Structure and energetics of arsenic(III) oxide intercalated by ionic azides

Supporting Information

Piotr A. Guńka,*,† Karol Kraszewski,† Yu-Sheng Chen,‡ and Janusz Zachara†

Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland, and ChemMatCARS, University of Chicago, Advanced Photon Source, Argonne, Illinois 60439, United States

E-mail: piogun@ch.pw.edu.pl

List of Figures

*To whom correspondence should be addressed
†Warsaw University of Technology
‡ChemMatCARS

List of Tables

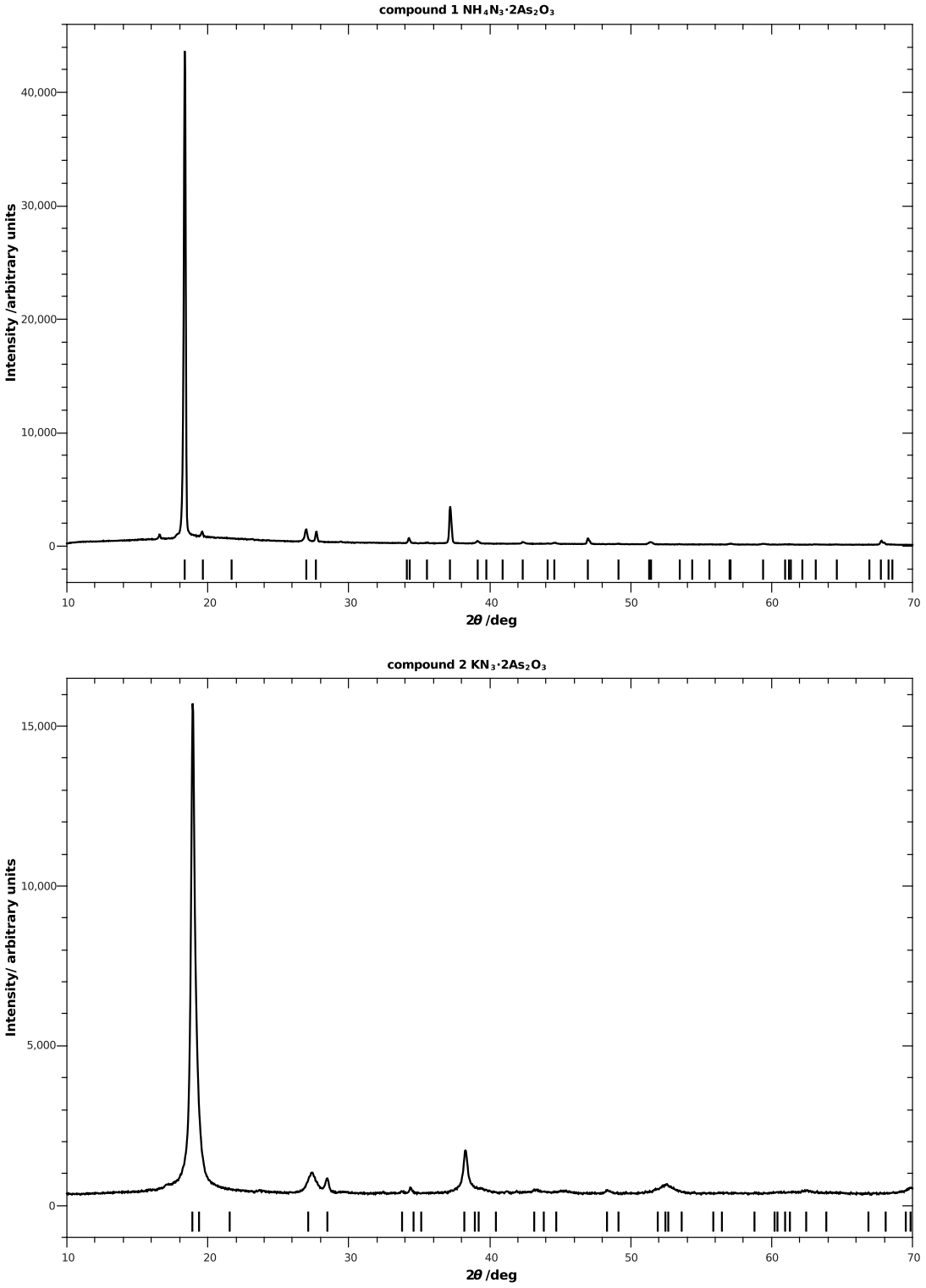

Figure S1: Powder diffraction patterns of compounds **1** and **2**. Substantial preferred orientation in the direction of (001) crystallographic planes is observed in the sample which is caused by the habit of crystals. Ticks below powder diffraction patterns represent positions of reflections calculated from crystal structure for compound **1** and resulting from Le-Bail fit of a low-temperature unit cell to the room-temperature powder pattern for intercalate **2**. The FullPROF programme suite was used for Le-Bail fitting.[1]

Table S1: Anisotropic and equivalent isotropic displacement parameters (in 10^3Å^2) for compound **2** at various temperatures. R^2 and slope are the result of linear least squares fit of U_{eq} vs. synchrotron X-ray dose (expressed in arbitrary units). Slope is given to indicate the relative extent of U_{eq} change upon irradiation for every atom.

atom	T/K	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
As1	45	6.1(2)	6.1(2)	19.0(4)	0	0	3.07(12)	10.4(2)
	35	6.6(3)	6.6(3)	22.4(5)	0	0	3.30(15)	11.9(3)
	25	7.4(4)	7.4(4)	26.1(6)	0	0	3.70(19)	13.6(4)
	15	8.2(4)	8.2(4)	30.2(7)	0	0	4.1(2)	15.6(4)
	30	9.7(4)	9.7(4)	35.9(8)	0	0	4.9(2)	18.4(5)
			R^2	*0.9908*			*slope*	*1.85(10)*
O1	45	11.2(11)	5.1(14)	19.5(18)	0	0	2.6(7)	12.6(7)
	35	7.1(17)	12.7(14)	23(2)	0	0	3.5(9)	15.0(9)
	25	7(2)	14.1(16)	27(3)	0	0	3.3(10)	16.7(10)
	15	8(2)	15.0(18)	30(3)	0	0	3.9(11)	18.5(11)
	30	9(3)	18(2)	36(4)	0	0	4.5(13)	22.3(13)
			R^2	*0.9839*			*slope*	*2.2(3)*
K1	45	11.8(7)	11.8(7)	26.0(16)	0	0	5.9(4)	16.5(6)
	35	11.9(9)	11.9(9)	30(2)	0	0	6.0(4)	17.9(7)
	25	12.8(10)	12.8(10)	33(2)	0	0	6.4(5)	19.5(8)
	15	13.7(12)	13.7(12)	37(3)	0	0	6.8(6)	21.6(10)
	30	15.8(13)	15.8(13)	42(3)	0	0	7.9(7)	24.5(11)
			R^2	*0.9808*			*slope*	*1.9(3)*
$N1_{middle}$	45	11(3)	11(3)	50(10)	0	0	5.3(16)	24(3)
	35	14(4)	14(4)	49(12)	0	0	7(2)	26(4)
	25	14(5)	14(5)	65(17)	0	0	7(3)	31(5)
	15	18(6)	18(6)	68(19)	0	0	9(3)	34(6)
	30	23(7)	23(7)	70(20)	0	0	11(4)	37(6)
			R^2	*0.9870*			*slope*	*3.3(14)*
$N2_{terminal}$	45	31(4)	31(4)	54(9)	0	0	15.4(18)	38(3)
	35	34(5)	34(5)	72(13)	0	0	17(2)	47(4)
	25	44(6)	44(6)	65(15)	0	0	22(3)	51(5)
	15	48(8)	48(8)	80(19)	0	0	24(4)	59(6)
	30	52(9)	52(9)	110(30)	0	0	26(5)	70(8)
			R^2	*0.9874*			*slope*	*7.3(16)*

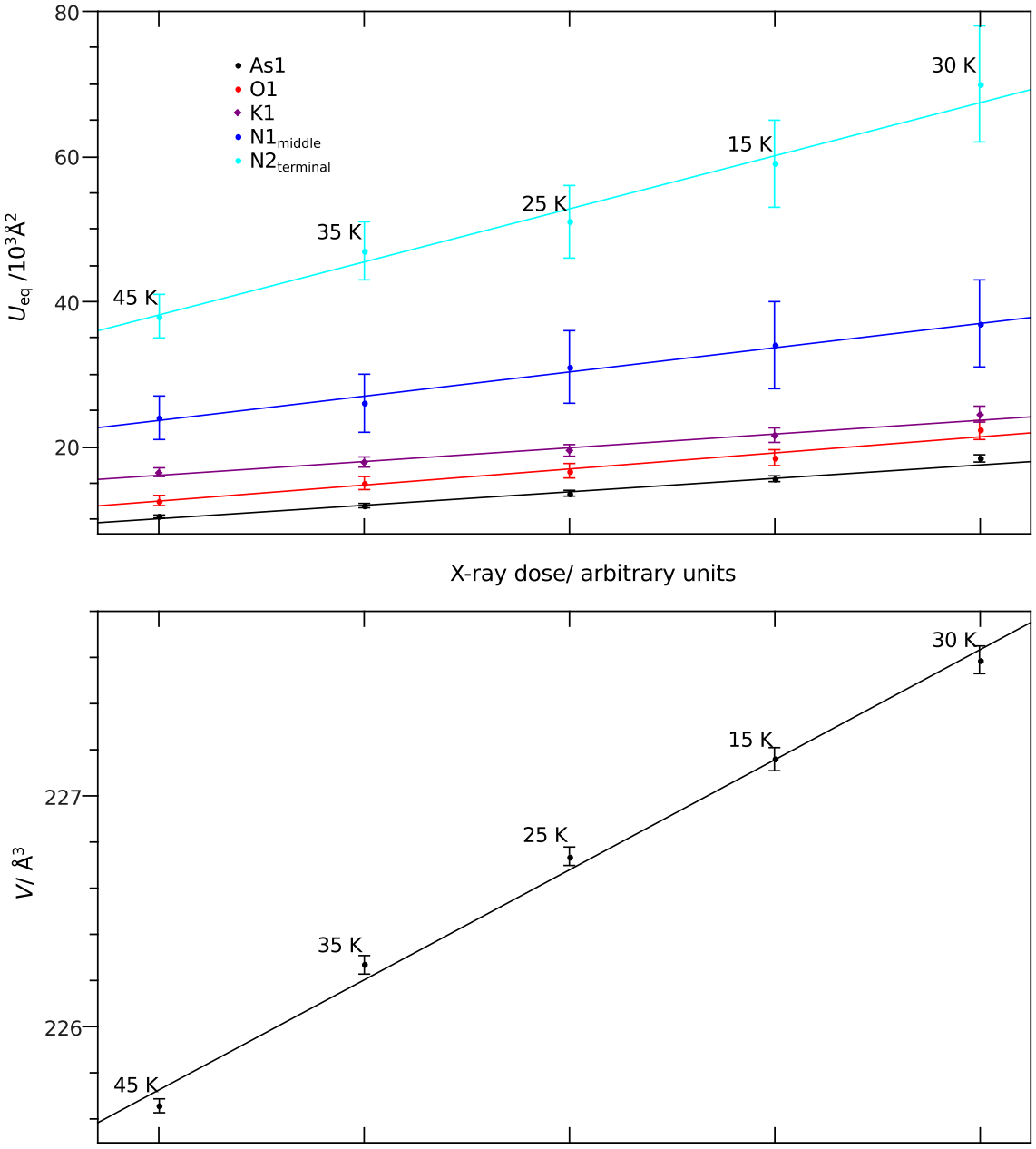

Figure S2: Equivalent isotropic displacement parameters (top) and unit cell volume (bottom) plotted as a function of synchrotron X-ray dose for compound **2**. Lines are drawn as a guide for the eyes and are a result of a least squares fit. See Table S1 for their slope.

Table S2: Formulae to compute interlayer interaction energies:

$$\begin{cases} E_{AC} = \mathcal{E}_0 - \mathcal{E}_{LCLA\_a} - \mathcal{E}_{CLAL\_b} - \mathcal{E}_{CLA\_c} + \mathcal{E}_{L\_c} \\ E_{CA} = \mathcal{E}_0 - \mathcal{E}_{LALC\_a} - \mathcal{E}_{ALCL\_b} - \mathcal{E}_{ALC\_d} + \mathcal{E}_{L\_d} \\ E_{LL\_O} = \mathcal{E}_{LL\_O} - \mathcal{E}_{L\_c} - \mathcal{E}_{L\_d} \\ E_{LL\_As} = \mathcal{E}_{LL\_As} - \mathcal{E}_{L\_c} - \mathcal{E}_{L\_d} \\ E_{CL} = \mathcal{E}_{ALCL\_b} - \mathcal{E}_{ALC\_d} - \mathcal{E}_{LL\_O} + \mathcal{E}_{L\_c} \\ E_{LC} = \mathcal{E}_{LCLA\_a} - \mathcal{E}_{CLA\_c} - \mathcal{E}_{LL\_O} + \mathcal{E}_{L\_d} \\ E_{AL} = \mathcal{E}_{CLAL\_b} - \mathcal{E}_{CLA\_c} - \mathcal{E}_{LL\_As} + \mathcal{E}_{L\_d} \\ E_{LA} = \mathcal{E}_{LALC\_a} - \mathcal{E}_{ALC\_d} - \mathcal{E}_{LL\_As} + \mathcal{E}_{L\_c} \end{cases}$$

Table S3: Optimised unit cell parameters and fractional coordinates of atoms for compound **1** together with computed B3LYP-D* energies of bulk structure and extracted layers. $\mathscr{E}$ is stands for energy; $\mathscr{E}^{\mathrm{c}}$ is the BSSE-corrected energy value (i.e. energy of layers computed along with ghost atoms). Energy values are given per unit cell.

$P31m$
$a = 5.33034$ Å
$c = 9.27083$ Å

atom	x	y	z
As	3.33333E−001	−3.33333E−001	2.68234E−001
As	3.33333E−001	−3.33333E−001	−2.70928E−001
O	−4.96769E−001	5.55112E−017	1.64290E−001
O	4.84493E−001	−2.77556E−017	−1.66136E−001
N	0	0	−3.76843E−001
N	0	0	4.94368E−001
N	0	0	3.65688E−001
N	0	0	5.37610E−003
H	0	0	1.15146E−001
H	0	1.81386E−001	−3.09757E−002

		$\mathscr{E}$ /Ha	$\mathscr{E}^{\mathrm{C}}$ /Ha
	bulk		−9616.017120699
a	LALC	−9615.895039513	−9615.901747913
	LCLA	−9615.908679925	−9615.916787999
b	CLAL	−9615.901918748	−9615.907280428
	ALCL	−9615.908735784	−9615.917012783
c	CLA	−4918.588873702	−4918.596125901
	L	−4697.295896109	−4697.301068184
d	ALC	−4918.582929431	−4918.590783260
	L	−4697.295068098	−4697.300629157
	LL_O	−9394.600539905	−9394.611240684
	LL_As	−9394.596355260	−9394.607656129

Table S4: Optimised unit cell parameters and fractional coordinates of atoms for compound **2** together with computed B3LYP-D* energies of bulk structure and extracted layers. $\mathscr{E}$ is stands for energy; $\mathscr{E}^{\mathrm{c}}$ is BSSE-corrected energy (i.e. energy of layers computed along with ghost atoms). Energy values are given per unit cell.

$P6/mmm$
$a = 5.31864$ Å
$c = 9.16580$ Å

atom	x	y	z
As	3.33333E−001	−3.33333E−001	2.68874E−001
O	5.00000E−001	−2.77556E−017	1.63013E−001
N	0	0	5.00000E−001
N	0	0	3.69729E−001
K	0	0	0

	$\mathscr{E}$ /Ha	$\mathscr{E}^{\mathrm{C}}$ /Ha
bulk		−10158.833156947
LALC	−10158.704874467	−10158.713284064
LCLA	−10158.722900556	−10158.731098256
CLA	−5461.391840756	−5461.401657343
L	−4697.295116943	−4697.299899609
LL_O	−9394.599797011	−9394.609460283
LL_As	−9394.595675481	−9394.606854681

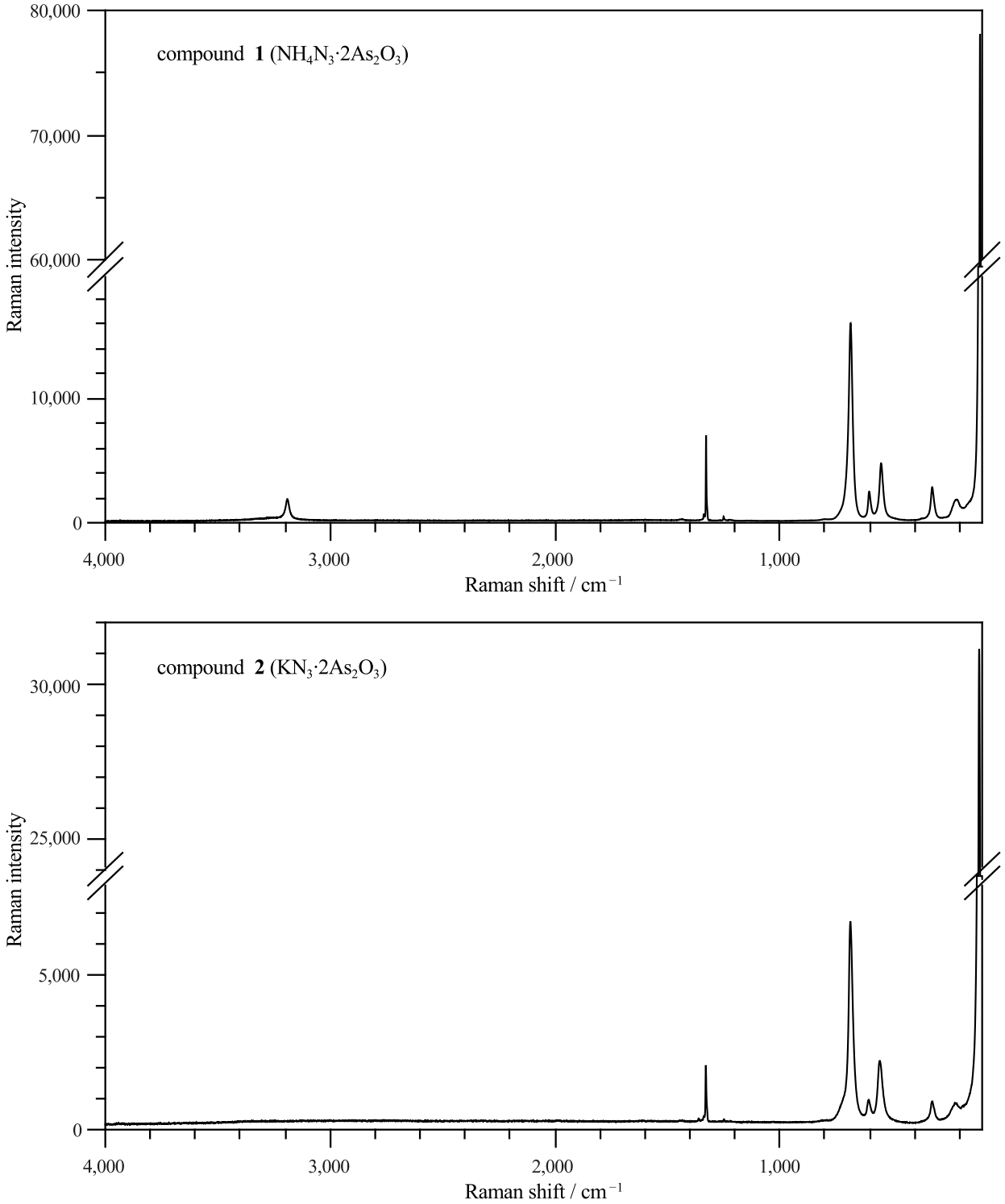

Figure S3: Experimental Raman spectra of compounds **1** and **2** in the whole measured range.

Table S5: Calculated frequencies of lattice vibrations at Γ point in compound **2**.

Eigenvalues / Ha^2	Wavenumber /cm^{-1}	Symmetry	IR	$Intensity_{IR}$ /km/mol	Raman
−2.62E−009	−11	A_{2u}	A	0	I
3.61E−009	13	E_{1u}	A	1	I
1.62E−008	28	E_{1g}	I	0	A
8.16E−008	63	E_{1g}	I	0	A
1.94E−007	97	A_{1g}	I	0	A
2.45E−007	109	A_{2u}	A	62	I
2.46E−007	109	E_{1u}	A	420	I
3.81E−007	136	B_{2g}	I	0	I
4.07E−007	140	B_{1u}	I	0	I
4.19E−007	142	E_{1u}	A	23	I
4.89E−007	154	A_{2u}	A	34	I
5.78E−007	167	E_{2u}	I	0	I
7.11E−007	185	E_{2g}	I	0	A
1.06E−006	226	B_{1g}	I	0	I
1.17E−006	237	B_{2u}	I	0	I
2.10E−006	318	E_{1g}	I	0	A
2.14E−006	321	E_{1u}	A	850	I
5.85E−006	531	E_{2u}	I	0	I
6.39E−006	555	E_{2g}	I	0	A
7.64E−006	607	E_{1g}	I	0	A
7.72E−006	610	E_{1u}	A	5167	I
8.40E−006	636	A_{2u}	A	663	I
8.61E−006	644	E_{1u}	A	15	I
9.64E−006	682	A_{1g}	I	0	A
1.34E−005	804	B_{1g}	I	0	I
1.40E−005	820	B_{2u}	I	0	I
3.63E−005	1323	A_{1g}	I	0	A
8.81E−005	2060	A_{2u}	A	2093	I

A and I denote active and inactive, respectively.

Table S6: Calculated frequencies of lattice vibrations at Γ point in compound **1**. The $P31m$ space group was used to circumvent ammonium cation disorder.

Eigenvalues / Ha^2	Wavenumber /cm^{-1}	Symmetry	IR	$Intensity_{IR}$ /km/mol	Raman
−3.09E−010	−4	E	A	0	A
1.41E−009	8	A_1	A	0	A
6.62E−009	18	E	A	3	A
6.30E−008	55	E	A	13	A
1.54E−007	86	A_1	A	3	A
1.83E−007	94	E	A	355	A
3.02E−007	121	A_1	A	64	A
4.98E−007	155	A_1	A	0	A
5.77E−007	167	A_1	A	3	A
5.82E−007	167	E	A	0	A
6.57E−007	178	E	A	0	A
8.16E−007	198	E	A	0	A
8.44E−007	202	A_1	A	182	A
1.01E−006	221	A_2	I	0	I
1.13E−006	234	E	A	0	A
1.31E−006	251	A_2	I	181	I
2.08E−006	317	E	A	75	A
2.25E−006	329	E	A	730	A
2.62E−006	355	A_2	I	0	I
5.78E−006	528	E	A	11	A
6.19E−006	546	E	A	4	A
7.36E−006	595	E	A	2090	A
7.66E−006	607	E	A	3316	A
8.28E−006	632	A_1	A	746	A
8.40E−006	636	E	A	2	A
9.52E−006	677	A_1	A	0	A
1.37E−005	812	A_2	I	0	I
1.42E−005	827	A_2	I	0	I
3.65E−005	1325	A_1	A	0	A
4.64E−005	1495	E	A	813	A
4.64E−005	1496	A_1	A	427	A
6.22E−005	1730	E	A	2	A
8.78E−005	2056	A_1	A	2127	A
2.34E−004	3359	A_1	A	252	A
2.43E−004	3422	E	A	1081	A
2.54E−004	3498	A_1	A	646	A

A and I denote active and inactive, respectively.

References

(1) Roisnel, T.; Rodriguez-Carvajal, J. FullProf.98 and WinPLOTR. 1998.