

Supplementary Information to accompany paper entitled ‘Near ultraviolet photolysis of deuterated pyrrole’ by Cronin *et al.*

Calculated (Gaussian03, 6-311G(d,p)) B3LYP harmonic and anharmonic wavenumbers for the fundamental modes of the C_{2v} optimised geometries of pyrrole-d₅ and the pyrrolyl-d₄ radical in their respective ground electronic states. (The layout of this table is chosen to emphasise the correlation between nuclear motions in the parent pyrrole-d₅ and the radical.)

Pyrrole-d ₅ X ¹ A ₁				Pyrrolyl-d ₄ X ² A ₂			
		Wavenumbers				Wavenumbers	
Mode	Symmetry	Harmonic	Anharmonic	Mode	Symmetry	Harmonic	Anharmonic
ν ₁	a1	2700.6	2576.6	ν ₁	a1	2421.6	2338.4
ν ₂	a1	2434.6	2359.9	ν ₂	a1	2369.8	2291.7
ν ₃	a1	2397.4	2312.6	ν ₄	a1	1379.8	1188.6
ν ₄	a1	1412.8	1382.2	ν ₃	a1	1490.5	1427.0
ν ₅	a1	1349.9	1321.0	ν ₅	a1	1097.8	1082.2
ν ₆	a1	1110.1	1082.7	ν ₇	a1	911.4	878.6
ν ₇	a1	924.4	913.0	ν ₆	a1	830.9	817.4
ν ₈	a1	793.2	782.5	ν ₈	a1	739.0	730.8
ν ₉	a1	743.4	739.7				
ν ₁₀	a2	740.9	732.4	ν ₉	a2	774.5	766.3
ν ₁₁	a2	550.5	544.9	ν ₁₀	a2	654.5	638.4
ν ₁₂	a2	516.4	504.6	ν ₁₁	a2	406.8	402.0
ν ₁₃	b2	2421.5	2346.6	ν ₁₂	b2	2381.2	2301.2
ν ₁₄	b2	2382.8	2301.6	ν ₁₃	b2	2356.9	2267.9
ν ₁₅	b2	1487.1	1458.0	ν ₁₄	b2	1212.7	1187.6
ν ₁₆	b2	1370.8	1332.4	ν ₁₅	b2	1040.8	1019.8
ν ₁₇	b2	1036.4	1019.1	ν ₁₆	b2	978.2	961.2
ν ₁₈	b2	904.0	890.1	ν ₁₈	b2	639.6	646.5
ν ₁₉	b2	817.1	803.9				
ν ₂₀	b2	777.9	768.4	ν ₁₇	b2	754.8	745.2
ν ₂₁	b1	688.0	679.6	ν ₁₉	b1	745.4	730.8
ν ₂₂	b1	574.4	570.1	ν ₂₀	b1	543.2	535.4
ν ₂₃	b1	510.6	499.2	ν ₂₁	b1	443.9	437.8
ν ₂₄	b1	368.4	365.1				

B3LYP harmonic and anharmonic wavenumbers for the fundamental modes of the pyrrolyl-d₄ radical resulting from Gaussian03 (6-311G(d,p)) and GAMESS (6-311G(d)) calculations. The % difference column gives an indication of the anharmonic correction; it shows the absolute difference between the calculated harmonic and anharmonic wavenumbers as a percentage of the calculated harmonic fundamental.

Pyrrolyl-d ₄ X ² A ₂							
Mode	Symmetry	Gaussian Wavenumbers			GAMESS Wavenumbers		
		Harmonic	Anharmonic	% Difference	Harmonic	PT2-VSCF	% Difference
ν ₁	a1	2421.6	2338.4	3.4	2412.6	2316.5	4.0
ν ₂	a1	2369.8	2291.7	3.3	2364.5	2272.2	3.9
ν ₄	a1	1379.8	1188.6	13.9	1386.5	1240.0	10.6
ν ₃	a1	1490.5	1427.0	4.3	1483.8	1474.9	0.6
ν ₅	a1	1097.8	1082.2	1.4	1101.8	1082.6	1.7
ν ₇	a1	911.4	878.6	3.6	920.1	881.2	4.2
ν ₆	a1	830.9	817.4	1.6	843.4	818.7	2.9
ν ₈	a1	739.0	730.8	1.1	746.1	745.4	0.1
ν ₉	a2	774.5	766.3	1.1	769.2	758.3	1.4
ν ₁₀	a2	654.5	638.4	2.5	651.0	659.0	1.2
ν ₁₁	a2	406.8	402.0	1.2	406.4	419.4	3.2
ν ₁₂	b2	2381.2	2301.2	3.4	2374.1	2272.9	4.3
ν ₁₃	b2	2356.9	2267.9	3.8	2349.7	2248.3	4.3
ν ₁₄	b2	1212.7	1187.6	2.1	1221.7	1199.4	1.8
ν ₁₅	b2	1040.8	1019.8	2.0	1043.3	1052.2	0.9
ν ₁₆	b2	978.2	961.2	1.7	989.2	975.3	1.4
ν ₁₈	b2	639.6	646.5	1.1	645.9	654.8	1.4
ν ₁₇	b2	754.8	745.2	1.3	767.5	777.1	1.3
ν ₁₉	b1	745.4	730.8	2.0	761.3	739.6	2.8
ν ₂₀	b1	543.2	535.4	1.4	539.4	544.7	1.0
ν ₂₁	b1	443.9	437.8	1.4	443.3	454.4	2.5

B3LYP harmonic and anharmonic wavenumbers for the fundamental modes of the C_{2v} optimised geometry of the pyrrolyl-d₄ radical in its ground electronic state were obtained with Gaussian03. The large anharmonic correction in ν₄ (~14%) was surprising and could not easily be explained by examining the nuclear motion involved in this vibration. Similar calculations were thus performed using the GAMESS package to check whether the result was an anomaly associated with the Gaussian code. Using GAMESS, the vibration still shows a large anharmonic correction (~11%) and the results from both methods match well for the harmonic and anharmonic calculations.