

Table S3: Evolution of vibration-rotation interaction constants (in MHz) related to the three rotational constants as a function of the quantum number v for the vibrational states of 2-trans-FF analysed from hot bands.

Vibrational state	A	B	C
$V_{27}=1$	76.33	0.34	2.45
$V_{27}=2$	70.7	0.96	3.39
$V_{27}=3$	64.76	1.92	4.34
$V_{27}=4$	59.02	0.41	2.25
$V_{27}=5$	61.16	1.00	2.94
$V_{26}=1$	-13.98	-0.60	-1.08
$V_{26}=2$	-19.13	-2.75	-1.01
$V_{26}=1, V_{27}=1$	95.34	0.01	-2.58
$V_{26}=1, V_{27}=2$	72.08	0.91	-3.24
$V_{26}=1, V_{27}=3$	65.70	2.04	-4.26
$V_{25}=1$	14.86	1.05	-0.24
$V_{25}=1, V_{27}=1$	76.10	-0.48	-2.30
$V_{25}=1, V_{27}=2$	77.22	-1.97	-4.48

Table S4 : Comparison between calculated energy levels of trans- and cis-furfural up to 700 cm⁻¹ using MP2/AVTZ method and experimental ones derived from microwave and far-IR experiments (this work).

v	Trans-furfural			Cis-furfural		
	Calc. Energy levels	vexp (FIR) This work	vexp(mw)	Calc. Energy levels	vexp (FIR) This work	vexp (mw)
V ₂₇ =1	148.680	146.19761	146.25	129.806		127.86 ^a
V ₁₉ =1	203.178	203.13242	207.5	200.575		195
V ₂₆ =1	247.487	235.82428	235.9(a)	288.323	280.25936	280.2 ^a
V ₂₇ =2	304.061	291.43	292.5	259.728		255.72
V ₂₇ =1, V ₁₉ =1	355.526		353.75	331.493		322.86
V ₂₇ =1, V ₂₆ =1	395.585	381.59	382.15	417.072		
V ₁₉ =2	407.650		415	402.397		
V ₂₆ =1, V ₁₉ =1	447.044			488.966		
V ₂₇ =3	455.767	435.70		389.769		383.58
V ₂₆ =2	486.035	469.84		577.108		
V ₁₈ =1	491.608	462.3		490.601		
V ₂₇ =2, V ₁₉ =1	507.658					
V ₂₇ =2, V ₂₆ =1	546.927	526.29				
V ₂₇ =1, V ₁₉ =2	560.208					
V ₂₇ =4	607.258	579.04		519.926		
V ₂₅ =1	609.901	595.97994		610.038	595.9	
V ₁₉ =3	613.417			605.464		
V ₂₄ =1	635.170	622.6		654.513		
V ₂₇ =1, V ₁₈ =1	647.928			619.057		
V ₁₉ =1, V ₁₈ =1	695.164			691.332		
V ₂₆ =3	726.020	704.0				
V ₂₆ =1, V ₁₈ =1	735.924	694.3				

(a) Little et al⁶

Table S5 : Deviation ($\Delta = \text{exp} - \text{calc}$) of the rotational constants in the ground and excited states of trans- and cis-2-FF.

		Calculated	Experimental	$\Delta = \text{exp} - \text{calc}$	ES constants corrected from GS deviation ^a
Trans-2-furfural					
GS	A	8196.98	8191.7732	-5.207	
	B	2045.85	2045.9296	+0.080	
	C	1637.24	1637.1839	-0.056	
V ₂₇	A	8111.15	8115.4201	+4.270	+9.477
	B	2046.00	2045.5834	-0.417	-0.497
	C	1639.89	1639.6275	-0.262	-0.206
V ₁₉	A	8270.58	8248.4062	-22.174	-16.967
	B	2048.13	2047.6262	-0.504	-0.584
	C	1637.13	1636.9856	-0.144	-0.088
V ₂₆	A	8201.56	8205.7582	+4.198	+9.405
	B	2046.54	2046.5305	-0.009	-0.089
	C	1638.42	1638.2701	-0.150	-0.094
V ₂₅	A	8183.01	8176.9316	-6.08	-0.873
	B	2044.87	2044.8710	+0.001	-0.081
	C	1637.55	1637.4168	-0.133	-0.077
Cis-2-furfural					
GS	A	8148.14	8143.7387	-4.401	
	B	2098.52	2098.7242	+0.204	
	C	1668.84	1668.8730	+0.033	
V ₂₇	A	8077.86	8077.8111	-0.049	+4.352
	B	2099.39	2099.5761	+0.186	-0.018
	C	1671.99	1672.0478	+0.058	+0.025
V ₁₉	A	8211.80	8201.813	-9.987	-5.586
	B	2099.96	2100.0479	+0.088	-0.116
	C	1668.15	1668.1878	+0.038	+0.005
V ₂₆	A	8141.98	8139.1325	-2.847	+1.554
	B	2098.58	2098.7948	+0.215	+0.011
	C	1669.77	1669.8018	+0.032	-0.001

^a Corrected rotational constant values correspond to calculated ES constants corrected from the GS

deviation according to the following relation : $X_v^{\text{corr}} = \frac{X_v^{\text{calc}}}{X_{\text{GS}}^{\text{calc}}} X_{\text{GS}}^{\text{exp}}$

where X= A, B, C.