

**Supporting information for:**

The role of amino acid side chains in stabilizing dipeptides: The  
laser ablation Fourier transform microwave spectrum of Ac-Val-  
NH<sub>2</sub>

I. León,<sup>a</sup> E. R. Alonso,<sup>a</sup> S. Mata,<sup>a</sup> C. Cabezas,<sup>a</sup> M. A. Rodríguez,<sup>a</sup> J. U. Grabow,<sup>b</sup> and J. L. Alonso<sup>\*a</sup>

<sup>a</sup>Grupo de Espectroscopía Molecular (GEM), Edificio Quifima, Laboratorios de Espectroscopia y Bioespectroscopia, Unidad Asociada CSIC, Parque Científico UVA, Universidad de Valladolid, 47011 Valladolid, Spain.

<sup>b</sup>Institut für Physikalische Chemie und Elektrochemie, Lehrgebiet A, Gottfried-Wilhelm-Leibniz-Universität, Callinstrasse 3A, D-30167 Hannover, Germany.

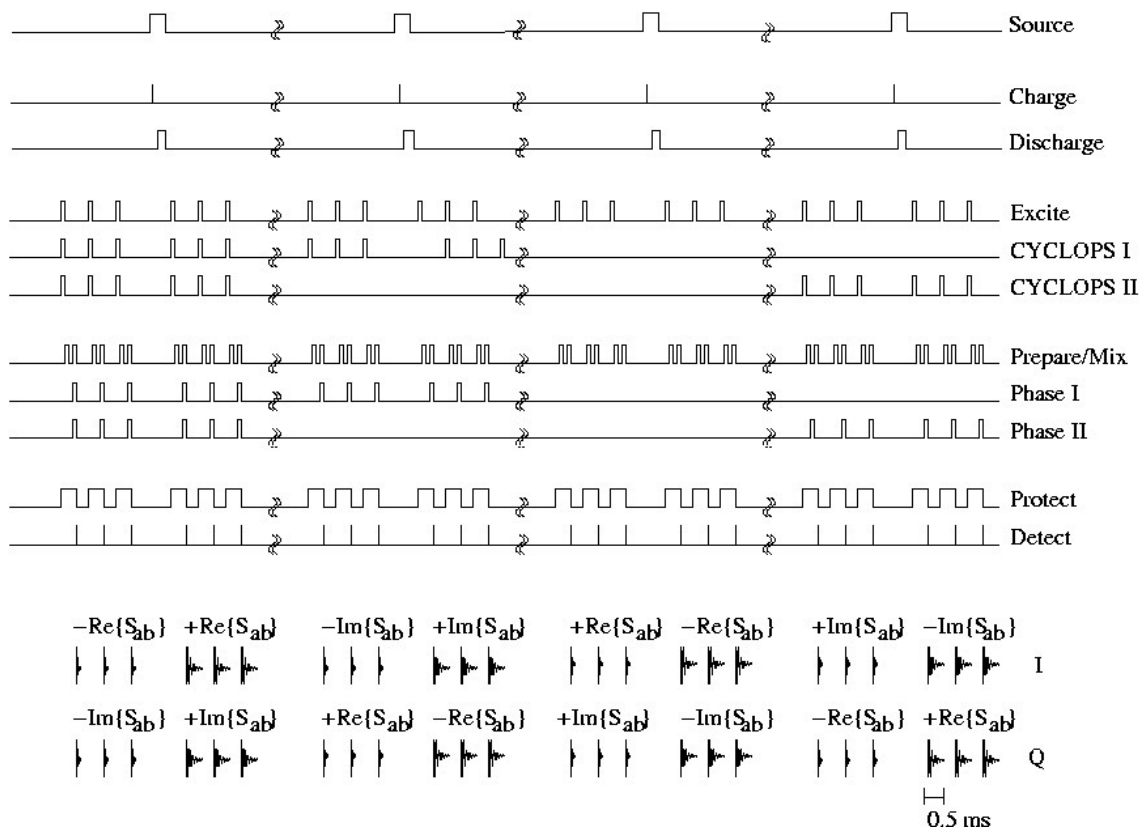
\*Corresponding Author:

Jose Luí­s Alonso, [jlalonso@qf.uva.es](mailto:jlalonso@qf.uva.es)

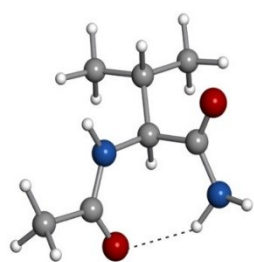
phones: +34 983 186344 / +34 983 186349

web: <http://www.gem.uva.es/>

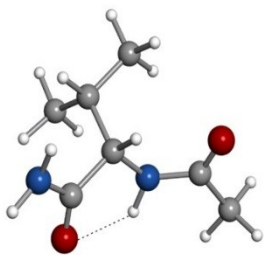
**Fig. S01** The pulse sequence depicted in Fig. S01 is generated using a 32-bit counter sourced by a 20 MHz or a 100 kHz base clock, depending on the required pulse duration. The clock of the A/D conversion is phase-stabilized to a 10 MHz base clock. The signal of a 10 MHz reference standard is used to generate these base frequencies either directly or after division of the 20 MHz output signal of a frequency doubler. The trigger signal is derived from the 100 kHz basis such that all harmonics of this frequency can be used in the system. Apart from the transistor-transistor-logic (TTL) pulse sequence for the internally singly triggered jet valve (SOURCE), LASER-photolysis, LASER-ablation or flash-lamp trigger (CHARGE), DC-discharge or Q-switch trigger (DISCHARGE), the internally retriggerable MW pulse (EXCITE), DR pulse (PREPARE/MIX), MW/DR protection (PROTECT), and start trigger of the transient recorder (DETECT), additional TTL control signals (CYCLOPS I, II) are provided for the generation of an optional quadrature-phase-shift-keying (QPSK) sequence to remove possible phase and amplitude asymmetries of the input channels (I, Q) and known as the cyclically-ordered-phase-sequence (CYCLOPS). Retriggerable without trigger-delay, the segmented memory of the transient recorder captures one FID per segment. At a flight time of about 1 ms for the jet propagating along the resonator's axis, about 4 FIDs can be recorded per gas pulse without compromising the resolution while an S/N improvement of x2 is achieved. For optional double resonance (DR) experiments, the relative phase between the DR pulses can be adjusted according to the requirements of a specific DR phase sequence (PHASE I,II). All TTL status signals for phase control are only active for the duration of the corresponding radiation pulse, so that remaining coherent leakage signals during the detection period are not subjected to the phase modulation and therefore are eliminated due to the Re/Im channel rotation and +/- sign alternation in the data-acquisition cycles.



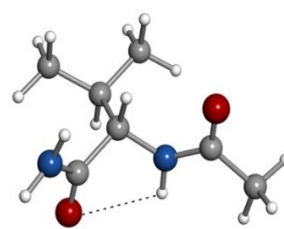
**Fig. S02** The predicted six low-energy conformers of Ac-Val-NH<sub>2</sub> in energetical order from lowest to highest. The rotational constants (in MHz) are also shown.



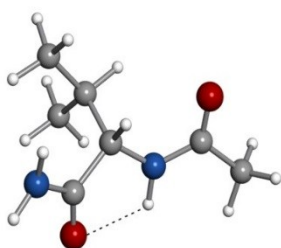
C<sub>7</sub>-III  
A = 1385.2  
B = 838.5  
C = 626.4



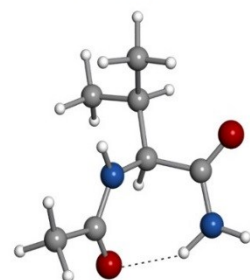
C<sub>5</sub>-III  
A = 1366.2  
B = 822.9  
C = 657.4



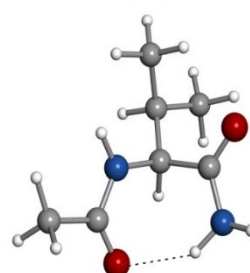
C<sub>5</sub>-I  
A = 1348.9  
B = 806.5  
C = 627.0



C<sub>5</sub>-II  
A = 1459.9  
B = 763.1  
C = 644.1



C<sub>7</sub>-I  
A = 1268.1  
B = 887.5  
C = 645.5



C<sub>7</sub>-II  
A = 1534.6  
B = 773.6  
C = 636.3

**Table S01.** Experimental and calculated spectroscopic parameters for the six lowest energy conformers of Ac-Val-NH<sub>2</sub>, including the observed rotamers (C<sub>7</sub>-III and C<sub>5</sub>-III conformers). Ab initio energies are included for the predicted species. All the calculations were done using the 6-311++G(d,p) basis set, except for B3LYP-D3BJ for which def2tzvp was used instead. A, B, and C represent the rotational constants (in MHz);  $\mu_a$ ,  $\mu_b$ , and  $\mu_c$  are the electric dipole moment components (in D);  $\chi_{aa}$ ,  $\chi_{bb}$ , and  $\chi_{cc}$  are the diagonal elements of the <sup>14</sup>N nuclear quadrupole coupling tensor (in MHz); N<sub>c</sub> and N<sub>t</sub> correspond to the central and terminal <sup>14</sup>N nuclei, respectively.  $\Delta E$  is the relative energies (in cm<sup>-1</sup>) with respect to the global minimum.  $\Delta E_{ZPE}$  is the relative energies (in cm<sup>-1</sup>) with respect to the global minimum, taking into account the zero point energy(ZPE).  $\Delta G$  is the Gibbs energies (in cm<sup>-1</sup>) calculated at 298K.

	Experimental		C <sub>7</sub> -III				C <sub>5</sub> -III				C5-I			
	Rotamer 1	Rotamer 2	MP2	M06-2X	B3LYP-D3	B3LYP-D3BJ	MP2	M06-2X	B3LYP-D3	B3LYP-D3BJ	MP2	M06-2X	B3LYP-D3	B3LYP-D3BJ
<b>A</b>	1388.6071(22)	1353.8151(58)	1385.186	1396.279	1378.672	1387.608	1366.223	1391.378	1336.571	1340.589	1348.950	1396.269	1352.620	1357.923
<b>B</b>	840.91159(42)	826.98719(28)	838.465	841.410	834.033	840.758	822.860	823.807	817.164	826.713	806.537	810.489	802.463	810.462
<b>C</b>	619.86354(17)	657.16182(21)	626.387	621.346	613.927	618.821	657.379	656.299	653.082	657.068	626.969	620.156	617.367	622.343
$ \mu_a $			1.2	1.4	1.4	1.4	2.2	2.5	2.5	2.6	0.7	1.7	1.6	1.6
$ \mu_b $			1.9	2.1	2.1	2.0	0.0	0.4	0.4	0.3	0.6	0.4	0.4	0.5
$ \mu_c $			0.8	0.8	0.8	0.8	0.3	0.2	0.2	0.2	0.1	0.3	0.3	0.3
N <sub>c</sub> / $\chi_{aa}$	2.0245(51)	2.170(11)	2.06	2.09	2.22	2.03	2.21	2.27	2.38	2.21	2.28	2.31	2.44	2.27
N <sub>c</sub> / $\chi_{bb}$	-2.987(11)	-2.286(14)	-3.22	-3.18	-3.37	-3.16	-2.29	-2.22	-2.72	-2.45	-3.46	-2.33	-3.18	-2.93
N <sub>c</sub> / $\chi_{cc}$	0.962(11)	0.116(14)	1.16	1.08	1.15	1.12	0.08	-0.05	0.34	0.24	1.18	0.01	0.74	0.65
N <sub>t</sub> / $\chi_{aa}$	-0.7689(71)	0.613(12)	-1.04	-0.80	-0.77	-0.71	0.38	0.88	0.59	0.50	-2.11	-0.76	-1.50	-1.51
N <sub>t</sub> / $\chi_{bb}$	1.902(13)	-0.925(15)	1.95	2.05	2.14	2.08	-1.23	-1.02	-1.2	-0.99	0.07	-0.76	-0.51	-0.37
N <sub>t</sub> / $\chi_{cc}$	-1.133(13)	0.312(15)	-0.91	-1.25	-1.37	-1.36	0.84	0.14	0.64	0.49	2.05	1.52	2.01	1.88
$\Delta E$			0	0	0	0	83	161	360	271	403	511	556	484
$\Delta E_{ZPE}$			0	51	0	0	45	0	187	122	267	388	372	321
$\Delta G$			113	190	115	168	154	0	0	0	0	298	122	118

**Table S01.** Cont.

	Experimental		C <sub>s</sub> -II				C <sub>7</sub> -I				C <sub>7</sub> -II			
	Rotamer 1	Rotamer 2	MP2	M06-2X	B3LYP-D3	B3LYP-D3BJ	MP2	M06-2X	B3LYP-D3	B3LYP-D3BJ	MP2	M06-2X	B3LYP-D3	B3LYP-D3BJ
<b>A</b>	1388.6071(22)	1353.8151(58)	1459.928	1478.124	1445.795	1452.532	1268.107	1296.690	1279.068	1287.992	1534.606	1555.722	1536.222	1546.055
<b>B</b>	840.91159(42)	826.98719(28)	763.069	769.803	758.491	766.400	887.512	886.970	878.761	885.804	773.625	771.279	763.985	770.868
<b>C</b>	619.86354(17)	657.16182(21)	644.125	642.501	639.507	641.934	645.512	638.250	630.885	636.035	636.289	633.483	627.149	631.908
$ \mu_a $			2.1	2.3	2.5	2.6	1.1	1.4	1.3	-1.3	1.3	1.5	1.5	-1.51
$ \mu_b $			0.7	0.4	0.4	-0.5	2.4	2.5	2.5	-2.5	2.4	2.4	2.4	-2.32
$ \mu_c $			0.5	0.3	0.3	-0.3	1.3	1.4	1.3	-1.3	0.4	0.5	0.5	-0.45
$N_c/\chi_{aa}$	2.0245(51)	2.170(11)	2.32	2.36	2.50	2.33	2.05	2.11	2.24	2.05	2.10	2.14	2.26	2.08
$N_c/\chi_{bb}$	-2.987(11)	-2.286(14)	-0.58	-0.40	-0.87	-0.63	-2.40	-2.47	-2.50	-2.24	-1.27	-1.52	-1.55	-1.37
$N_c/\chi_{cc}$	0.962(11)	0.116(14)	-1.74	-1.96	-1.62	-1.70	0.36	0.37	0.26	0.19	-0.84	-0.62	-0.71	-0.71
$N_t/\chi_{aa}$	-0.7689(71)	0.613(12)	0.14	0.74	0.55	0.55	0.83	1.04	1.03	0.98	-0.05	0.10	0.12	0.14
$N_t/\chi_{bb}$	1.902(13)	-0.925(15)	-0.37	-0.05	-0.40	-0.12	1.83	2.03	2.11	2.03	1.58	1.70	1.78	1.70
$N_t/\chi_{cc}$	-1.133(13)	0.312(15)	0.23	-0.69	-0.15	-0.43	-2.67	-3.07	-3.14	-3.01	-1.52	-1.80	-1.90	-1.84
$\Delta E$			342	293	417	313	440	182	193	144	588	457	406	402
$\Delta E_{ZPE}$			272	241	271	179	429	176	155	134	629	497	414	416
$\Delta G$			351	298	169	84	602	287	225	265	811	468	547	593

**Table S02.** Measured frequencies and residuals (in MHz) for the nuclear quadrupole coupling hyperfine components of the C<sub>7</sub>-III conformer of Ac-Val-NH<sub>2</sub>.

J'	K' <sub>-1</sub>	K' <sub>+1</sub>	J''	K'' <sub>-1</sub>	K'' <sub>+1</sub>	I'	F'	I''	F''	$\nu_{\text{obs.}}$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$
3	0	3	2	0	2	1	2	1	1	4182.7061	0.0034
3	0	3	2	0	2	2	4	2	3	4182.7511	0.0027
3	0	3	2	0	2	2	3	2	2	4182.8731	0.0024
3	0	3	2	0	2	1	3	0	2	4182.9342	0.0043
3	0	3	2	0	2	2	5	2	4	4182.9879	0.0046
3	0	3	2	0	2	1	4	1	3	4183.1587	0.0032
3	2	2	2	2	1	2	2	2	1	4381.6986	-0.0021
3	2	2	2	2	1	1	3	1	2	4381.8243	-0.0003
3	2	2	2	2	1	1	4	1	3	4382.0074	-0.0016
3	2	2	2	2	1	2	5	2	4	4382.2344	-0.0014
3	2	2	2	2	1	0	3	0	2	4382.2853	-0.0009
3	2	2	2	2	1	2	3	2	2	4382.7738	-0.002
3	2	2	2	2	1	2	4	2	3	4382.8690	0.0028
3	2	2	2	2	1	1	2	1	1	4382.9496	-0.0008
4	0	4	3	1	3	1	3	1	2	5207.0316	0.0007
4	0	4	3	1	3	2	5	2	4	5207.0804	0.0008
4	0	4	3	1	3	0	4	0	3	5207.1285	0.0012
4	0	4	3	1	3	2	6	2	5	5207.1414	-0.0009
4	0	4	3	1	3	1	4	1	3	5207.2195	-0.0014
4	0	4	3	1	3	1	5	1	4	5207.2854	-0.0008
4	0	4	3	1	3	2	3	2	2	5207.3294	0.0021
4	0	4	3	0	3	1	5	2	4	5425.1573	-0.0007
4	0	4	3	0	3	1	5	1	4	5425.2329	-0.0030
4	0	4	3	0	3	2	3	2	2	5425.2401	0.0008
4	0	4	3	0	3	2	6	2	5	5425.3965	-0.0027
4	0	4	3	0	3	0	4	0	3	5425.4600	-0.0027
4	0	4	3	0	3	2	5	1	4	5425.5869	-0.0016
4	0	4	3	0	3	1	3	2	2	5425.6772	-0.0024

**Table S03.** Measured frequencies and residuals (in MHz) for the nuclear quadrupole coupling hyperfine components of the C<sub>5</sub>-III conformer of Ac-Val-NH<sub>2</sub>.

J'	K' <sub>-1</sub>	K' <sub>+1</sub>	J''	K'' <sub>-1</sub>	K'' <sub>+1</sub>	I'	F'	I''	F''	$\nu_{\text{obs.}}$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$
3	1	3	2	1	2	1	4	1	3	4177.6912	-0.0001
3	1	3	2	1	2	2	5	2	4	4177.7269	-0.0001
3	1	3	2	1	2	2	3	0	2	4177.7400	-0.0001
3	0	3	2	0	2	2	3	2	2	4321.5734	-0.0028
3	0	3	2	0	2	2	4	2	3	4321.6002	0.0001
3	0	3	2	0	2	1	2	1	1	4321.6137	-0.0014
3	0	3	2	0	2	2	5	2	4	4321.7529	-0.0002
3	0	3	2	0	2	0	3	0	2	4321.9104	0.0020
3	1	2	2	1	1	2	5	2	4	4682.5783	0.0016
3	1	2	2	1	1	1	4	1	3	4682.6382	0.0045
3	1	2	2	1	1	1	2	1	1	4682.6952	-0.0045
3	1	2	2	1	1	2	4	2	3	4682.7236	0.0053
3	1	2	2	1	1	2	3	2	2	4682.8164	0.0029
4	1	4	3	1	3	2	6	2	5	5538.8507	0.0055
4	1	4	3	1	3	2	5	2	4	5538.8758	-0.0020
4	2	2	3	2	1	0	4	0	3	6193.7977	-0.0009
4	2	2	3	2	1	2	6	2	5	6193.8758	-0.0001
4	2	2	3	2	1	1	5	1	4	6194.0125	-0.0025
4	2	2	3	2	1	2	5	2	4	6194.2932	-0.0001
4	2	2	3	2	1	2	4	2	3	6194.4250	-0.0029
5	1	5	4	1	4	2	3	0	4	6883.0983	-0.0018
5	1	5	4	1	4	2	5	2	4	6883.1050	0.0034
5	1	5	4	1	4	2	6	2	5	6883.1136	-0.0013
5	1	5	4	1	4	2	7	2	6	6883.1221	0.0022
5	1	5	4	1	4	1	5	1	4	6883.1319	0.0035
5	0	5	4	0	4	1	6	1	5	6952.2332	0.0016
5	0	5	4	0	4	2	4	2	3	6952.2637	-0.0042
5	0	5	4	0	4	2	7	2	6	6952.2772	-0.0038
5	0	5	4	0	4	0	5	0	4	6952.2869	-0.0015

**Fig. S03** Calculated MP2/6-311++G(d,p) potential energy surface (PES) for the torsional coordinate of the isopropyl group of Ac-Val-NH<sub>2</sub>. From left to right: Conformers C<sub>5</sub>-II, C<sub>5</sub>-I and C<sub>5</sub>-III.

