Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

A conformation selective IR-UV study of dipeptides Ac-Phe-Ser-NH_2 and Ac-Phe-Cys-NH_2: probing the SH···O and OH···O hydrogen bond strengths

Supporting Information

Bin Yan, Sander Jaeqx, Wim J. van der Zande and Anouk M. Rijs*

Radboud University Nijmegen, Institute for Molecules and Materials, FELIX Facility,

Toernooiveld 7, 6525 ED Nijmegen, The Netherlands.

*E-mail: a.rijs@science.ru.nl

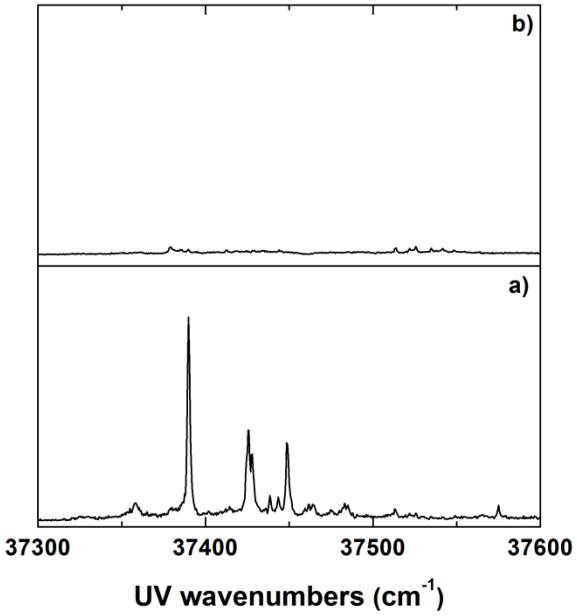

Fig. SI-1 REMPI spectrum of Ac-Phe-Ser-NH_2 (panel a) and IR-UV hole burning spectra (panel b, scanning UV wavelength while IR burning laser is fixed at any vibrational frequency of the 5 modes showed in Fig. 3A). All REMPI signal is depleted, indicating that they originate from the same conformer.

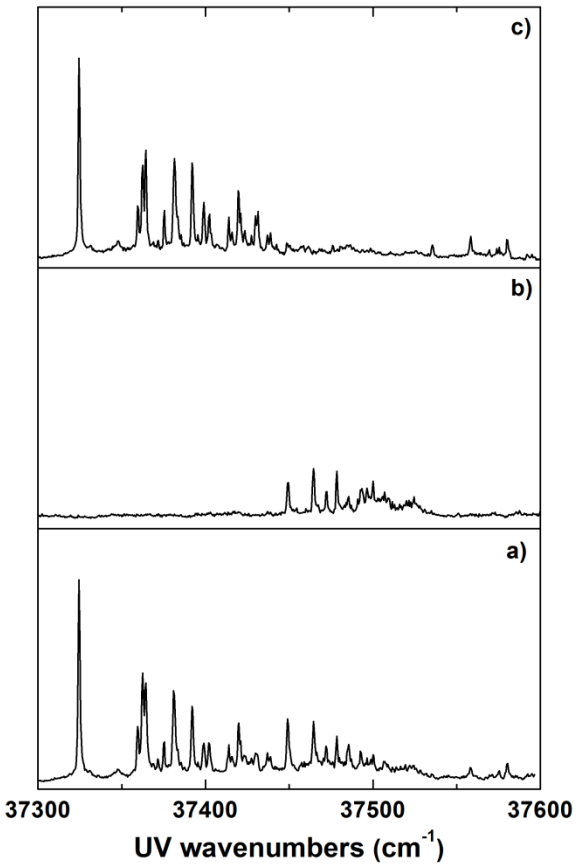

Fig. SI-2 REMPI spectrum of Ac-Phe-Cys-NH_2 (panel a) and IR-UV hole burning spectra (Scanning UV wavelength while IR burning laser is fixed at 3362 cm^{-1} for panel b and 3395 cm^{-1} for panel c). In panel b (or c), REMPI peaks originate from the same conformer are depleted.

Table SI-1 Relative Electronic Energies (Eelec), Zero-point corrected Energies (ZPE) and Gibbs Free Energies at 300 K (ΔG) in kcal/mol for the five lowest energy Structures of Ac-Phe-Cys-NH_2 and Ac-Phe-Ser-NH_2

	B97D			B3LYP		
	E_{elec}	ZPE	ΔG	E_{elec}	ZPE	ΔG
FC1	0.00	0.00	0.00	0.27	0.32	0.43
FC2	0.60	0.57	1.18	0.66	0.60	0.59
FC3	0.78	0.88	1.88	2.09	2.00	2.06
FC4	1.64	1.64	1.20	0.00	0.00	0.00
FC5	1.82	1.86	2.23	1.69	1.80	2.12
FS1	0.00	0.00	0.00	0.00	0.00	0.00
FS2	1.27	1.41	0.93	0.06	0.29	0.38
FS3	2.08	1.98	1.45	2.17	2.08	2.01
FS4	3.37	3.18	2.17	1.66	1.58	1.62
FS5	4.61	4.28	2.55	1.81	1.72	0.85

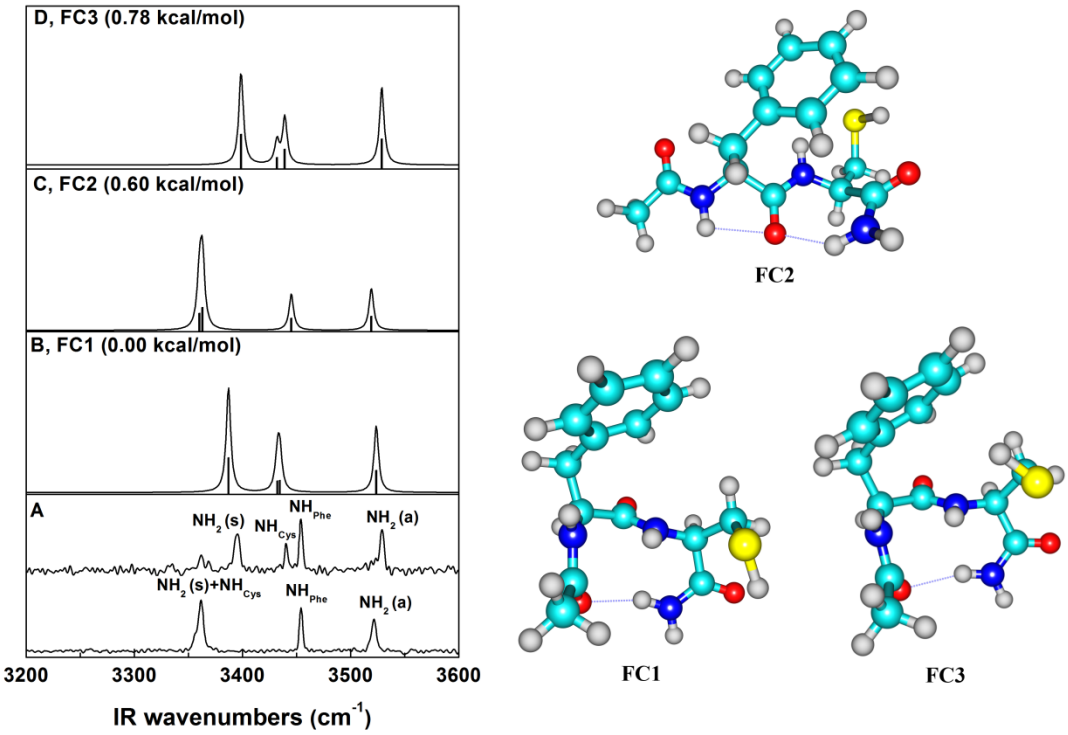

Fig. SI-3 IR-UV ion dip spectra of FC (panel A) and the theoretical spectra of three lowest energy structures (panel B-D), calculated at the B97-D/6-311+G(d,p) level of theory. The frequencies of theoretical spectra are corrected by mode-dependent scaling factors. FC2 in β_L-γ_L type is assigned to the prominent conformer (bottom trace in panel A) while FC3 in β-turn type is assigned to the minor conformer (top trace in panel A) according to the spectra matching. Lowest energy structure FC1 is not observed probably because it is converted to the similar one FC3 during supersonic expansion since they only differs with each other in the direction of SH group.