

UV Resonance Raman Investigation of the Aqueous Solvation Dependence of Primary Amide Vibrations

Supporting Information

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X-ray Crystal Structure of Propanamide

X-ray crystal diffraction was performed using a Bruker X8 Prospector Ultra equipped with a copper micro-focus tube ($\lambda = 1.54178 \text{ \AA}$). A propanamide crystal specimen with approximate dimensions of 0.020 mm x 0.090 mm x 0.110 mm was used for structure determination. The crystal was mounted and placed in a cold N_2 stream ($\sim 230 \text{ K}$) for data collection. Crystals were not well-formed, showing diffuse diffraction spots; however, we were able to determine a unit cell and solve a crystal structure.

The frames were integrated with the Bruker SAINT software package. The integration of the data using a monoclinic unit cell yielded a total of 2212 reflections to a maximum θ angle of 68.09° (0.83 \AA resolution), of which 689 were independent (average redundancy 3.210, completeness = 83.5%, $R_{int} = 8.52\%$, $R_{sig} = 7.03\%$) and 364 (52.83%) were greater than $2\sigma(F^2)$.

The final cell constants (Table S1) of $a = 8.851(4) \text{ \AA}$, $b = 5.750(2) \text{ \AA}$, $c = 9.766(3) \text{ \AA}$, $\beta = 114.780(15)^\circ$, volume = $451.3(3) \text{ \AA}^3$, are based upon the refinement of the XYZ-centroids of reflections above $20 \sigma(I)$. Unit-cell parameters and analysis of systematic absences indicated propanamide crystallized in a $\text{P2}_1/c$ space group.

The structure (Figure S1) was solved via direct methods, which located all of the non-hydrogen atoms. Idealized atom positions were calculated for all hydrogen atoms, except for NH_2 hydrogen atoms (see Tables S2-S6). The final anisotropic least-squares refinement on F^2 converged at $R1 = 9.53\%$, for the observed data and $wR2 = 24.72\%$ for all data, and the goodness-of-fit was 1.304. The final Fourier map contained no significant residual electron density.

Deconvolution of UVRR Spectra

UVRR spectra of propanamide in different acetonitrile and water mixtures were deconvoluted into a sum of a minimum number of Gaussian or Lorentzian bands on a linear background using the GRAMS/AI 8.0 software suite (Thermo Fisher). Figures S2 and S3 show the deconvolution of the 204 nm excitation UVRR spectra of propanamide in pure acetonitrile and pure water.

Table S 1: Summary of Crystallographic Data for CH₃CH₂CONH₂

Molecular formula	C ₃ H ₇ NO
Temperature (K)	230(2)
Wavelength (Å)	1.54178
Theta range (°)	9.18-68.09
Cell setting	monoclinic
Space group	P2 ₁ /c
a (Å)	8.851(4)
b (Å)	5.750(2)
c (Å)	9.766(3)
α (°)	90
β (°)	114.780(15)
γ (°)	90
V (Å ³)	451.259
Z	4
Calc. density (g·cm ⁻³)	1.076
R1	0.0953
wR2	0.2472

Table S 2: Atomic Coordinates and Equivalent Isotropic Atomic Displacement Parameters (\AA^2)

	x/a	y/b	z/c	U(eq)
O9	0.6355(5)	0.7687(5)	0.6186(3)	0.1029(15)
N10	0.6057(7)	0.8705(7)	0.3890(4)	0.0958(16)
C1	0.8330(8)	0.3790(10)	0.6341(7)	0.120(2)
C2	0.7834(9)	0.5471(11)	0.5093(6)	0.121(2)
C6	0.6678(7)	0.7373(7)	0.5094(5)	0.0867(16)

Table S 3: Anisotropic Atomic Displacement Parameters (\AA^2)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O9	0.166(3)	0.095(2)	0.0723(19)	0.0141(14)	0.075(2)	0.0239(18)
N10	0.159(4)	0.084(3)	0.067(2)	0.004(2)	0.069(3)	0.014(3)
C1	0.152(6)	0.092(3)	0.116(4)	0.007(3)	0.055(4)	0.018(3)
C2	0.169(6)	0.121(4)	0.098(4)	0.022(3)	0.080(4)	0.047(4)
C6	0.135(4)	0.072(3)	0.070(2)	0.002(2)	0.060(3)	0.004(2)

Table S 4: Comparison of Bond Lengths (\AA) Between the DFT-optimized and X-ray Crystal Structure

	Crys. Struc.	DFT Calc.
r(C6=O9)	1.228(6)	1.223
r(C6-N10)	1.315(5)	1.353
r(C6-C2)	1.498(8)	1.519
r(C2-C1)	1.470(8)	1.521
r(C1-H3)	0.97	1.090
r(C1-H4)	0.97	1.091
r(C1-H5)	0.97	1.091
r(C2-H7)	0.98	1.095
r(C2-H8)	0.98	1.093
r(N10-H11)	0.83(5)	1.007
r(N10-H12)	0.97(6)	1.008

Table S 5: Comparison of Torsion Angles ($^{\circ}$) Between the DFT-optimized and X-ray Crystal Structure

	Crys. Struc.	DFT Calc.
τ (N10C6C2C1)	-171.5(5)	169.60
τ (O9C6C2C1)	9.8(7)	-10.89
τ (H12N10C6O9)	-16(4)	-2.69
τ (H12N10C6C2)	166(4)	176.83
τ (H11N10C6O9)	-176(3)	-178.79
τ (H11N10C6C2)	5(3)	0.72
τ (H5C1C2H8)	-56.4	-58.32
τ (H5C1C2H7)	59.5	59.54
τ (H5C1C2C6)	-178.4	179.58
τ (H3C1C2H8)	-176.4	-178.37
τ (H3C1C2H7)	-60.4	-60.51
τ (H3C1C2C6)	61.6	59.54
τ (H4C1C2H8)	63.6	61.64
τ (H4C1C2H7)	179.6	179.50
τ (H4C1C2C6)	-58.4	-60.46
τ (H8C2C6O9)	-112.2	-134.50
τ (H8C2C6N10)	66.5	-45.99

Table S 6: Comparison of Bond Angles ($^{\circ}$) Between the DFT-optimized and X-ray Crystal Structure

	Crys. Struc.	DFT Calc.
$\theta(\text{H12N10H11})$	121(4)	118.56
$\theta(\text{H12N10C6})$	118(3)	119.60
$\theta(\text{H11N10C6})$	118(3)	121.73
$\theta(\text{H5C1H3})$	109.4	108.43
$\theta(\text{H5C1H4})$	109.5	108.32
$\theta(\text{H5C1C2})$	109.5	110.17
$\theta(\text{H3C1H4})$	109.5	107.97
$\theta(\text{H3C1C2})$	109.5	110.90
$\theta(\text{H4C1C2})$	109.5	110.17
$\theta(\text{C1C2H8})$	108.2	111.15
$\theta(\text{C1C2H7})$	108.2	110.72
$\theta(\text{C1C2C6})$	116.5(5)	112.88
$\theta(\text{H8C2H7})$	107.3	106.26
$\theta(\text{H8C2C6})$	108.2	108.44
$\theta(\text{H7C2C6})$	108.2	107.09
$\theta(\text{O9C6N10})$	121.9(4)	122.07
$\theta(\text{O9C6C2})$	121.1(4)	122.91
$\theta(\text{N10C6C2})$	117.0(4)	115.02

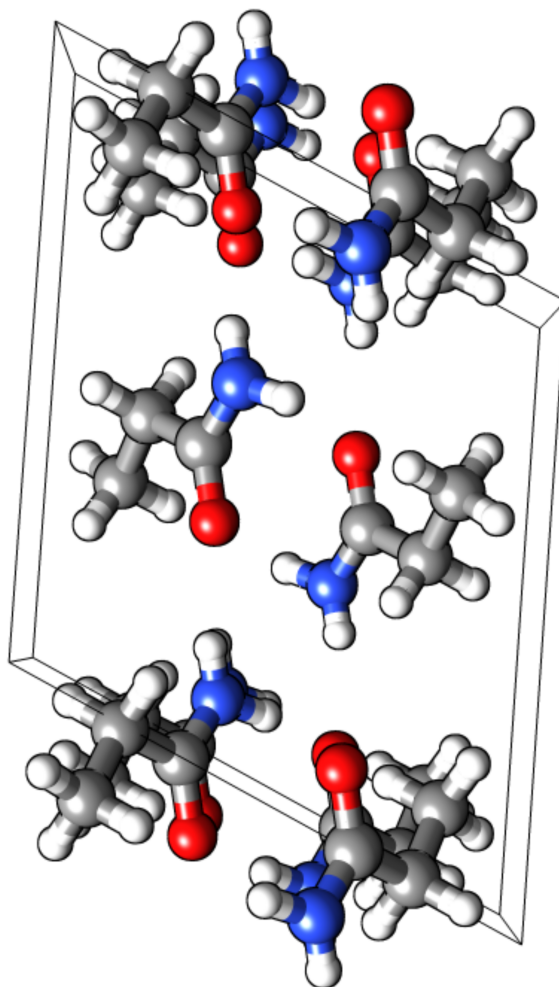


Figure S 1: Crystal structure of propanamide.

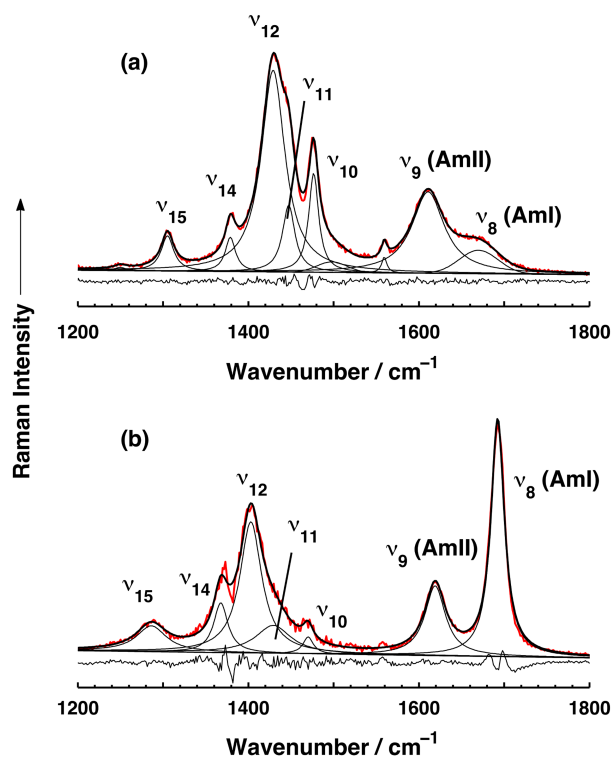


Figure S 2: Spectral deconvolution of the 204 nm UVRR spectrum of propanamide in (a) water and (b) acetonitrile in the region from 1200-1800 cm⁻¹.

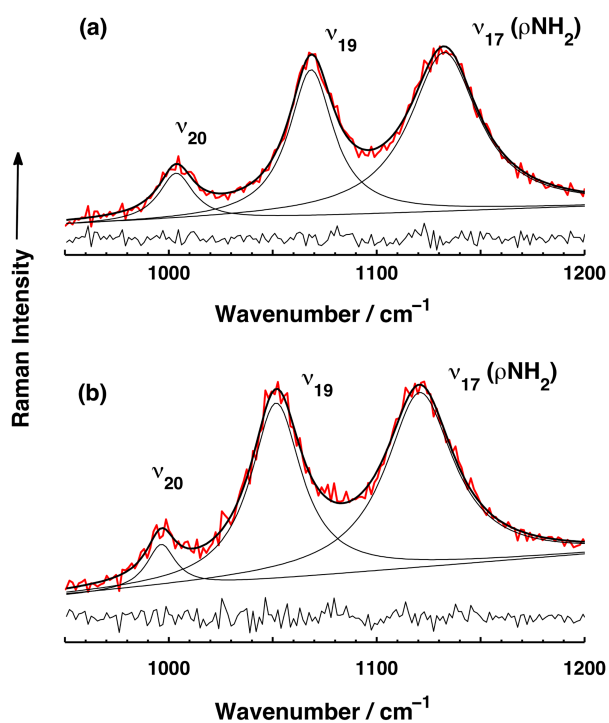


Figure S 3: Spectral deconvolution of the 204 nm UVRR spectrum of propanamide in (a) water and (b) acetonitrile in the region from 800-1200 cm⁻¹.