accuracy and validation of the conformational landscape predicted by the theoretical computations of quantum chemistry.
- The next step would be to exploit these results in the rovibrational analysis of infrared spectra recorded in the experimental setups Jet-AILES (FT-FIR, SOLEIL) and SPIRALES (Low temperature EC-QCL Laser spectroscopy in the mid infrared domain, MONARIS Laboratory, Pierre and Marie Curie University, Paris, France).

