Supplementary material

Table S1: Spectroscopic constants of 4-nitroanisole determined experimentally and via quantum-chemical calculations. The value in square brackets was taken directly from calculations.

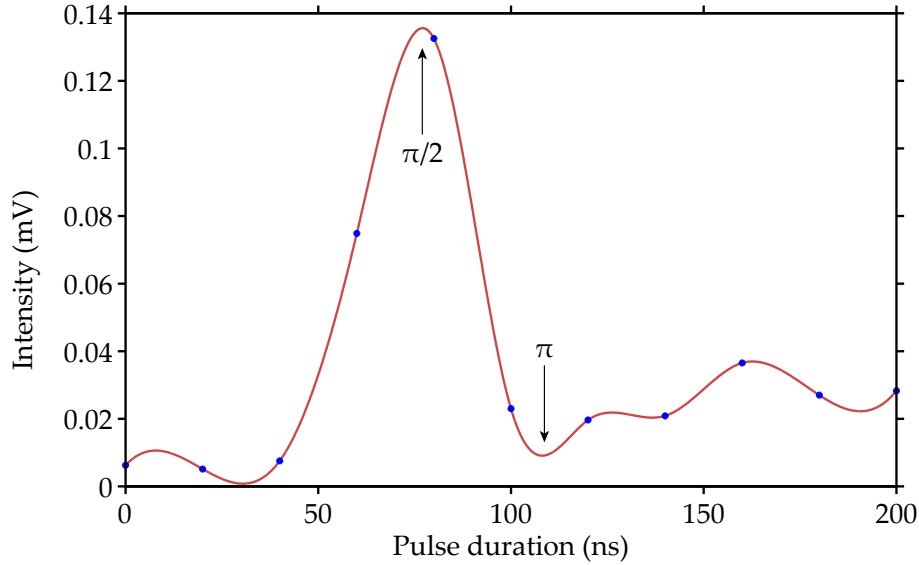| Parameter	Experiment	B3LYP/ aug-cc-pVTZ	B3LYP/ aug-cc-pVTZ (GD3BJ)	B3LYP/ def2-TZVP (GD3BJ)	MP2/ 6-311++G(d,p)
A (MHz)	3533.8097(5)	3565.90	3563.30	3565.43	3514.65
B (MHz)	587.03009(5)	586.25	588.15	588.07	584.66
C (MHz)	505.37812(5)	505.09	506.45	506.44	502.89
D_K (kHz)	0.33(8)	–	–	–	–
D_{JK} (kHz)	$-0.031(5)$	–	–	–	–
D_J (kHz)	0.006(1)	–	–	–	–
χ_{aa} (MHz)	$-1.164(2)$	-1.2409	-1.2494	-1.2813	-0.5915
χ_{bb-cc} (MHz)	$-0.569(3)$	-1.0179	-1.0172	-1.0495	1.3711
χ_{ab} (MHz)	$[-0.1145]$	-0.1145	-0.1168	-0.1200	-0.1336
μ_a (D)	–	6.15	6.14	6.09	5.45
μ_b (D)	–	0.78	0.78	0.78	0.92
μ_c (D)	–	0	0	0	0
N_{lines}	169	–	–	–	–
σ (kHz)	4.9	–	–	–	–

Figure S1: Nutation curve of the $2_{02} \leftarrow 1_{01}$ transition at 2183.17 MHz with a step-width of 20 ns. All pulses were amplified with the TWT amplifier at 100% gain. Both the π and $\pi/2$ pulse durations are also indicated in the plot.
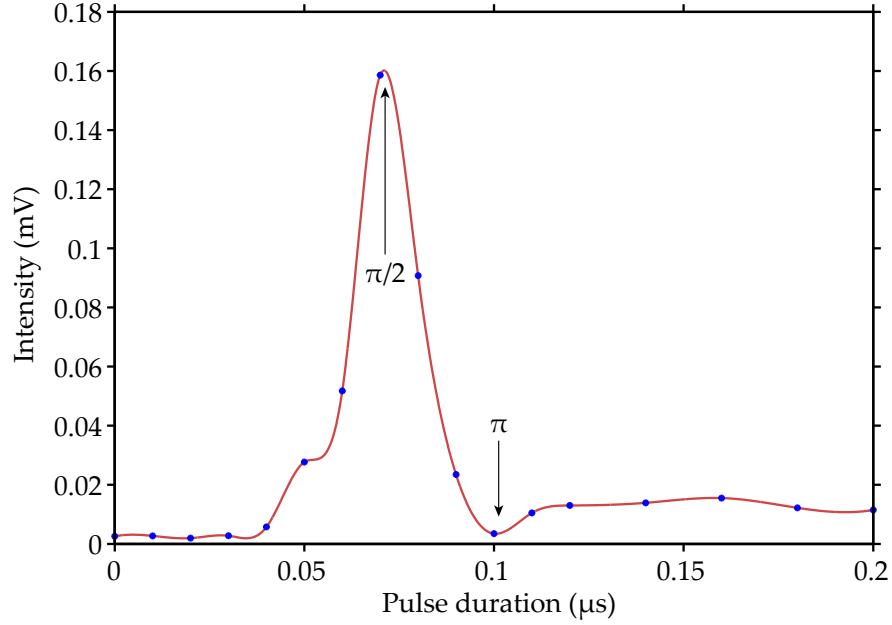
Figure S2: Nutation curve of the $2_{02} \leftarrow 1_{01}$ transition at 2183.17 MHz with a step-width of 10 ns until a pulse duration of 120 ns, then a 20 ns step-width thereafter. All pulses were amplified with the TWT amplifier at 100% gain. Both the π and $\pi/2$ pulse durations are also indicated in the plot.
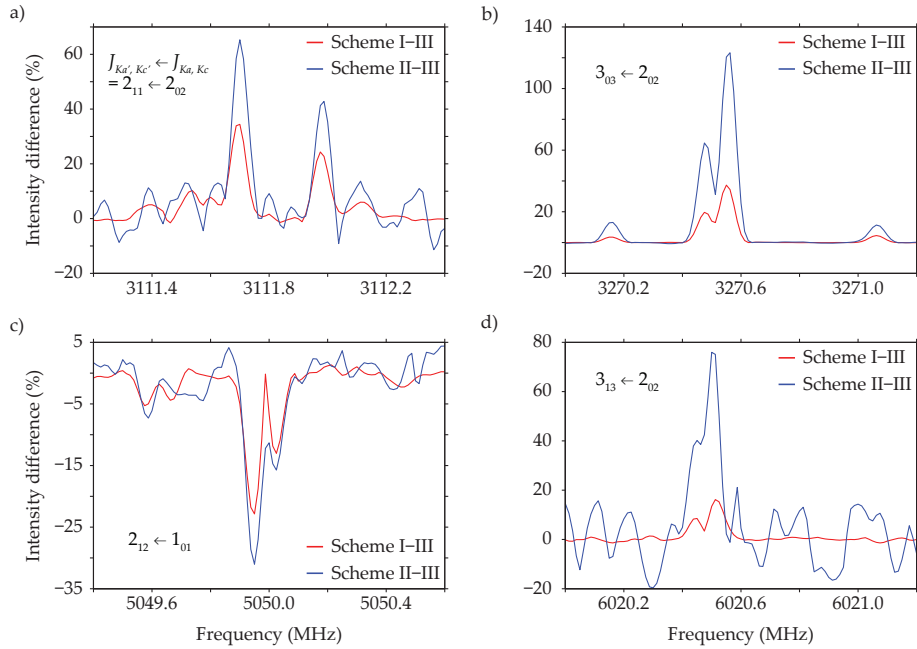

Figure S3: Percentage difference for each signal transition and the two different pulse schemes. Percentages determined by calculating intensity differences relative to the maximum intensity recorded using Scheme III alone.