Supplemental Material

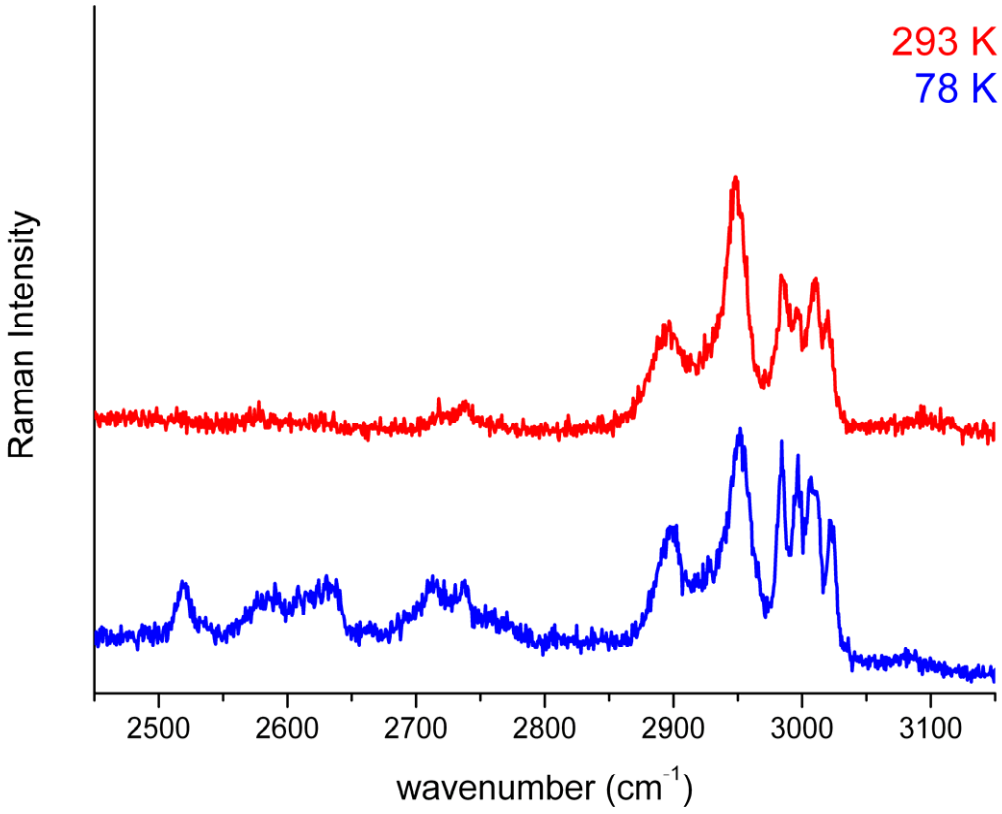

Figure S1. High-frequency region of L-alanine alaninium nitrate. Raman spectra between 2400 – 3200 cm^{-1} at 293 K (red, upper) and at 78 K (blue, lower) showing the distribution of the hydrogen stretching spectral features.

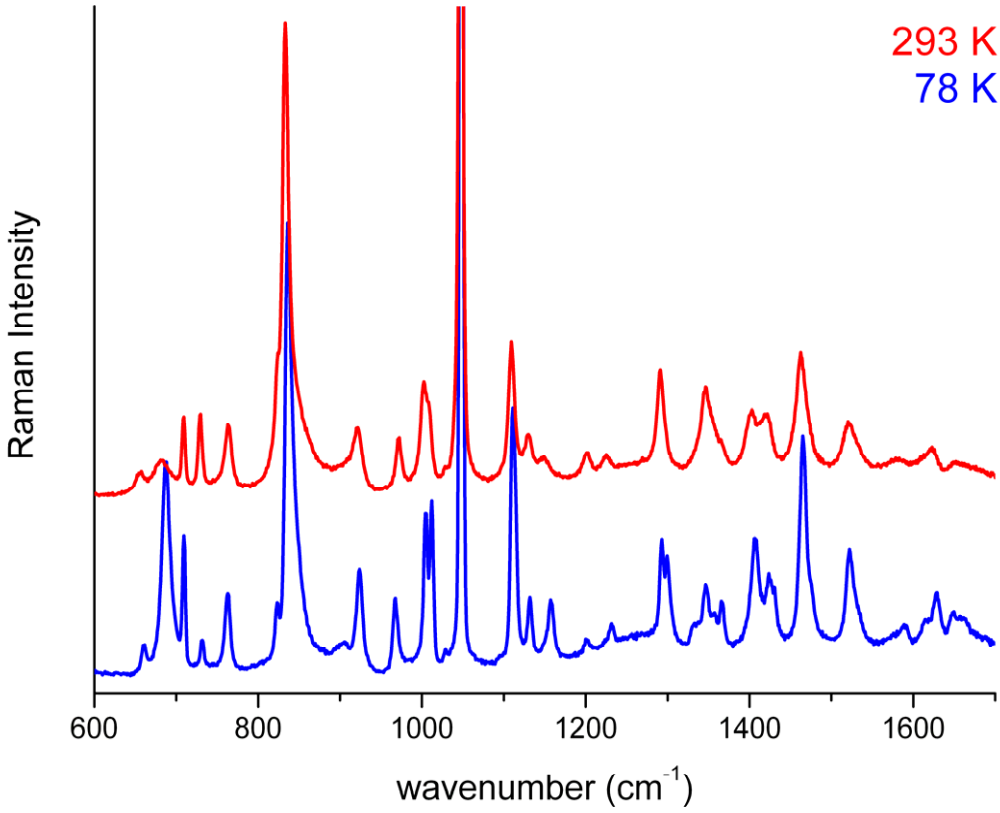

Figure S2. Raman spectra of L-alanine alaninium nitrate between 600 – 1700 cm^{-1} at 293 K (red, upper) and at 78 K (blue, lower). Raman intensity has been scaled to show low intensity modes resulting in the truncation of the most intense spectral feature at 1048 cm^{-1}, the origin of which is discussed in the text.

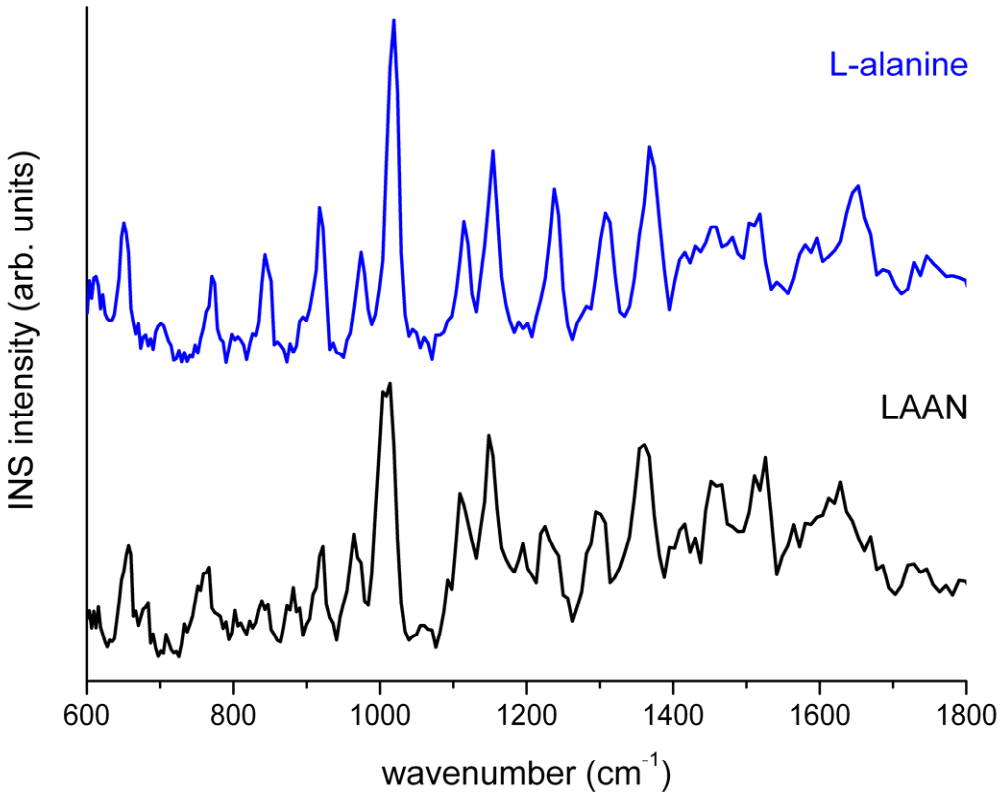

Figure S3. Comparison of the INS spectra of L-alanine (blue, upper) with L-alanine alaninium nitrate (black, lower) between 600 – 1700 cm^{-1}.

X-ray Crystallography

X-ray measurements were performed on a Bruker-AXS SMART-CCD diffractometer at low-temperature (90 K) using graphite-monochromated Mo Kα radiation ($\lambda_{Mo\ K\alpha}$= 0.71073 Å).[11] The data were corrected for Lorentz and polarization effects and absorption using SADABS.[12] The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. After all of the non-hydrogen atoms were located, the model was refined against F^2, initially using isotropic and later anisotropic thermal displacement parameters. Hydrogen atoms were refined and allowed for isotropically. Neutral atom scattering coefficients and anomalous dispersion corrections were taken from the *International Tables*, Vol. C.[13] All calculations were performed using SHELXTL crystallographic software programs.[14, 15] Atomic positional parameters, full tables of bond lengths and angles, and anisotropic temperature factors are available in CCDC 720351.

Table S1. Crystal data and structure refinement for L-alanine alaninium nitrate.

Identification code	p21	
Empirical formula	C6 H15 N3 O7	
Formula weight	241.21	
Temperature	90(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 7.7153(6) Å	α= 90°
	b = 5.4523(5) Å	β= 94.607(2)°
	c = 12.7639(11) Å	γ = 90°
Volume	535.19(8) $Å^3$	
Z	2	
Density (calculated)	1.497 Mg/m^3	
Absorption coefficient	0.136 mm^{-1}	
F(000)	256	
Crystal size	0.30 x 0.28 x 0.26 mm^3	
Theta range for data collection	2.65 to 28.07°	
Index ranges	-10<=h<=10, -7<=k<=7, -16<=l<=16	
Reflections collected	5351	
Independent reflections	1438 [R(int) = 0.0270]	
Completeness to theta = 28.07°	99.7 %	
Absorption correction	multiscan	
Max. and min. transmission	0.9654 and 0.9603	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1438 / 1 / 176	
Goodness-of-fit on F^2	1.252	
Final R indices [I>2σ(I)]	R1 = 0.0508, wR2 = 0.1178	
R indices (all data)	R1 = 0.0515, wR2 = 0.1181	
Largest diff. peak and hole	0.414 and -0.317 $e.Å^{-3}$	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for L-alanine alaninium nitrate. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(5)	8263(3)	1192(5)	2971(2)	19(1)
O(4)	2599(3)	-264(4)	2115(2)	15(1)
O(1)	2493(3)	1841(5)	3805(2)	19(1)
O(2)	1417(3)	-1415(4)	4623(2)	13(1)
O(3)	3184(3)	115(4)	450(2)	11(1)
O(6)	6595(3)	2792(5)	1711(2)	19(1)
O(7)	7314(3)	-1065(5)	1656(2)	18(1)
N(1)	1367(4)	1175(5)	6447(2)	10(1)
N(2)	3615(3)	5007(5)	562(2)	8(1)
N(3)	7371(3)	996(6)	2108(2)	12(1)
C(1)	2058(4)	629(6)	4619(2)	10(1)
C(2)	2522(4)	2013(6)	5635(2)	10(1)
C(3)	4414(4)	1510(7)	6024(2)	16(1)
C(4)	2859(4)	1007(6)	1309(2)	10(1)
C(5)	2652(4)	3788(6)	1385(2)	9(1)
C(6)	723(4)	4464(6)	1223(3)	17(1)

Table S3. Bond lengths [Å] and angles [°] for L-alanine alaninium nitrate.

O(5)-N(3)	1.256(3)
O(4)-C(4)	1.270(4)
O(1)-C(1)	1.298(4)
O(1)-H(1)	0.82(7)
O(2)-C(1)	1.220(4)
O(3)-C(4)	1.243(4)
O(6)-N(3)	1.235(4)
O(7)-N(3)	1.262(4)
N(1)-C(2)	1.492(4)
N(1)-H(1B)	0.86(4)
N(1)-H(1C)	0.92(5)
N(1)-H(1A)	0.90(4)
N(2)-C(5)	1.491(4)
N(2)-H(2B)	0.84(4)
N(2)-H(2A)	0.89(4)
N(2)-H(2C)	0.90(4)
C(1)-C(2)	1.518(4)
C(2)-C(3)	1.528(4)
C(2)-H(2)	1.0000
C(3)-H(3A)	0.9800
C(3)-H(3B)	0.9800
C(3)-H(3C)	0.9800
C(4)-C(5)	1.529(5)
C(5)-C(6)	1.531(4)
C(5)-H(5A)	1.0000
C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800
C(6)-H(6C)	0.9800
C(1)-O(1)-H(1)	113(5)
C(2)-N(1)-H(1B)	108(2)
C(2)-N(1)-H(1C)	111(3)
H(1B)-N(1)-H(1C)	112(4)
C(2)-N(1)-H(1A)	107(3)
H(1B)-N(1)-H(1A)	111(4)
H(1C)-N(1)-H(1A)	108(4)
C(5)-N(2)-H(2B)	110(2)
C(5)-N(2)-H(2A)	109(2)
H(2B)-N(2)-H(2A)	113(4)
C(5)-N(2)-H(2C)	110(3)
H(2B)-N(2)-H(2C)	105(4)
H(2A)-N(2)-H(2C)	111(3)
O(6)-N(3)-O(5)	120.4(3)
O(6)-N(3)-O(7)	121.4(2)
O(5)-N(3)-O(7)	118.2(3)
O(2)-C(1)-O(1)	126.8(3)
O(2)-C(1)-C(2)	121.3(3)
O(1)-C(1)-C(2)	111.9(3)
N(1)-C(2)-C(1)	109.2(2)
N(1)-C(2)-C(3)	109.1(2)
C(1)-C(2)-C(3)	110.0(2)
N(1)-C(2)-H(2)	109.5
C(1)-C(2)-H(2)	109.5
C(3)-C(2)-H(2)	109.5

C(2)-C(3)-H(3A)	109.5
C(2)-C(3)-H(3B)	109.5
H(3A)-C(3)-H(3B)	109.5
C(2)-C(3)-H(3C)	109.5
H(3A)-C(3)-H(3C)	109.5
H(3B)-C(3)-H(3C)	109.5
O(3)-C(4)-O(4)	123.9(3)
O(3)-C(4)-C(5)	118.3(3)
O(4)-C(4)-C(5)	117.8(3)
N(2)-C(5)-C(4)	109.7(3)
N(2)-C(5)-C(6)	109.3(3)
C(4)-C(5)-C(6)	109.6(3)
N(2)-C(5)-H(5A)	109.4
C(4)-C(5)-H(5A)	109.4
C(6)-C(5)-H(5A)	109.4
C(5)-C(6)-H(6A)	109.5
C(5)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
C(5)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for L-alanine alaninium nitrate. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2} U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(5)	32(1)	12(1)	12(1)	1(1)	-6(1)	-4(1)
O(4)	28(1)	7(1)	10(1)	0(1)	3(1)	-1(1)
O(1)	31(1)	16(1)	9(1)	-1(1)	4(1)	-7(1)
O(2)	14(1)	13(1)	12(1)	-2(1)	-1(1)	-3(1)
O(3)	14(1)	9(1)	12(1)	-1(1)	3(1)	0(1)
O(6)	19(1)	14(1)	24(1)	4(1)	-3(1)	2(1)
O(7)	28(1)	13(1)	13(1)	-3(1)	-1(1)	1(1)
N(1)	13(1)	10(1)	6(1)	-3(1)	1(1)	-2(1)
N(2)	11(1)	5(1)	10(1)	0(1)	3(1)	2(1)
N(3)	15(1)	11(1)	11(1)	2(1)	2(1)	-1(1)
C(1)	6(1)	12(2)	12(1)	-1(1)	-1(1)	2(1)
C(2)	12(1)	6(1)	11(1)	0(1)	1(1)	-3(1)
C(3)	12(1)	20(2)	14(1)	-4(1)	-2(1)	-5(1)
C(4)	8(1)	7(1)	13(1)	2(1)	0(1)	1(1)
C(5)	11(1)	8(1)	9(1)	-1(1)	4(1)	-2(1)
C(6)	8(1)	12(2)	30(2)	-3(1)	7(1)	3(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for L-alanine alaninium nitrate.

	x	y	z	U(eq)
H(2)	2356	3812	5511	11
H(3A)	4726	2493	6654	23
H(3B)	5173	1951	5473	23
H(3C)	4557	-234	6194	23
H(5A)	3130	4356	2095	11
H(6A)	589	6239	1308	25
H(6B)	79	3605	1743	25
H(6C)	268	3983	514	25
H(2B)	3400(50)	6520(80)	550(30)	0(8)
H(1B)	1670(40)	1920(80)	7030(30)	1(8)
H(1C)	1420(60)	-510(100)	6520(30)	18(11)
H(1A)	280(50)	1590(90)	6210(30)	16(10)
H(2A)	4750(50)	4680(80)	690(30)	7(9)
H(2C)	3220(50)	4450(80)	-80(30)	10(9)
H(1)	2410(80)	1030(150)	3260(50)	60(20)

Table S6. Torsion angles [°] for L-alanine alaninium nitrate.

O(2)-C(1)-C(2)-N(1)	-27.2(4)
O(1)-C(1)-C(2)-N(1)	155.4(3)
O(2)-C(1)-C(2)-C(3)	92.5(3)
O(1)-C(1)-C(2)-C(3)	-84.9(3)
O(3)-C(4)-C(5)-N(2)	-24.6(4)
O(4)-C(4)-C(5)-N(2)	158.9(2)
O(3)-C(4)-C(5)-C(6)	95.4(3)
O(4)-C(4)-C(5)-C(6)	-81.0(4)

Table S7. Calculated vibrational frequencies (cm^{-1}) for L-alanine alaninium dimer from isolated molecule DFT with corresponding calculated infrared and Raman intensities.

		Calculated activity				Calculated activity	
MODE	Freq. (1/cm)	IR	Raman	MODE	Freq. (1/cm)	IR	Raman
1	16.5	4.6	0.1	39	1213.5	23.4	1.2
2	35.6	14.3	0.2	40	1276.0	217.4	5.3
3	47.4	7.8	0.1	41	1296.8	14.4	3.6
4	64.8	4.6	0.2	42	1319.4	631.6	1.9
5	80.2	5.5	0.2	43	1344.9	31.2	6.8
6	102.7	5.0	0.1	44	1370.7	685.2	6.0
7	116.8	4.8	0.8	45	1378.7	27.2	3.1
8	164.6	46.0	0.5	46	1388.8	215.7	12.9
9	238.9	3.0	0.3	47	1410.1	207.8	5.0
10	251.4	0.9	0.2	48	1427.0	63.6	3.2
11	260.7	1.6	0.4	49	1432.7	32.1	1.4
12	294.8	55.5	0.4	50	1492.6	1.6	7.0
13	300.1	0.9	0.5	51	1497.8	6.9	8.4
14	338.8	15.2	0.6	52	1501.9	16.2	6.1
15	359.0	103.7	1.5	53	1508.7	14.8	7.0
16	384.1	79.0	0.4	54	1530.9	146.1	3.3
17	389.2	43.4	0.5	55	1631.5	12.7	5.8
18	399.3	33.3	0.7	56	1632.3	23.1	8.6
19	517.8	41.8	2.9	57	1652.0	29.0	3.9
20	551.0	222.2	5.2	58	1665.6	32.8	4.3
21	646.6	3.5	3.0	59	1730.5	775.8	16.0
22	656.8	16.6	4.0	60	1803.1	183.9	6.6
23	743.6	22.9	1.5	61	2445.4	3234.2	117.3
24	764.4	6.9	1.5	62	2509.3	320.0	39.6
25	813.3	46.4	11.0	63	2799.8	421.9	27.3
26	828.8	35.0	8.1	64	3038.4	7.9	117.6
27	866.2	50.6	2.6	65	3039.3	12.2	144.7
28	874.9	73.4	2.5	66	3093.9	5.5	80.0
29	980.7	5.4	1.6	67	3101.8	6.9	85.0
30	989.3	13.2	1.1	68	3111.2	9.9	50.4
31	1003.4	74.5	3.2	69	3118.5	4.4	28.9
32	1015.0	80.8	2.9	70	3138.0	2.9	47.5
33	1077.6	37.7	2.0	71	3145.8	4.6	69.8
34	1087.0	11.1	2.7	72	3469.4	69.2	77.3
35	1115.9	98.5	1.1	73	3477.2	55.2	105.7
36	1118.3	74.3	2.4	74	3535.5	77.6	38.4
37	1123.9	61.2	0.4	75	3548.7	69.5	46.4
38	1211.7	14.7	1.8				

Table S8. Calculated vibrational frequencies (cm^{-1}) for an isolated nitrate ion from isolated molecule DFT with corresponding calculated Raman intensities.

MODE	Freq. (1/cm)	Calculated Raman activity
1	716	5.0
2	716	5.0
3	843	0.0
4	1068	18.7
5	1430	1.0
6	1433	1.0