

Supporting Information

Pseudorotation in pyrrolidine: rotational coherence spectroscopy and *ab initio* calculations of a large amplitude intramolecular motion

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I. Further details on the fitted simulation of fs DFWM spectra

The dependences of the required molecular properties on the pseudorotational angle were parametrized in the fitted simulation as follows. The potential function was characterized by three parameters: φ_{max} , the pseudorotational angle that corresponds to the barrier V_{max} and the energy difference ΔV_{ax-eq} between the axial ($\varphi=0^\circ$) and the equatorial ($\varphi=180^\circ$) conformers. These parameters were subsequently transformed into the three terms V_i (see equation (4) of the article). The pseudorotational constant B_p and centrifugal distortion constants Δ_J , Δ_{JK} were considered as being independent of the pseudorotational angle ϕ . The functions of the rotational constants A and B were parameterized by four equidistant points along the pseudorotational path: $R(0^\circ)$, $R(60^\circ)$, $R(120^\circ)$, $R(180^\circ)$, where $R=A,B$. Finally, the expansion terms R_n (equation (6) of the article) were calculated. Since the fs DFWM signal is highly insensitive to the rotational constant C , it was considered as being independent on the pseudorotational angle and fixed to the value of 3.895 GHz, which is an average of C constants of the axial and equatorial conformers taken from microwave spectroscopy.¹ This choice is also justified by the fact that the calculated dependence of the rotational constant C on the pseudorotational angle is, to a good approximation, a line that connects the values corresponded to the axial (0°) and equatorial (180°) forms. The dependence of the polarizability parameter φ on the pseudorotational angle was parameterized by two points $\varphi(0^\circ)$ and $\varphi(180^\circ)$. A depletion of the signal with time due to molecular collisions was treated by a single exponential decay. The populations of the pseudorotational and rotational levels under supersonic expansion were described by means of vibrational and rotational temperatures.

The fitting procedure is based on the Differential Evolution minimization algorithm developed by R. Storn and K. Price.² The algorithm is thought to be applicable for finding the global minimum of the chi-square function. The MINUIT optimization package³ was further used for the final precise optimization in the global minimum region.

The fitted parameters from the simulation of the fs-DFWM spectrum of pyrrolidine at room temperature are collected in Table S1.

Table S1 The fitted parameters of the simulation of the fs DFWM spectrum of PYR at room temperature with consideration of PR.

$\phi_{max}/^\circ$	94.5(2)	$\varphi(0^\circ)/\text{grad}$	0.6(3)	$A(0^\circ)/\text{GHz}$	6.835(4)	$B(0^\circ)/\text{GHz}$	6.678(4)
V_{max}/cm^{-1}	220(20)	$\varphi(180^\circ)/\text{grad}$	-0.01(20)	$A(60^\circ)/\text{GHz}$	6.828(4)	$B(60^\circ)/\text{GHz}$	6.729(4)
$\Delta V_{ax-eq}/\text{cm}^{-1}$	29(10)	Δ_J/kHz	1.18(20)	$A(120^\circ)/\text{GHz}$	6.840(4)	$B(120^\circ)/\text{GHz}$	6.793(4)
B_p/cm^{-1}	3.8(1)	Δ_{JK}/kHz	-0.5(6)	$A(180^\circ)/\text{GHz}$	6.870(4)	$B(180^\circ)/\text{GHz}$	6.786(4)

II. Dependence of the maximum pseudorotational amplitude q on the pseudorotational angle ϕ

The maximum amplitude q and the pseudorotational angle ϕ (see equation (3) of the article) were calculated⁴ from the geometries optimized by the STQN method^{5,6} using the aug-cc-pVD(T)Z basis sets at B3LYP and MP2 levels of theory. The dependences of q on the pseudorotational angle ϕ are shown in Fig. S1. The calculations at both B3LYP and MP2 levels of theory indicate the equatorial conformer to have the largest puckering amplitude. The puckering amplitudes calculated at the MP2 level of theory are systematically larger than the ones calculated with the B3LYP method.

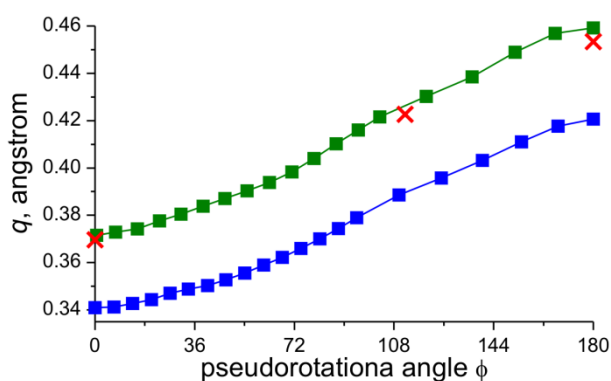


Fig. S1 Dependence of the pseudorotational amplitude q on the pseudorotational angle ϕ : blue – B3LYP/aug-cc-pVDZ, green – MP2/aug-cc-pVDZ, red crosses – MP2/aug-cc-pVTZ

III. The energy difference between the axial and equatorial conformers of pyrrolidine calculated with different methods and basis sets

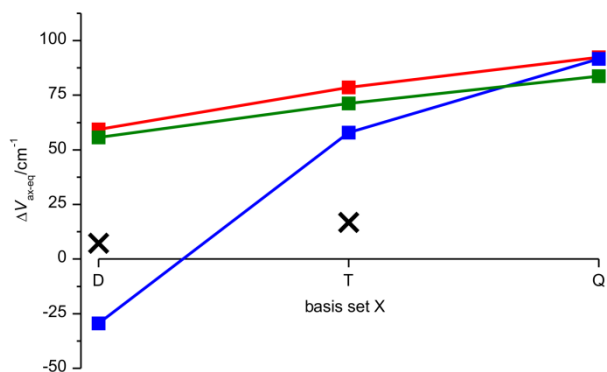


Fig. S2 Dependence of the energy difference between the axial and equatorial conformers on a basis set at the MP2 level of theory: blue – cc-pCVXZ, red – aug-cc-pCVXZ, green – aug-cc-pVXZ . The values calculated at CCSD(T) level of theory with aug-cc-pVXZ are shown by black crosses.

IV. The experimental and calculated rotational constants of the axial and equatorial conformers of pyrrolidine

Table S2 The experimental and calculated rotational constants (GHz) of the axial and equatorial conformers of pyrrolidine

	axial			equatorial		
	<i>A</i>	<i>B</i>	<i>C</i>	<i>A</i>	<i>B</i>	<i>C</i>
microwave ¹	6.834536(8)	6.677856(8)	3.888062(8)	6.864704(6)	6.791908(5)	3.9004(42)
this work (cell)	6.835(4)	6.682(4)	- ^a	6.866(4)	6.787(4)	- ^a
HF/aug-cc-pVDZ						
harm. ^b	6.880	6.756	3.909	6.918	6.853	3.912
anharm. ^b (0K)	6.807	6.687	3.867	6.859	6.803	3.870
MP2/aug-cc-pVXZ						
X=D/harm. ^b	6.799	6.629	3.872	6.835	6.752	3.898
X=D/anharm. ^b (0K)	6.725	6.556	3.825	6.756	6.681	3.852
X=T	6.901	6.728	3.928	6.935	6.851	3.950
X=Q	6.924	6.752	3.941	6.958	6.875	3.962
MP2/aug-cc-pCVXZ						
X=D	6.824	6.650	3.887	6.858	6.772	3.912
X=T	6.927	6.756	3.944	6.963	6.878	3.965
X=Q	6.953	6.783	3.958	6.987	6.906	3.979
CCSD(T)/aug-cc-pVDZ						
harm.	6.751	6.587	3.842	6.786	6.701	3.863

^a – rotational constant *C* was fixed in the fit to the value of 3.895 GHz.

^b – harm./anharm. means that the rotational constants were **not corrected/corrected** for anharmonic effects.

V. SCRF calculations of the pseudorotational pathway of PYR

21 points along the pseudorotational path of PYR were optimized in the presence of solvent like water (SCRF method⁶) using the STQN approach at B3LYP/aug-cc-pVDZ. It is shown in Fig. S3. In contrast to the isolated pyrrolidine molecule, the presence of the polar solvent stabilizes the axial conformer.

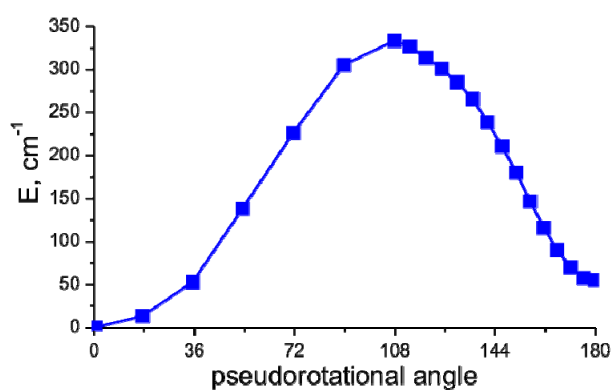


Fig. S3 Pseudorotational potential of PYR in the presence of solvent like water (SCRF B3LYP/aug-cc-pVDZ).

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