Terzo Workshop sull'Astronomia Millimetrica in Italia

Laboratory data in support of astronomical detection of molecules

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CNR Area della Ricerca a Bologna - Sala 216

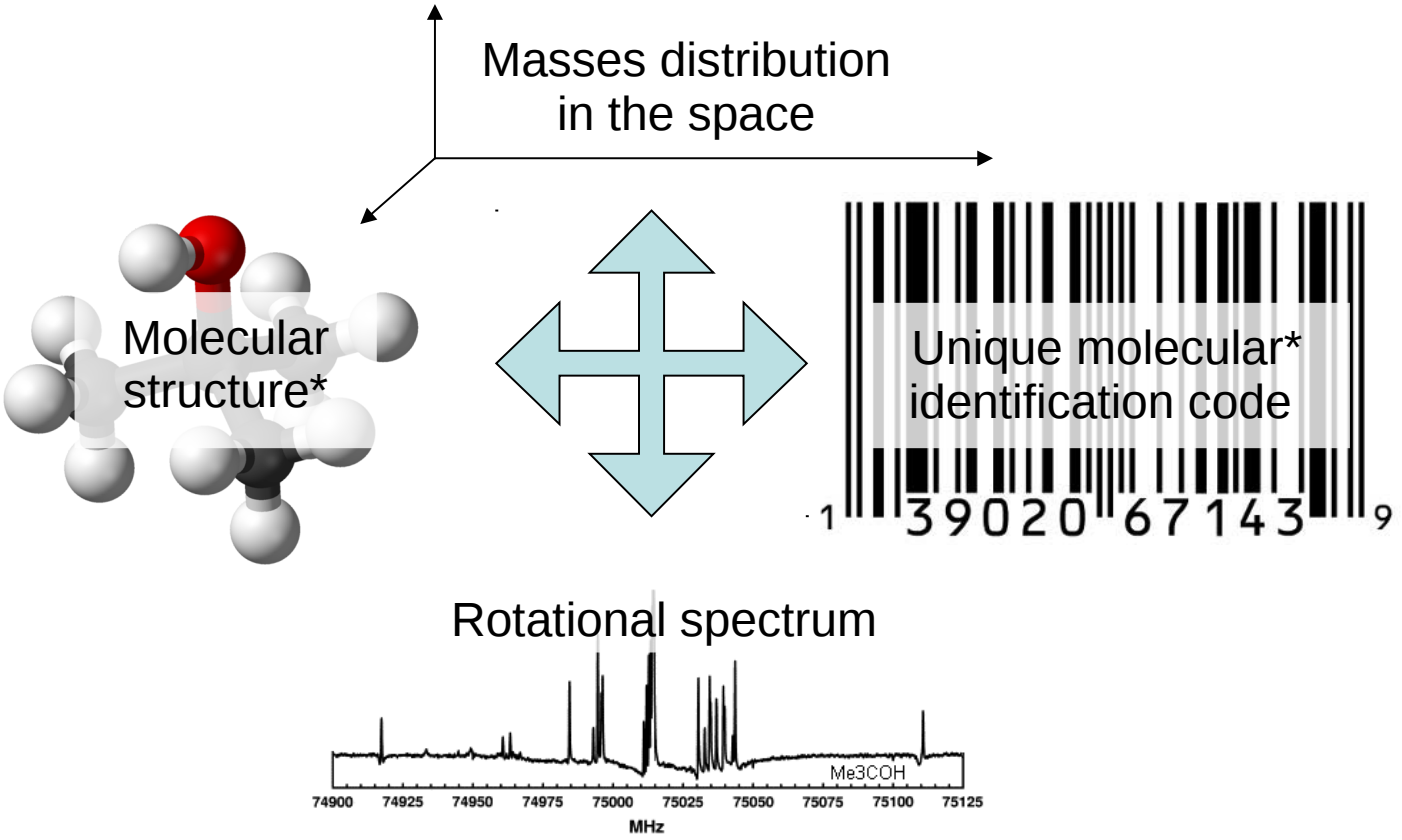
Rotational spectroscopy

- The research of molecules in space is essential to understand the chemistry of the Universe
- Astrochemical models are based on:

  - identification of the molecules

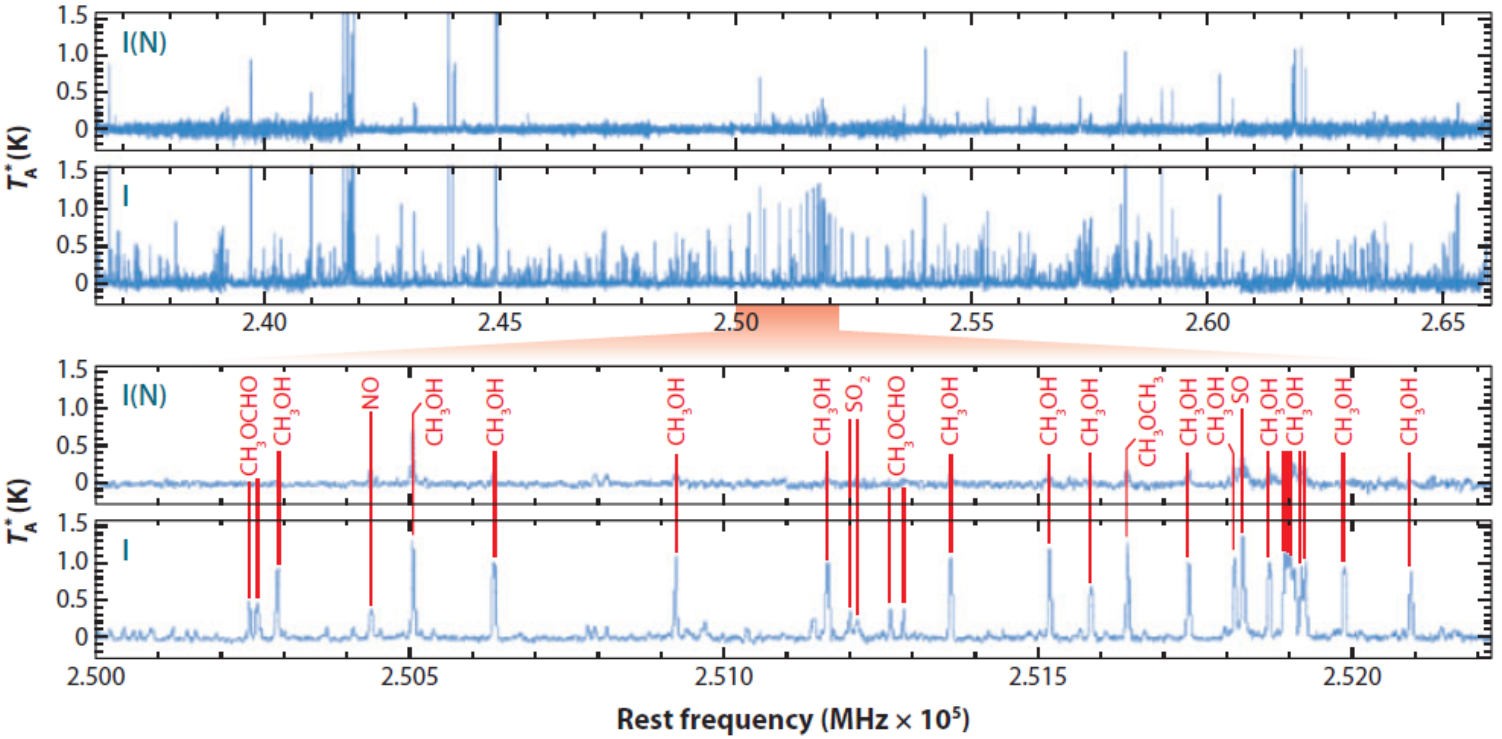
  - abundance

  - isotopic variations and other details
- Rotational spectroscopy is one of the main techniques for observation and identification of molecules in space



(*including: tautomers; isotopomers; conformers; vibrational and electronic excited states; ionized species)

Molecules in space (184+deuterated+unconfirmed)

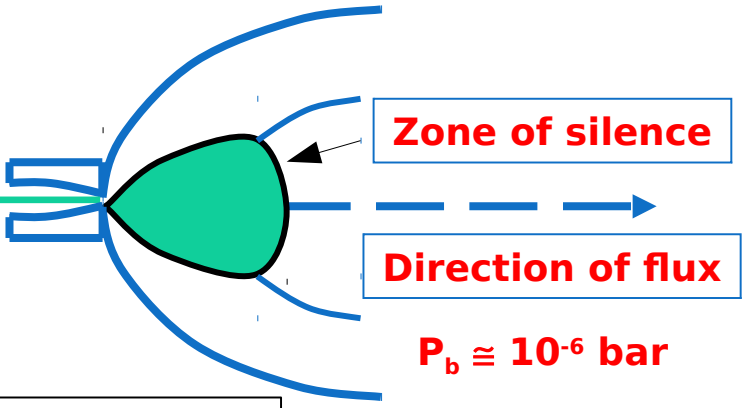


Line surveys in the 1 mm atmospheric window toward two massive young stellar objects, I(N) (top) and I (bottom), in the NGC 6334 star-forming region.

Herbst & van Dishoeck, Annu. Rev. Astron. Astrophys. 47 (2009) 427

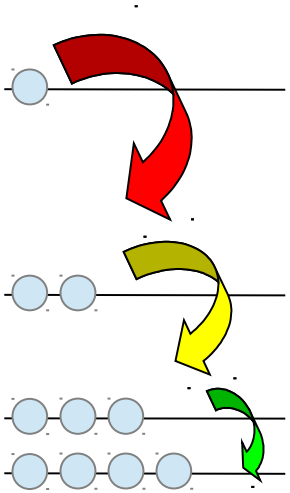
Mix of sample (ca. 1-2%) in rare gas

P_0 = 0.2 - 4 bar



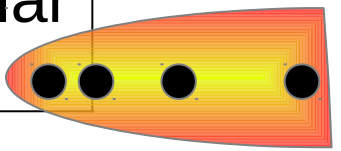
If $P_0 >> P_b$ (ca. 10^5)

Supersonic expansion



Cooling of the degrees of freedom

Stop of the intermolecular collisions



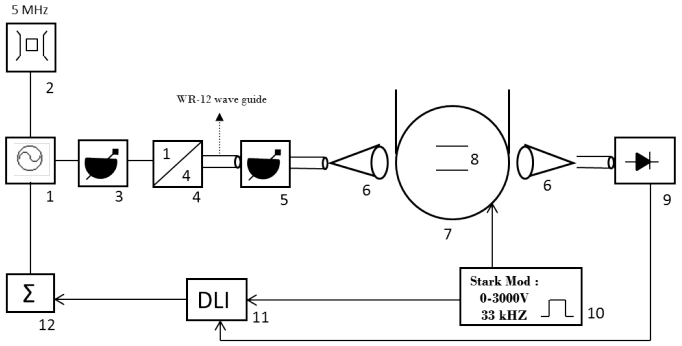
Depopulation of the excited vibrational states

More intense, more simple rotational spectra

Longer lifetime of kinetically unstable species

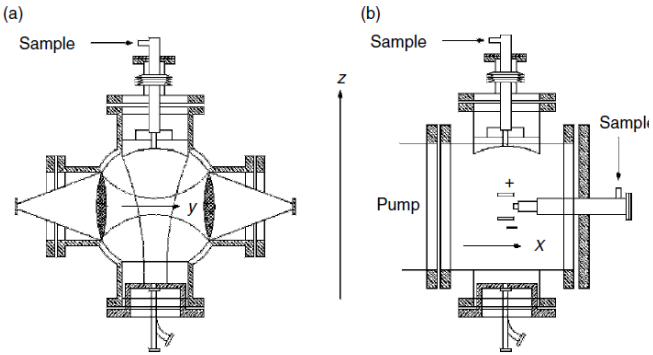
Free Jet Absorption MilliMeter Wave spectrometer (FJ-AMMW, 52-74.4 GHz)

- Sweep rate: 10 GHz per day
- Sensitivity: 10^{-7} - 10^{-8} cm^{-1}
- Resolution : 200 kHz
- Accuracy: < 50 kHz



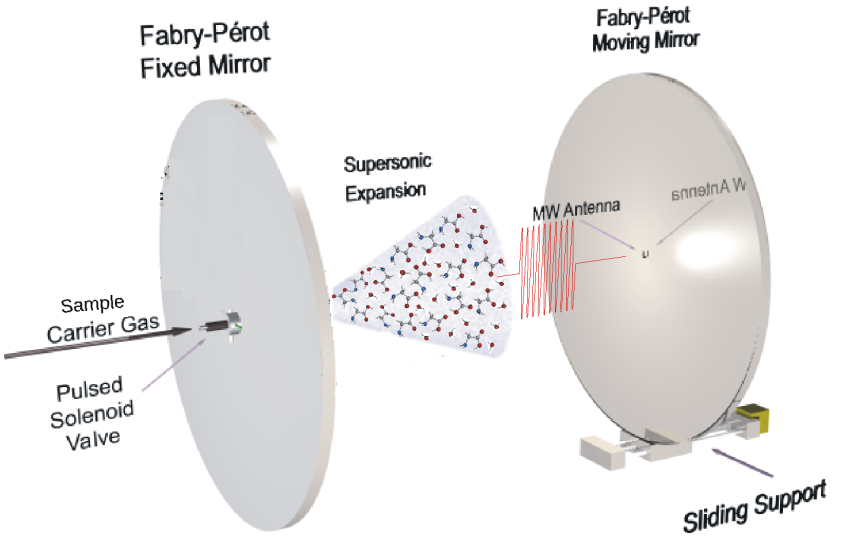
- *S. Melandri et al. J. Mol. Struct. 352/353 (1995) 253*
- *S. Melandri et al. Chem. Phys. Lett. 261 (1996) 267*
- *C. Calabrese et al. JPC-A 117 (2013) 13712*

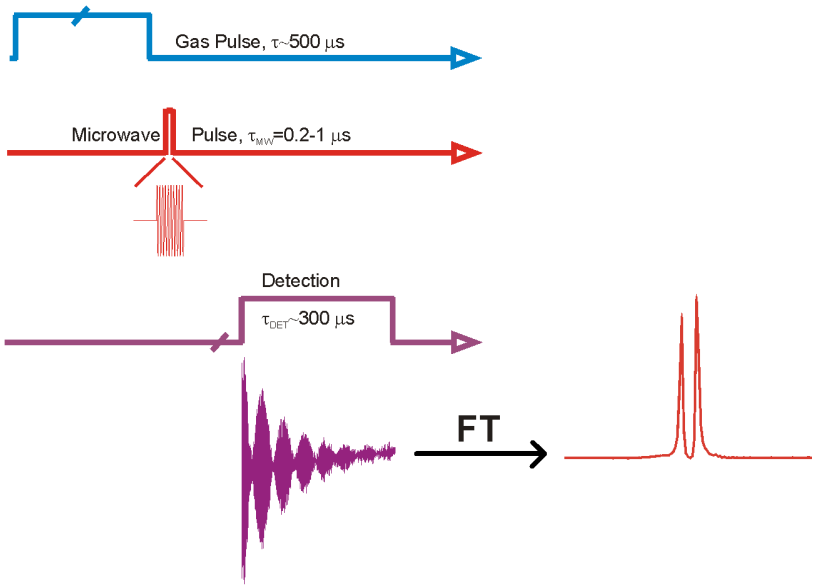
- Typical conditions:
- P_0=200-500 mbar, P_b=0.001 mbar
- T_{rot} ≈ 10 K, T_{sample} up to 160°
- Jet length: 16 cm



Molecular Beam Fourier Transform MW spectrometer (MBFTMW, 6-18 GHz)

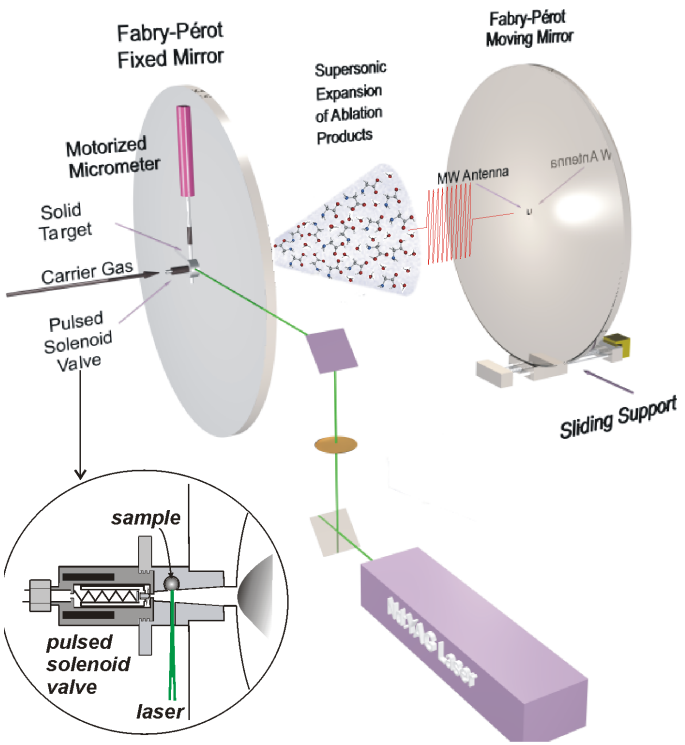
- Sweep rate: 0.2 GHz per day
- Sensitivity: 10^{-11} - 10^{-12} cm^{-1}
- Sub Doppler resolution: few kHz
- Accuracy: < 3 kHz
- $T_{rot} \approx 1$ K

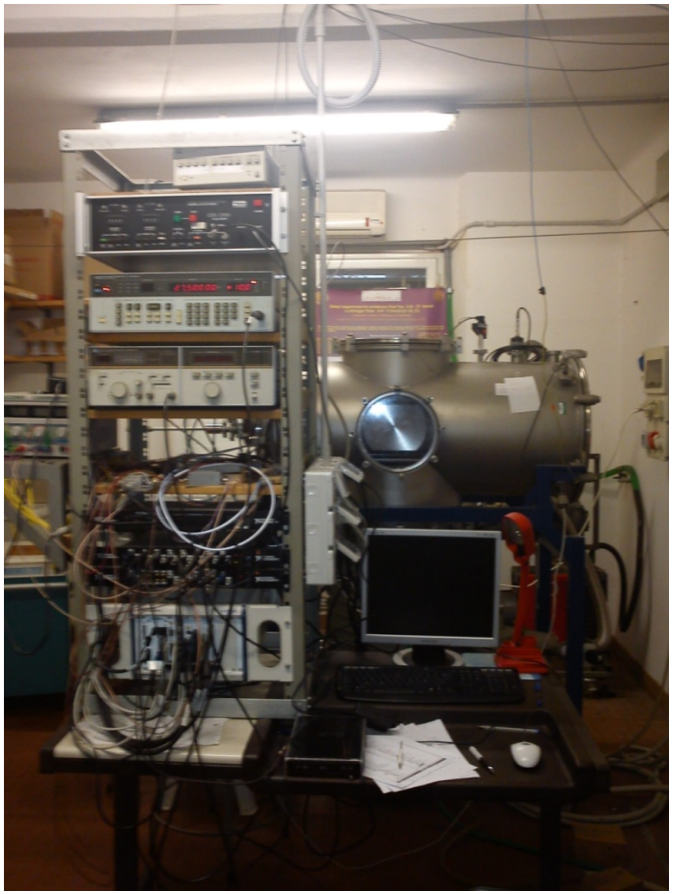


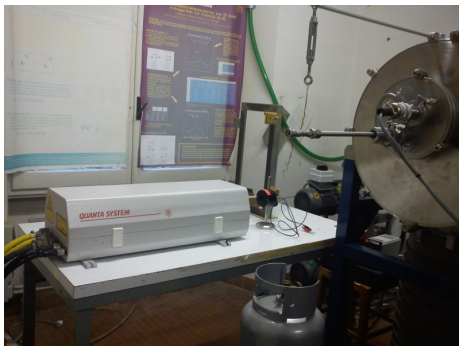


- *Caminati et al., Chem. Phys. Letters 392 (2004) 1*
- *Operated according to: Jens-Uwe Grabow, Habilitationsschrift, Universität Hannover (2004)*

Experimental Perspective: MBFTMW + Laser ablation/desorption



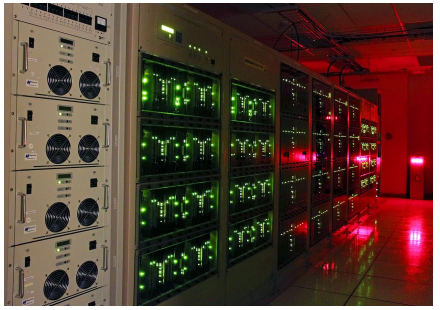


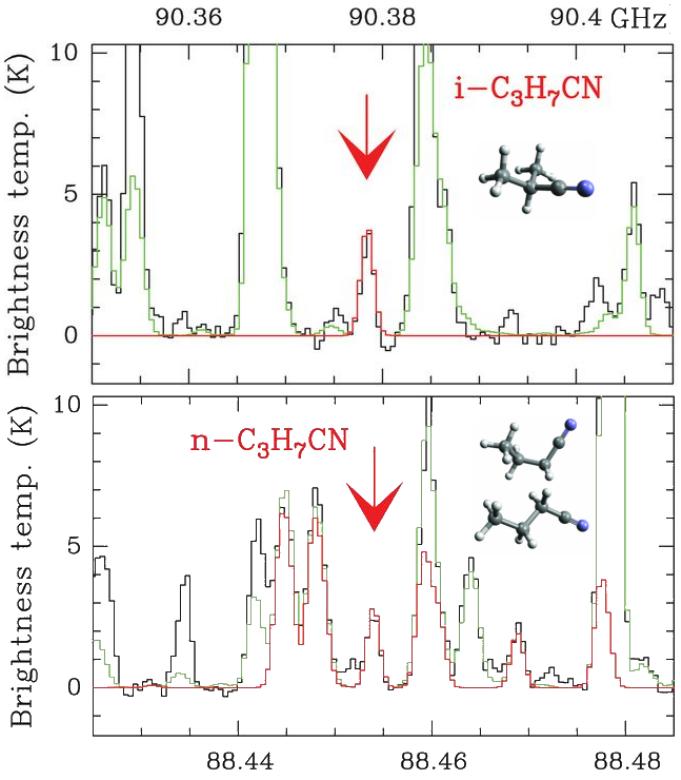


- Laser Nd-YAG (Quanta Systems) 532 nm 10 ns:
- Vaporization without decomposition of solid compounds and biomolecules
- Vaporization of metals

Atacama Large Millimeter/submillimeter Array
ALMA: 31 - 950 GHz

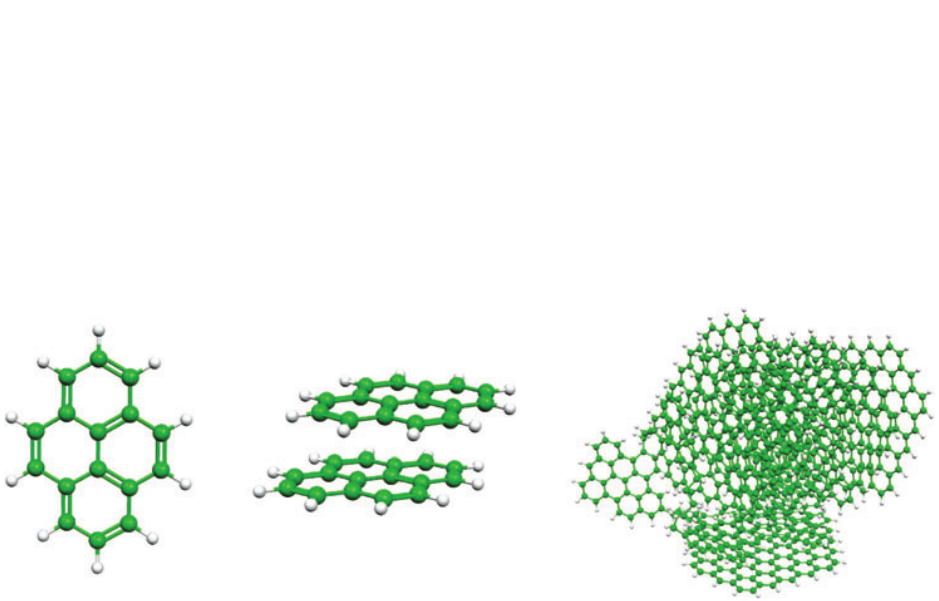
- High sensitivity and resolution
- The interpretation of the plethora of data that will be obtained requires a large number of laboratory data

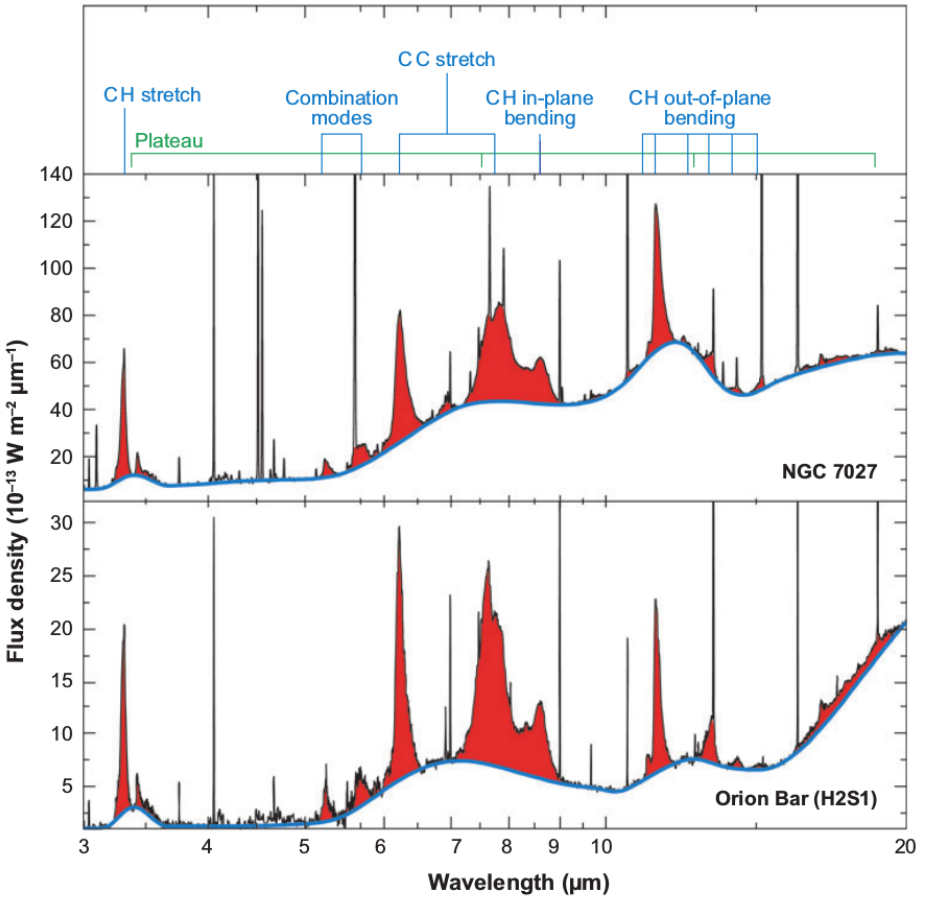




- **Examples of transitions of propyl cyanide toward the northern hot core of Sgr B2(N):**
- **Black**: continuum-subtracted spectrum observed with ALMA
- **Green**: preliminary model including all identified molecules
- **Red**: synthetic spectra of i-PrCN and n-PrCN
- *Belloche et al. Science 345 (2014) 1584*
- *Müller et al. J. Mol. Spectr. 267 (2011) 100*
- *Durig & Li, J. Mol. Struct. 21 (1974) 289*

Polycyclic Aromatic Hydrocarbon Molecules





e.g. Tielens, Annu. Rev. Astron. Astrophys. 46 (2008) 289

Fluorenone

	MHz	e-c		MHz	e-c
24 (24) - 23 (23)	68458.54	-0.08	33 (18) - 32 (17)	66173.33	0.01
25 (24) - 24 (23)	69467.34	-0.06	34 (18) - 33 (17)	67165.88	-0.08
23 (23) - 22 (22)	65567.13	-0.02	35 (18) - 34 (17)	68156.00	0.05
22 (21) - 21 (20)	60793.18	0.19	36 (18) - 35 (17)	69143.00	0.00
23 (21) - 22 (20)	61801.85	0.12	37 (18) - 36 (17)	70126.78	-0.02
23 (20) - 22 (19)	59918.70	-0.04	29 (17) - 28 (16)	60285.52	0.00
24 (20) - 23 (19)	60927.10	0.06	30 (17) - 29 (16)	61283.11	0.02
25 (20) - 24 (19)	61935.03	0.02	31 (17) - 30 (16)	62278.44	0.01
26 (20) - 25 (19)	62942.62	0.08	32 (17) - 31 (16)	63271.25	-0.02
27 (20) - 26 (19)	63949.57	0.03	33 (17) - 32 (16)	64261.29	-0.02
28 (20) - 27 (19)	64956.00	0.10	34 (17) - 33 (16)	65248.17	-0.05
29 (20) - 28 (19)	65961.58	0.07	35 (17) - 34 (16)	66231.64	-0.02
30 (20) - 29 (19)	66966.27	0.02	36 (17) - 35 (16)	67211.27	0.03
31 (20) - 30 (19)	67969.99	0.01	37 (17) - 36 (16)	68186.59	0.05
32 (20) - 31 (19)	68972.52	-0.05	38 (17) - 37 (16)	69157.13	0.03
33 (20) - 32 (19)	69973.88	0.01	39 (17) - 38 (16)	70122.45	0.05
19 (19) - 18 (18)	54001.04	-0.02	31 (16) - 30 (15)	60366.61	0.00
20 (19) - 19 (18)	55009.78	-0.11	32 (16) - 31 (15)	61353.36	-0.01
25 (19) - 24 (18)	60050.56	-0.05	33 (16) - 32 (15)	62336.32	-0.07
26 (19) - 25 (18)	61057.34	-0.04	34 (16) - 33 (15)	63315.20	-0.04
27 (19) - 26 (18)	62063.40	-0.03	35 (16) - 34 (15)	64289.43	0.01
28 (19) - 27 (18)	63068.61	-0.02	36 (16) - 35 (15)	65258.36	-0.04
29 (19) - 28 (18)	64072.85	0.01	32 (15) - 31 (14)	59419.03	0.09
30 (19) - 29 (18)	65075.90	-0.01	33 (15) - 32 (14)	60391.80	0.00
31 (19) - 30 (18)	66077.63	-0.04	34 (15) - 33 (14)	61358.95	0.07
32 (19) - 31 (18)	67078.04	0.07	35 (15) - 34 (14)	62319.56	-0.11
19 (18) - 18 (17)	52118.29	-0.02	36 (15, 22) - 35 (14, 21)	63272.68	0.02
20 (18) - 19 (17)	53126.95	-0.07	36 (15, 21) - 35 (14, 22)	63273.56	0.02
25 (18) - 24 (17)	58165.07	-0.01	37 (15, 23) - 36 (14, 22)	64217.45	0.07
27 (18) - 26 (17)	60175.44	-0.02	37 (15, 22) - 36 (14, 23)	64219.39	0.09
28 (18) - 27 (17)	61179.04	0.01	27 (14) - 26 (13)	52577.06	0.02
29 (18) - 28 (17)	62181.27	-0.02	28 (14) - 27 (13)	53563.41	0.02
30 (18) - 29 (17)	63181.95	-0.11	29 (14) - 28 (13)	54545.41	0.07
31 (18) - 30 (17)	64181.15	0.02	30 (14) - 29 (13)	55522.37	0.09
32 (18) - 31 (17)	65178.30	0.00			

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Accurate spectroscopy of polycyclic aromatic compounds: From the rotational spectrum of fluoren-9-one in the millimeter wave region to its infrared spectrum

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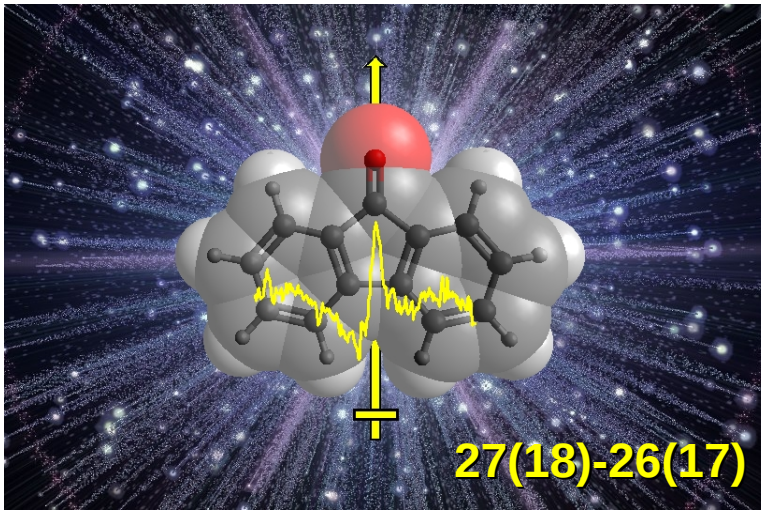
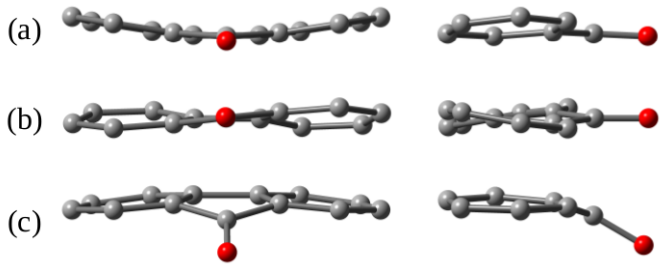
The rotational spectrum of fluoren-9-one, a small oxygenated polycyclic aromatic hydrocarbon, has been recorded and assigned in the 52-74.4 GHz region. The determined small negative value of the inertia defect (−0.3 u Å^2) has been explained in terms of vibrational-rotational coupling constants calculated at the B3LYP/cc-pVTZ level of theory. Vibrational anharmonic analysis together with second-order vibrational perturbation theory approximation was applied both to fluorenone and its reduced form, fluorene, to predict the mid- and near-infrared spectra. The data presented here give precise indication on the fluorenone ground state structure, allow for an accurate spectral characterization in the millimeter wave and infrared regions, and hopefully will facilitate extensive radio astronomical searches with large radio telescopes. © *2015 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4905134]



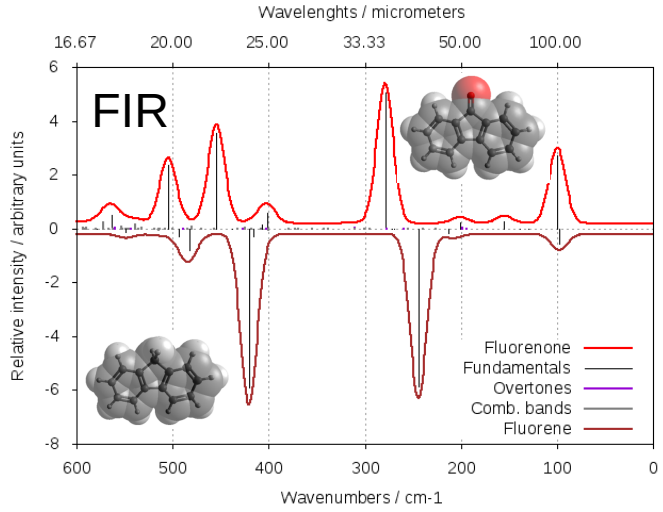
Microwave spectrum of fluorene:
Thorwirth et al. ApJ 662 (2007) 1309

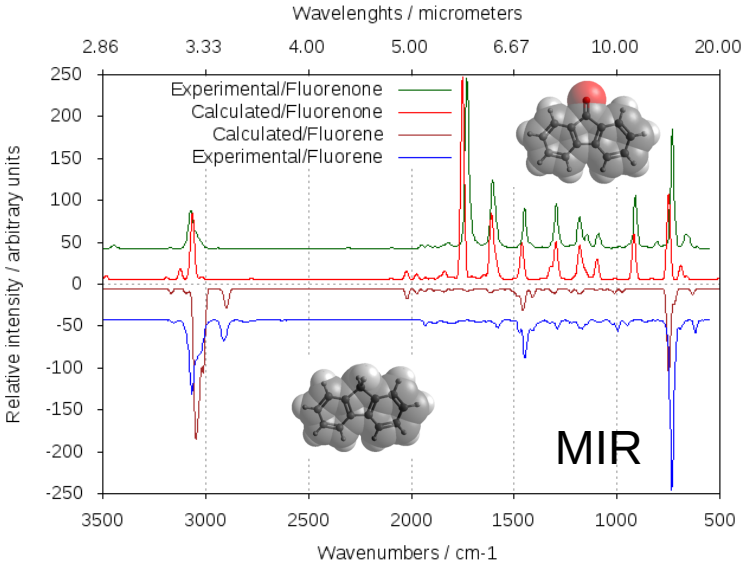
Fluorene and fluorenone: infrared spectra prediction (B3LYP/cc-pVTZ)

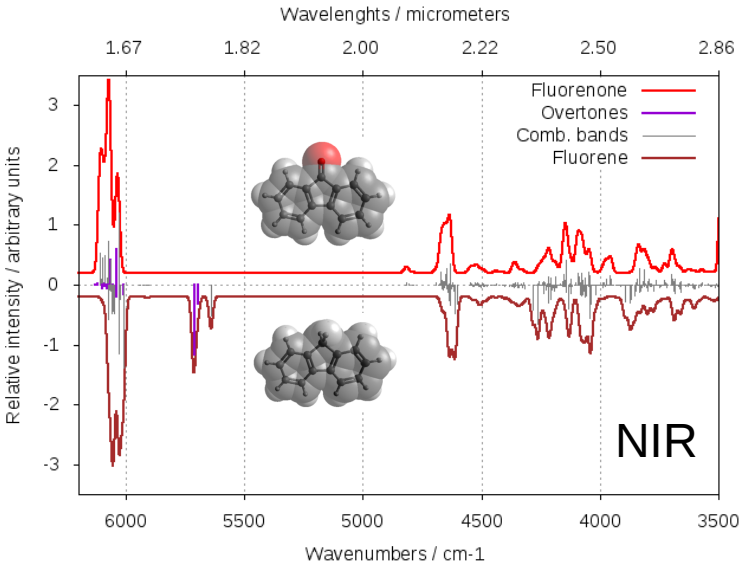


Irreducible representations of the fundamental vibrational normal modes (Γ_{fv}) and of the 1:1 combination bands (Γ_{cb})

9HF					F9O				
Γ_{fv}	22 a_1	10 a_2	11 b_1	20 b_2	Γ_{fv}	21 a_1	9 a_2	10 b_1	20 b_2
22 a_1	231 a_1	220 a_2	242 b_1	440 b_2	21 a_1	210 a_1	189 a_2	210 b_1	420 b_2
10 a_2		45 a_1	110 b_2	200 b_1	9 a_2		36 a_1	90 b_2	180 b_1
11 b_1			55 a_1	220 a_2	10 b_1			45 a_1	200 a_2
20 b_2				190 a_1	20 b_2				190 a_1
Γ_{cb}	521 a_1	440 a_2	442 b_1	550 b_2	Γ_{cb}	481 a_1	389 a_2	390 b_1	510 b_2





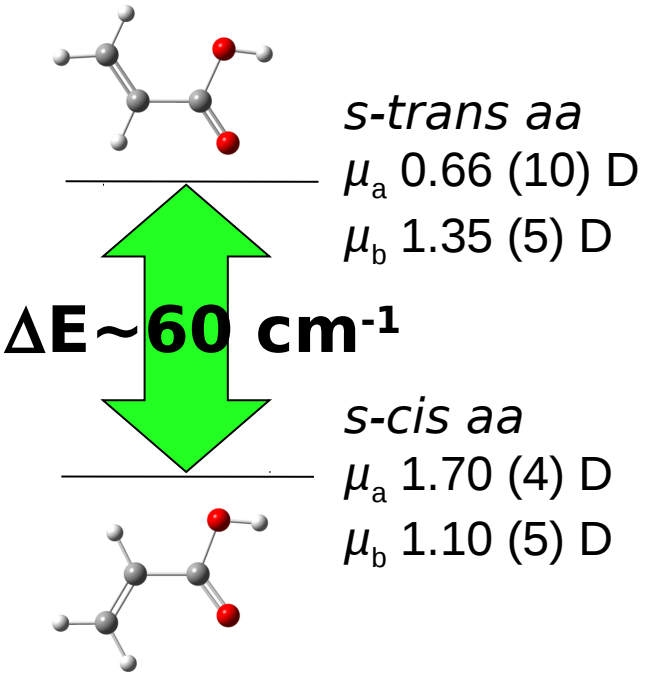


Acrylic acid

- Already detected in the interstellar medium or circumstellar shells:
- formic acid H-COOH
- acetic acid CH_3-COOH
- acrylonitrile CH_2=CH-CN
- acrolein CH_2=CH-CHO

MAYBE? → **CH_2=CH-COOH**

- A possible formation pathway of acrylic acid in interstellar ices containing CH4 and CO2 could be:
- $\cdot H + CO_2 \rightarrow \cdot COOH$
- $\cdot CH{=}CH_2 + \cdot COOH \rightarrow CH_2CHCOOH$



Bolton et al., J.Chem.Soc.Far.Trans. 270 (1974) 113

Acrylic acid

Journal of Molecular Spectroscopy 295 (2014) 37–43

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Laboratory rotational spectrum of acrylic acid and its isotopologues in the 6–18.5 GHz and 52–74.4 GHz frequency ranges

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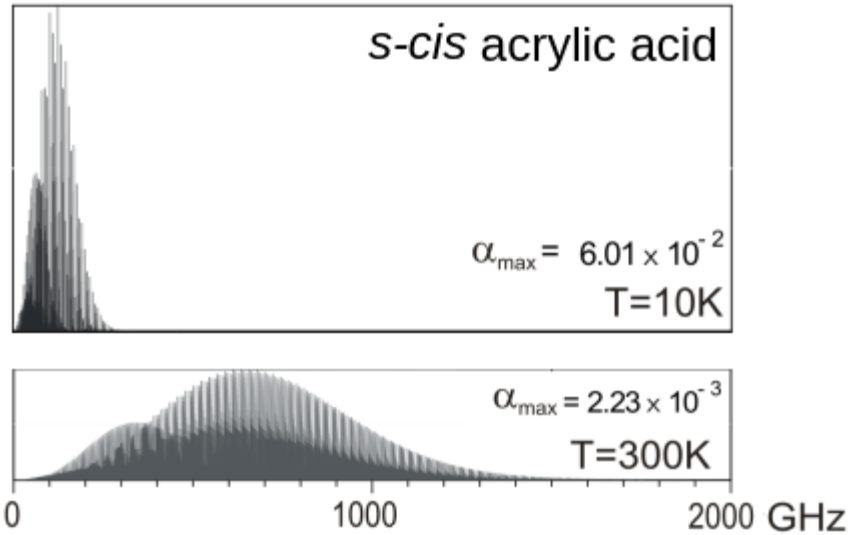
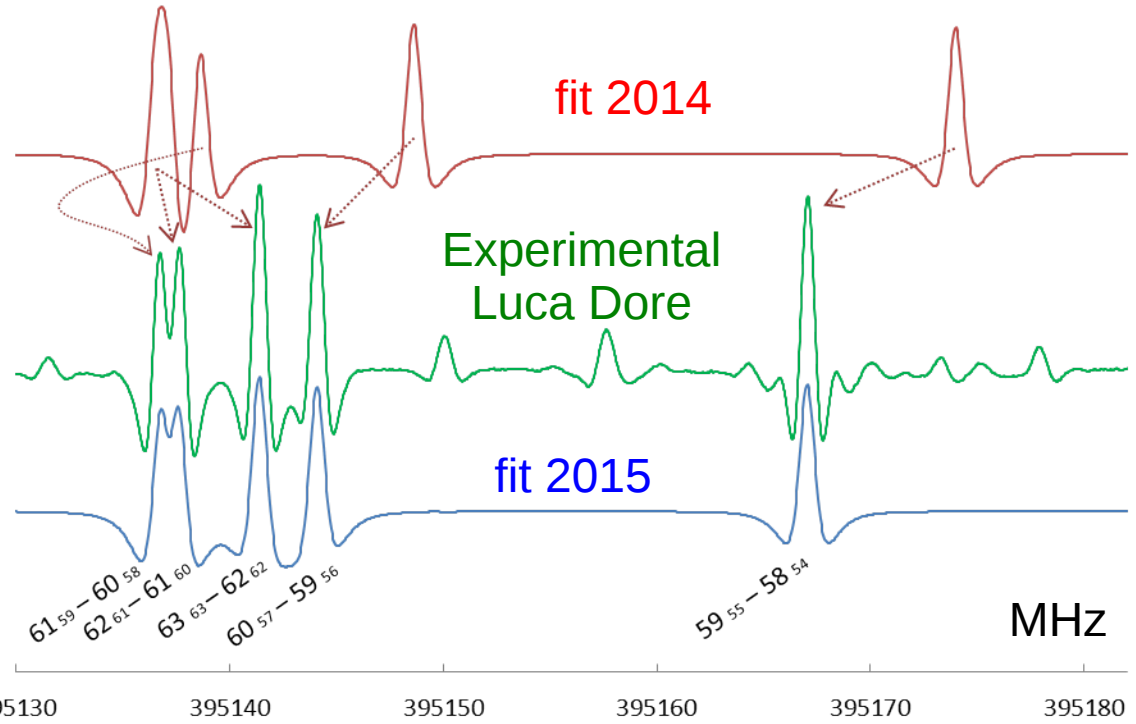
ABSTRACT

In order to facilitate the detection of acrylic acid in space, for which a possible mechanism of formation is proposed, we extended the measurements of the rotational spectrum of this molecule to the 6–18.5 GHz (time domain Fourier transform) and 52–74.4 GHz (frequency domain) ranges in supersonic expansions. 77 new lines were assigned to the *s-cis* conformer and 83 new lines to the *s-trans* conformer. In addition, the rotational spectra of the three single ^{13}C isotopologues have been measured in natural abundance for both conformers. High resolution measurements of the carboxylic deuterated isotopologues allowed for the determination of the deuterium nuclear quadrupole coupling constants. All the spectroscopic experimental parameters were compared to the ones obtained with quantum chemical methods at the MP2(fc)/aug-cc-pVTZ and B3LYP/aug-cc-pVTZ levels of calculation.

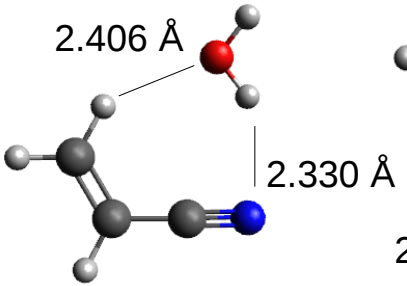
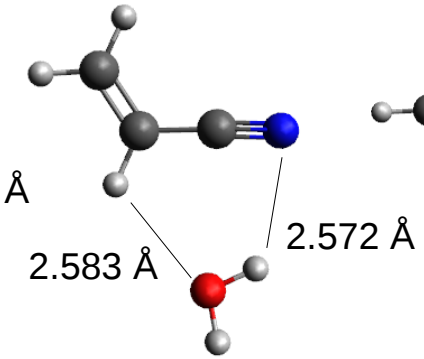
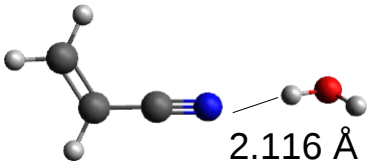
		s-cis	^{13}COOH	^{13}CH	$^{13}CH_2$	OD	All isotopologues		
A	MHz	11078.8707 (18)	11078.4874 (28)	10978.6648 (28)	11078.6840 (27)	11068.1939 (22)	D_J	kHz	0.638 (5)
B	MHz	4251.9700 (5)	4245.6528 (8)	4226.0138 (8)	4113.5180 (11)	4075.5367 (5)	D_{JK}	kHz	5.186 (7)
C	MHz	3073.3984 (6)	3070.0691 (9)	3052.1501 (9)	3000.3935 (13)	2979.5035 (6)	D_K	kHz	4.0 (2)
Δ_c	uÅ^2	0.03754 (5)	0.03766 (8)	0.03916 (8)	0.0378 (1)	0.04500 (6)	d_1	kHz	-0.206 (3)
χ_{aa}	MHz	-	-	-	-	0.150 (6)	d_2	kHz	-0.073 (2)
χ_{bb}	MHz	-	-	-	-	0.003 (12)	N		
χ_{cc}	MHz	-	-	-	-	-0.153 (12)	σ	kHz	46
		s-trans	^{13}COOH	^{13}CH	$^{13}CH_2$	OD	All isotopologues		
A	MHz	10716.1909 (19)	10715.2655 (33)	10615.8802 (28)	10715.3980 (30)	10242.1273 (16)	D_J	kHz	0.627 (13)
B	MHz	4388.2996 (6)	4379.1118 (25)	4360.4908 (14)	4245.7304 (15)	4307.8639 (7)	D_{JK}	kHz	5.3 (1)
C	MHz	3114.3105 (7)	3109.6045 (20)	3091.8579 (13)	3041.7619 (13)	3033.3856 (7)	D_K	kHz	2.4 (5)
Δ_c	uÅ^2	0.04906 (6)	0.0492 (2)	0.0507 (1)	0.0493 (1)	0.05303 (7)	d_1	kHz	-0.239 (9)
χ_{aa}	MHz	-	-	-	-	0.235 (5)	d_2	kHz	-0.086 (6)
χ_{bb}	MHz	-	-	-	-	-0.092 (7)	N		
χ_{cc}	MHz	-	-	-	-	-0.143 (7)	σ	kHz	41

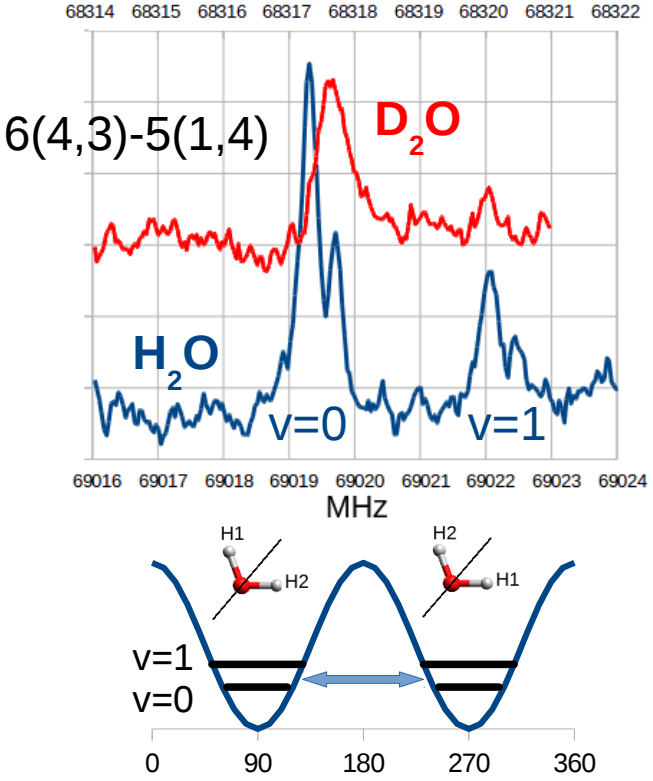




Acrylonitrile (vinyl cyanide) - water

MP2/6-311++G** results:

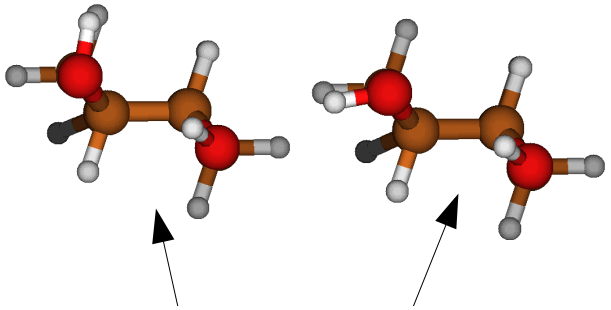
D_0=17.8 kJ/mol	D_0=15.5 kJ/mol	D_0=14.7 kJ/mol
		
A=5225 MHz	A=6669 MHz	A=27674 MHz
B=3517 MHz	B=2701 MHz	B=1241 MHz
C=2105 MHz	C=1924 MHz	C=1196 MHz

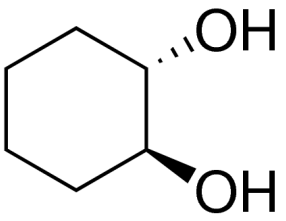


Experimental results:

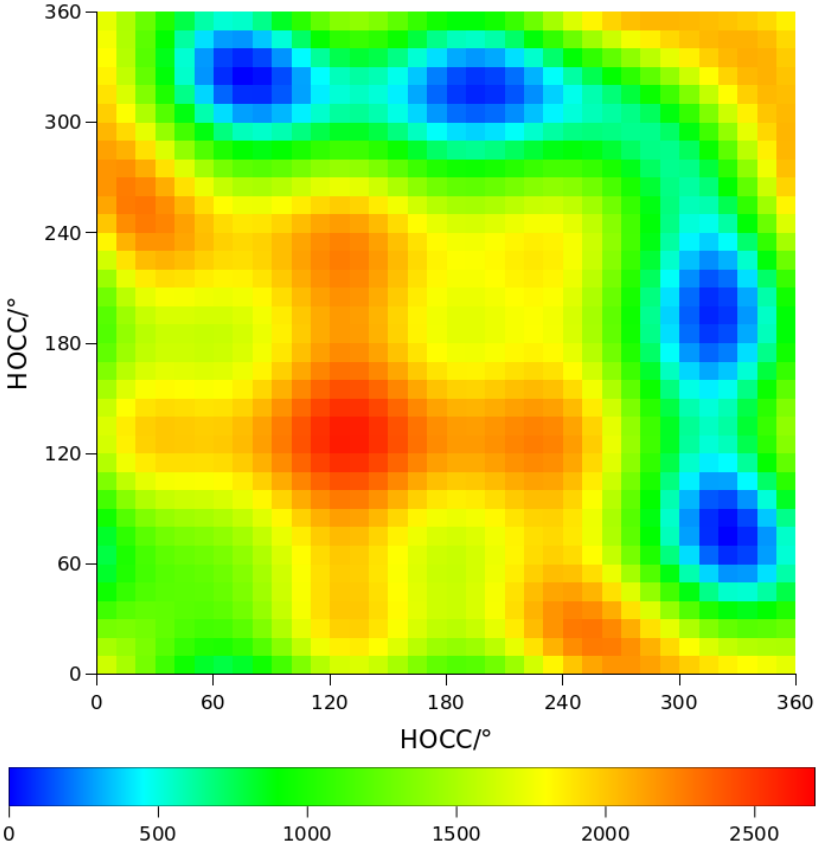
A_0=5282.022 (2) MHz	D_J=8.74 (1) kHz	χ_{aa}=-0.38 (10) MHz	M_{cc}=-0.12 uÅ² H_2O
B_0=3422.840 (3) MHz	D_{JK}=-4.00 (3) kHz	χ_{bb}=-1.47 (9) MHz	M_{cc}=-0.13 uÅ² $H_2{}^{18}OH$
C_0=2074.858 (4) MHz	D_K=15.79 (6) kHz	χ_{cc}=1.84 (9) MHz	M_{cc}=-0.08 uÅ² D_BOH_F
A_1=5282.195 (2) MHz	d_1=-4.089 (2) kHz		M_{cc}=-0.12 uÅ² D_2O
B_1=3422.986 (3) MHz	d_2=-0.758 (2) kHz		
C_1=2074.841 (4) MHz			

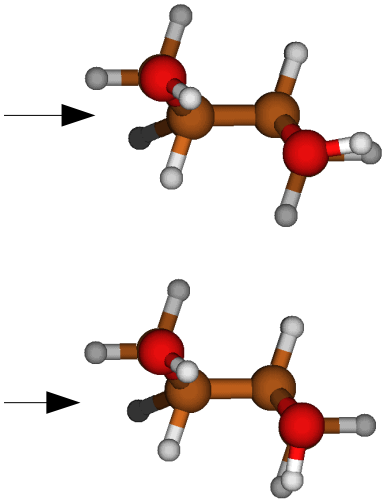
(1S,2S)-trans-1,2-Cyclohexanediol



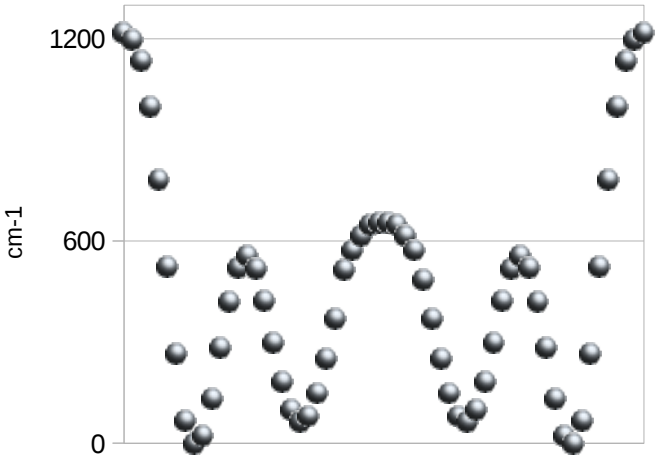


B3LYP/6-31G*
PES





ΔE01/MHz	1278.88 (4)
A0/A1 /MHz	2793.655/.671(1)
B0/B1 /MHz	1946.339/.307 (2)
C /MHz	1238.933 (4)
DJ /kHz	0.040 (9)
DJK /kHz	0.19(2)
DK /kHz	0.26 (1)
d1 /kHz	-0.056 (8)
d2 /kHz	0.011 (9)



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Uscendo: primo poster a destra

Organic and prebiotic molecules