Protein Side Chain Absorptions in the Infrared Finger Print Region

Excerpted from: Lauren DeFlores, *Multi-mode Vibrational Spectroscopy of Peptides and Proteins,* Ch. 6 (PhD Thesis, Massachusetts Institute of Technology, 2008)

See also:

Andreas Barth and Christian Zscherp, "What vibrations tell us about proteins," *Quarterly Reviews of Biophysics* **35** (2002) 369–430

Andreas Barth, "The infrared absorption of amino acid side chains," *Progress in Biophysics & Molecular Biology* **74** (2000) 141–173

Table 1. Extinction coefficients and peak frequencies of amino acids that absorb between 1200 cm^{-1} and 1800 cm^{-1} in H_2O and D_2O. Frequencies are tabulated as a function of pH relative to the pK_a value determined from the isolated amino acid. For vibrations with no pH dependence appear in the central column.

Table 1a. Side Chain Absorptions in H_2O

Amino Acid	cm^{-1} (H_2O) < pK_s low pH		cm^{-1} (H_2O)		cm^{-1} (H_2O) > pK_s high pH		Mode	pK_s
Arginine ARG R	460	1652	-	-	-	-	$\nu_{as}CN_3H_5^+$	11.6 - 12.6
	320	1630	-	-	-	-	$\nu_{s}CN_3H_5^+$	
Aspartic Acid ASP D	-	-	280	1716			$\nu C{=}O$	4.0 - 4.8
	-	-	-	-	235	1577	$\nu_{as}COO^-$	
	-	-	-	-	256	1402	$\nu_{s}COO^-$	
	-	-	-	1375	-	-	$\delta_{s}CH_3$	
Asparagine ASN N	-	-	320	1677	-	-	$\nu C{=}O$	
	-	-	150	1617	-	-	δNH_2	
Cysteine CYS C	-	-	-	2551	-	-	νSH	9.0-9.5
Glutamic Acid GLU E	-	-	220	1712		-	$\nu C{=}O$	4.4 - 4.6
	-	-	-	-	460	1558	$\nu_{as}COO^-$	
	-	-	-	-	316	1404	$\nu_{s}COO^-$	
Glutamine GLN Q	-	-	370	1680	-	-	$\nu C{=}O$	
	-	-	230	1595	-	-	δNH_2	
	-	-	-	1410	-	-	νCN	
Histindine HIS H	250	1631	-	-	-	-	$\nu C{=}C$ (H_2^+)	6.0-7.0
	70	1575, 1594	-	-	-	-	$\nu C{=}C$ (H)	
	-	-	-	-	-	1439	δCH_3, νCN ($^-$)	
Lysine LYS K	80	1626	-	-	-	-	$\delta_{as}NH_3^+$	10.4-11.1
	85	1526	-	-	-	-	$\delta_{s}NH_3^+$	
Phenylalanine PHE F	-	-	80	1494	-	-	νCC ring	
	-	-	-	1460	-	-	$\delta_{as}CH_3$	
Proline PRO P	-	-	-	1432	-	-	νCN	
	-	-	-	1450	-	-	δCH_2	
Tryptophan TRP W	-	-	-	1622	-	-	νCC, $\nu C{=}C$	
	-	-	-	1509	-	-	νCN, δCH, δNH	
	-	-	-	1496	-	-	νCC, δCH	
	-	-	-	1462	-	-	δCH, νCC, νCN	
	-	-	-	1427	-	-	dNH, νCC, δCH	
Tyrosine TYR Y	120	1617	-	-	-	-	νCC, νCH	9.8 - 10.4
	85	1598	-	-	160	1601	νCC	
	385	1515	-	-	-	-	νCC, δCH	
	-	-	-	-	700	1499	νCC, δCH	
	-	-	-	-	580	1270	νCO, δCC	
	200	1250	-	-	-	-	νCO, δCC	

Table 1b. Side Chain Absorptions in D_2O

Amino Acid	cm^{-1} (D_2O) <pK_s low pH		cm^{-1} (D_2O)		cm^{-1} (D_2O) > pK_s high pH		Mode	pK_s (pH)
Arginine ARG R	460	1605	-	-	-	-	$\nu_{as}CN_3D_5^+$	11.6 - 12.6
	500	1586	-	-	-	-	$\nu_{s}CN_3D_5^+$	
Aspartic Acid ASP D	-	-	290	1713	-	-	$\nu C{=}O$	4.0 - 4.8
	-	-	-	-	820	1584	$\nu_{as}COO^-$	
	-	-	-	-	-	1404	$\nu_{s}COO^-$	
Asparagine ASN N	-	-	570	1648	-	-	$\nu C{=}O$	
Cysteine CYS C	-	-	-	1849	-	-	νSD	9.0-9.5
Glutamic Acid GLU E	-	-	280	1706	-	-	$\nu C{=}O$	4.4 - 4.6
	-	-	-	-	830	1567	$\nu_{as}COO^-$	
	-	-	-	-	-	1407	$\nu_{s}COO^-$	
Glutamine GLN Q	-	-	550	1640	-	-	$\nu C{=}O$	
	-	-	-	1163	-	-	δND_2	
	-	-	-	1409	-	-	νCN	
Histindine HIS H	35	1600	-	-	-	-	$\nu C{=}C$ (D_2^+)	6.0-7.0
	70	1569, 1575	-	-	-	-	$\nu C{=}C$ (D)	
	-	-	-	-	-	1439	δCD_3, νCN ($^-$)	
Lysine LYS K	-	1200	-	-	-	-	$\delta_{as}ND_3^+$	10.4-11.1
	-	1170	-	-	-	-	$\delta_{s}ND_3^+$	
Tryptophan TRP W	-	-	-	1618	-	-	νCC, $\nu C{=}C$	
	-	-	200	1455	-	-	δCD, νCC, νCN	
	-	-	-	1382	-	-	δND, νCC, δCD	
Tyrosine TYR Y	160	1615	-	-	-	-	νCC, νCD	9.8 - 10.4
	50	1590	-	-	350	1630	νCC	
	500	1515	-	-	-	-	νCC, δCD	
	-	-	-	-	650	1499	νCC, δCD	
	150	1255	-	-	-	-	νCO, δCC	

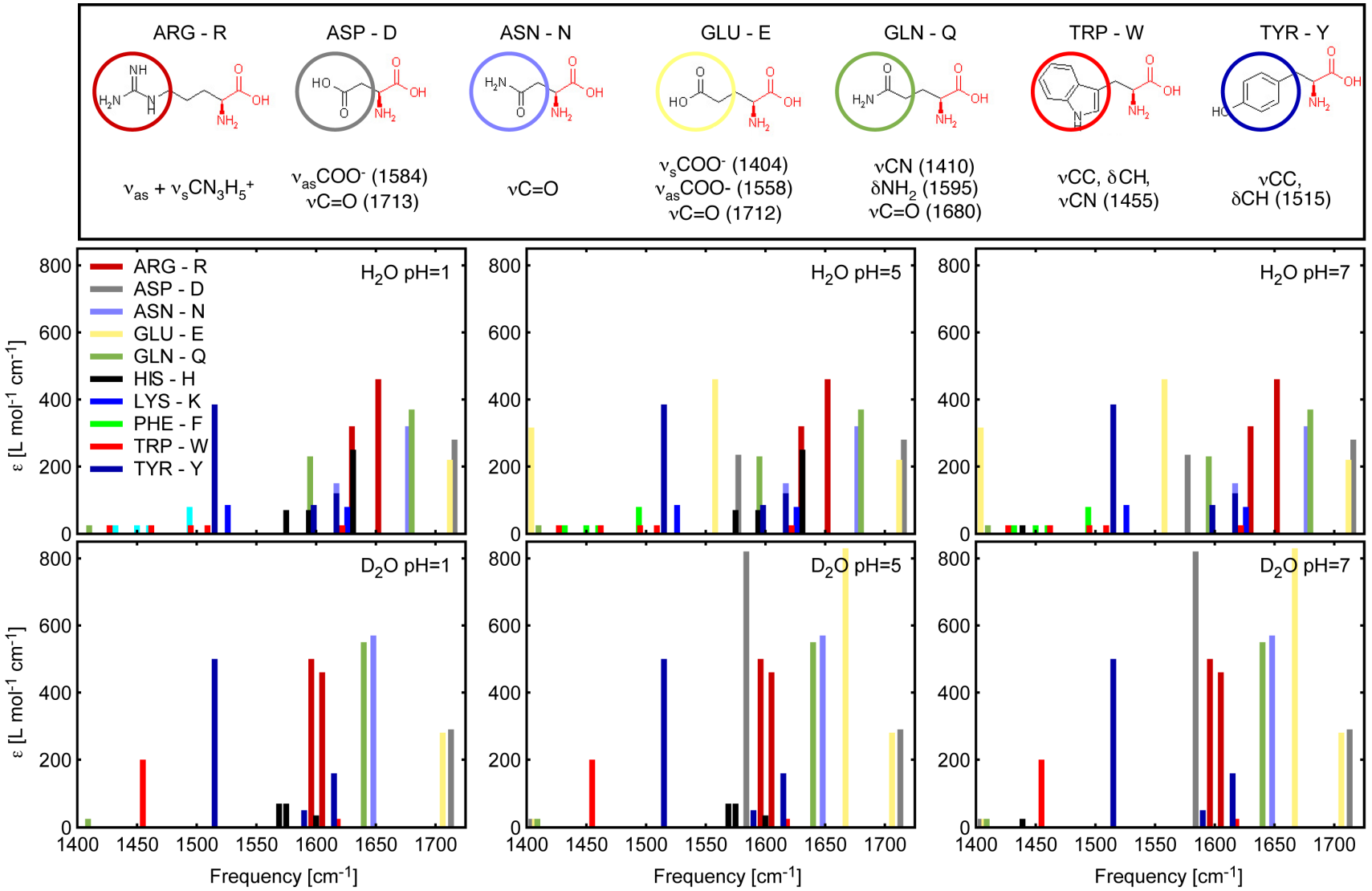

Figure 1. (Top) Atomic structures of predominant side chains in the amide finger region. (Bottom) Stick plots of side chain absorption from Table 1 in the amide finger print region as a function of solvent and pH. Major changes occur due to the protonation state of ASP, GLU and HIS. Isotopic sensitivity of the vibrational absorption is seen in TRP, ARG, GLU and ASP.