Supplementary material

Structure and vibrational spectra of formamidinium bromide

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Table S1. Structural parameters of FABr optimized by DFT computations with PW basis sets
Space symmetry group $P2_1/c$

a=4.6838 Å, b=13.4591 Å, c=6.6887 Å, □=90.30˚

Atom	*x/a*	*y/b*	*z/c*
H1	0.7213	0.4263	0.5664
H2	0.4923	0.4861	0.7429
H3	0.1055	0.2515	0.8037
H4	0.1248	0.3731	0.9091
H(C)	0.5658	0.2741	0.6017
C	0.4265	0.3369	0.6926
N1	0.5673	0.4215	0.6769
N2	0.2080	0.3203	0.8125
Br	0.8868	0.3939	0.2353

Table S2. Structural parameters of FABr optimized by DFT computations with AO basis sets
Space symmetry group $P2_1/c$

a=4.4774 Å, b=13.1454 Å, c=6.5691 Å, □=93.96˚

H1	0.7467	0.4259	0.55081
H2	0.5586	0.4866	0.7487
H3	0.1096	0.2540	0.7892
H4	0.1568	0.3760	0.9054
H(C)	0.4920	0.2756	0.5763
C	0.4403	0.3386	0.6780
N1	0.6000	0.4218	0.6662
N2	0.2281	0.3225	0.8034
Br	0.8747	0.3936	0.2143

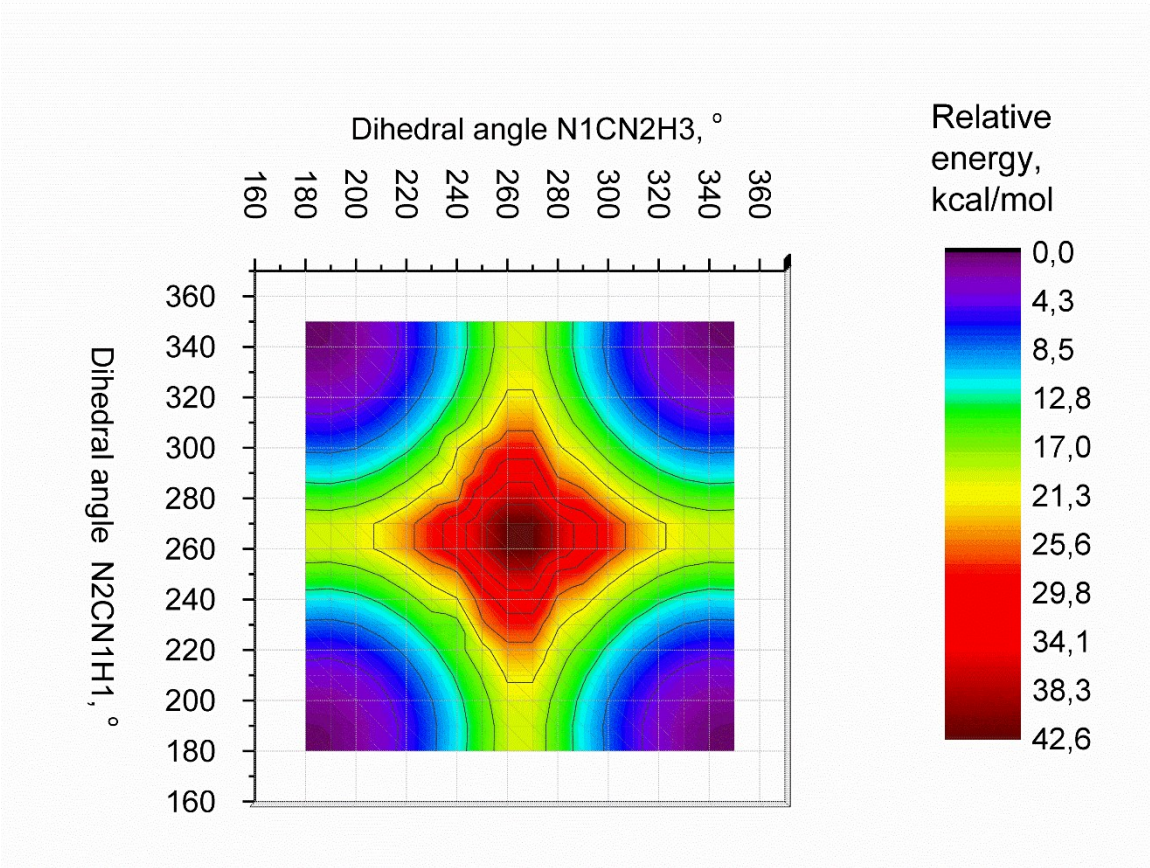


Figure S1. 2D scan of potential energy with respect to the FA torsion deformations determined by NCNH dihedral angles. Zero energy level corresponds to equilibrium FA configuration. For atomic labels see Figure 1.

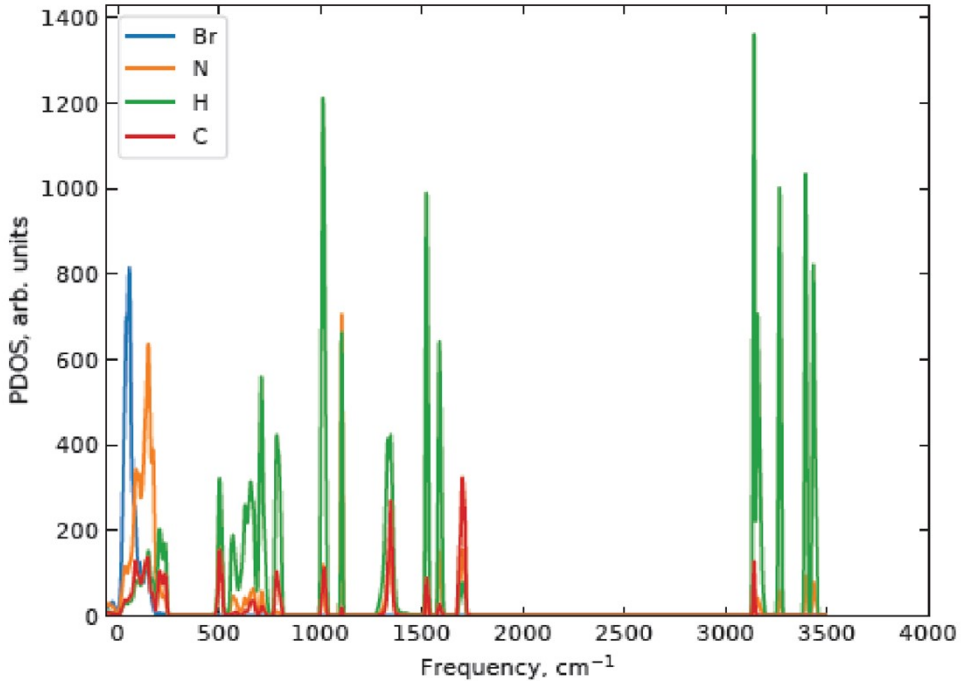


Figure S2. The FABr crystal partial (joined) density of vibrational states

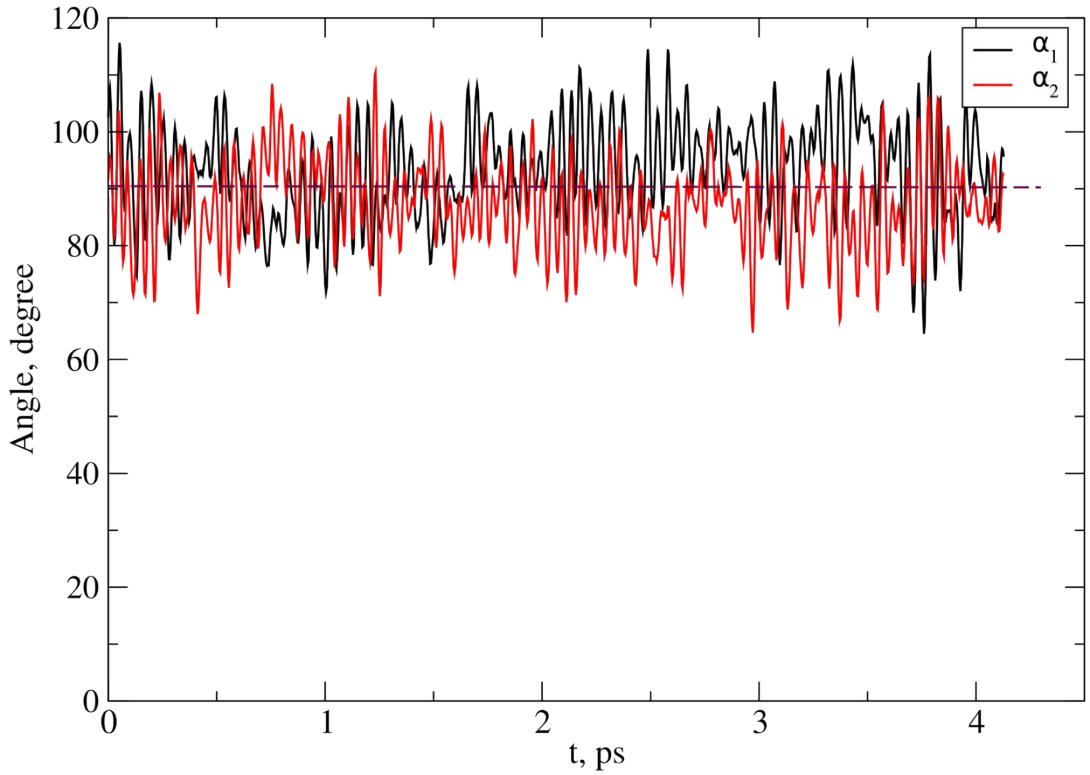


Figure S3. The MD-simulated temporary dependence of angles between H-H vectors and the normal to the N1-C-N2 plane for a selected cation in FABr crystal. Black (a1) and red (a2) lines corresponds to the H1-H2 and H3-H4 (a2) vectors, respectively. The mean values for both angles are shown by dashed line. For atomic labels see Figure 1

Table S3. Raman active modes of FABr crystal

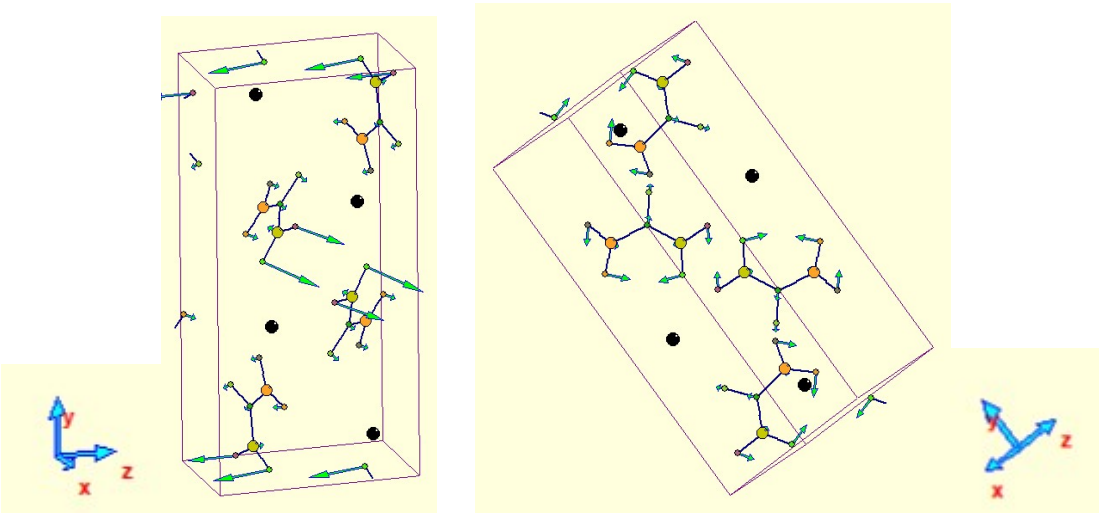
Calculation with AO basis			Calculation with PW basis		
symm	Freq. cm^{-1}	Intensity* arb.unit	symm	Freq. cm^{-1}	Intensity $Å^4$/amut
Ag	25	0.94	Ag	29	0.36
Bg	25	0.59	Bg	30	0.21
Ag	50	0.26	Ag	41	0.48
Bg	51	0.59	Bg	42	0.76
Ag	57	0.50	Ag	55	0.93
Bg	72	1.09	Ag	62	2.50
Ag	80	0.64	Bg	69	1.04
Bg	102	0.81	Bg	87	0.87
Bg	106	0.25	Bg	96	5.24
Ag	123	1.32	Ag	114	20.63
Ag	139	7.62	Ag	126	7.57
Bg	158	0.56	Bg	136	2.94
Ag	165	6.72	Ag	154	42.61
Bg	172	0.40	Bg	156	6.16
Ag	179	7.88	Ag	160	39.94
Bg	194	1.50	Bg	183	4.50
Ag	202	11.14	Ag	194	33.87
Bg	227	14.38	Bg	216	26.76
Ag	503	17.89	Ag	511	87.77
Bg	509	28.94	Bg	512	80.56
Bg	653	5.46	Ag	630	17.03
Ag	667	10.00	Bg	630	5.23
Bg	674	7.10	Bg	681	68.92
Ag	677	4.37	Ag	683	60.21
Ag	754	20.97	Ag	695	77.06
Bg	755	8.24	Bg	709	48.56
Ag	797	15.46	Ag	778	63.96
Bg	823	1.04	Bg	791	4.72
Bg	995	7.32	Bg	999	23.38
Ag	1003	9.13	Ag	1009	16.89
Bg	1012	12.33	Ag	1021	12.00
Ag	1026	5.96	Bg	1024	24.59
Ag	1110	66.34	Ag	1104	356.55
Bg	1121	1.80	Bg	1106	21.57
Ag	1325	67.45	Ag	1316	209.71
Bg	1326	3.04	Bg	1318	7.57
Bg	1338	8.52	Ag	1342	510.38
Ag	1341	104.67	Bg	1344	8.47
Ag	1507	42.30	Ag	1510	127.54
Bg	1508	34.11	Bg	1515	104.51
Ag	1568	18.04	Ag	1575	62.25
Bg	1581	8.47	Bg	1584	49.15
Ag	1711	5.90	Ag	1679	23.75
Bg	1725	3.35	Bg	1685	1.12
Ag	3032	334.87	Ag	3025	1291.05
Bg	3078	396.49	Bg	3058	879.89
Ag	3092	227.27	Ag	3058	1154.62
Bg	3099	81.00	Bg	3070	1343.83
Ag	3171	780.21	Bg	3145	104.95
Bg	3181	33.62	Ag	3153	3884.61
Ag	3244	1000.00	Ag	3230	2669.07
Bg	3277	37.81	Bg	3243	877.43
Bg	3308	116.01	Ag	3244	3281.98
Ag	3309	355.20	Bg	3255	923.87

*Raman intensities under Placzek approximation are computed as isotropic (polycrystalline powder)

Table S4. IR-active modes of FABr crystal

Calculation with AO basis			Calculation with PW basis			
symm	freq. cm^{-1}	IR intensity* km/mol	symm	freq. cm^{-1}	IR intensity $(D/A)^2/amu$	IR intensity km/mol
Au	35	1.31	Au	29	0.033	1.39
Bu	37	69.28	Au	35	0.078	3.30
Au	45	1.03	Bu	46	1.488	62.88
Bu	76	103.38	Bu	63	1.363	57.60
Au	88	4.49	Au	74	0.009	0.38
Au	108	102.32	Au	97	1.870	79.02
Bu	109	51.12	Bu	103	0.559	23.62
Bu	140	67.67	Bu	115	2.971	125.54
Au	143	6.72	Au	116	0.278	11.75
Bu	153	42.84	Bu	145	1.495	63.17
Bu	168	310.38	Au	158	1.928	81.47
Au	170	0.36	Au	168	2.553	107.88
Au	180	155.68	Bu	175	4.928	208.24
Bu	228	3.28	Bu	207	0.006	0.25
Au	251	12.26	Au	231	0.093	3.93
Au	506	89.25	Au	516	1.881	79.48
Bu	509	28.21	Bu	521	0.088	3.72
Au	614	208.47	Au	596	1.907	80.58
Bu	619	2154.52	Bu	598	55.634	2350.88
Bu	687	489.77	Bu	662	8.486	358.59
Au	690	12.22	Au	668	0.047	1.99
Bu	770	277.95	Bu	711	7.379	311.81
Au	784	101.32	Au	741	1.926	81.39
Bu	803	206.11	Bu	790	2.324	98.20
Au	821	6.84	Au	794	0.190	8.03
Bu	995	377.54	Au	1003	1.761	74.41
Au	1001	28.00	Au	1017	0.304	12.85
Au	1011	75.98	Bu	1017	6.324	267.23
Bu	1039	189.32	Bu	1020	4.856	205.20
Bu	1110	13.94	Bu	1103	0.236	9.97
Au	1112	5.02	Au	1107	0.089	3.76
Bu	1320	85.70	Bu	1316	4.077	172.28
Au	1325	166.57	Au	1316	5.459	230.68
Bu	1338	63.28	Bu	1341	1.105	46.69
Au	1347	52.70	Au	1347	1.303	55.06
Bu	1510	54.08	Bu	1514	0.806	34.06
Au	1515	66.72	Au	1515	0.004	0.17
Bu	1565	439.21	Bu	1571	8.122	343.20
Au	1577	115.64	Au	1579	3.048	128.80
Au	1704	1036.29	Au	1673	23.165	978.86
Bu	1713	2549.55	Bu	1678	50.879	2149.95
Au	3038	5663.64	Au	3028	156.174	6599.30
Bu	3045	4696.36	Bu	3038	101.924	4306.91
Bu	3092	52.23	Bu	3058	0.626	26.45
Au	3094	240.34	Au	3059	2.285	96.56
Au	3164	9.09	Au	3141	7.321	309.36
Bu	3170	3700.91	Bu	3147	45.641	1928.61
Bu	3244	1695.51	Au	3229	63.796	2695.77
Au	3248	2325.44	Bu	3230	53.162	2246.42
Au	3326	649.07	Bu	3271	77.207	3262.47
Bu	3332	1990.78	Au	3273	1.881	79.48

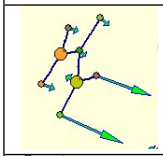
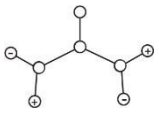
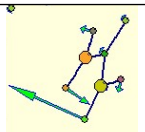
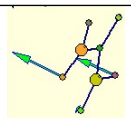
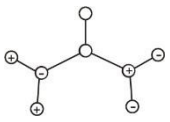
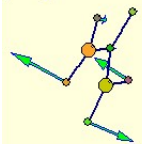
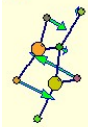
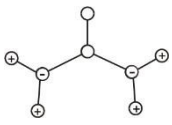
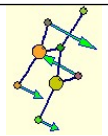
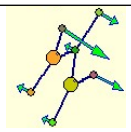
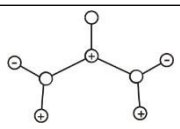
*integrated IR intensities, in units KM/MOL, are computed under the hypothesis of of isotropic response (i.e for a powder ample)



(a) (b)

Figure S4. Unit cell orientations used to depict atomic displacements for vibration modes involving the out-of-plane (a) and in-plane (b) oscillations of cations. The cations used in Tables S5 and S6 are highlighted by blue rectangles.

Table S5. Out-of-plane vibrational modes of FA cation in FABr crystal and in isolated state

FABr crystal			Isolated FA+			
Form	□ (cm^{-1})	Assignment	Form	□ (cm^{-1})	IR	Assignment
	614, 619, 652	□(H1+H2)		542	A2	□$_{as}$(NH2)
	667	□(H1-H4)				
	677	□(H2+H4)		616	A2	□$_{as}$(NH2)
	674, 687, 690	□(□1-□2-□4)				
	754, 755	□(□2-□3-□4)		639	B1	□$_{s}$(NH2)
	770, 784	□(□2-□3)				
	797, 804	□$_{s}$(NH_2)		714	B1	□$_{s}$(NH_2)

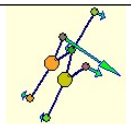
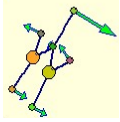
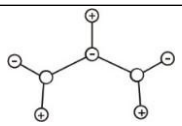
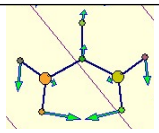
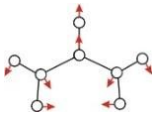
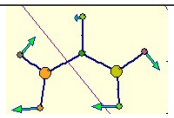
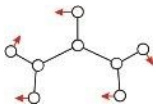
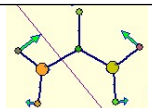
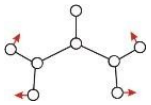
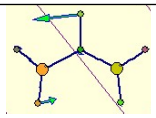
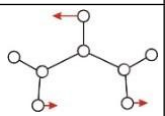
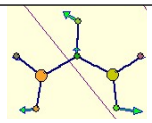
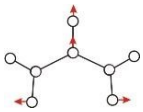
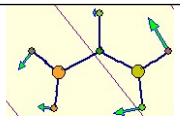
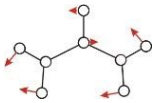
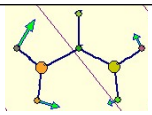
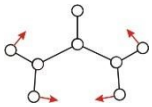
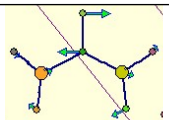
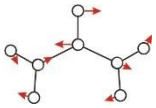
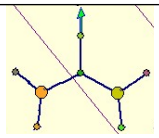
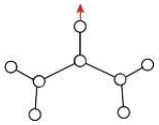
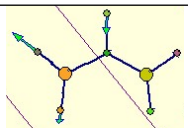
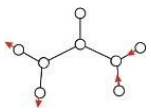
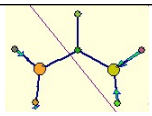
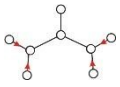
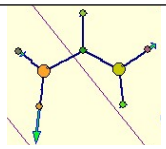
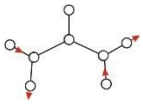
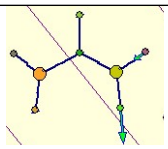
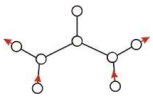
	821, 823					
	1011, 1012, 1026, 1039	□(CH)		1022	B1	□(CH)

Table S6. In-plane bending modes of FA cation in FABr crystal and in isolated state

FABr crystal			Isolated FA+			
Form	□ (cm^{-1})	Assignment	Form	□ (cm^{-1})	symm	Assignment
	503-510	□(NCN)		502	A1	□(NCN)
	994-1003	$\square_{as}(NH_2)$		991	B2	$\square_{as}(NH_2)$
	1110-1121	$\square_{s}(NH_2)$		1091	A1	$\square_{s}(NH_2)$
	1322-1326	□(CH)		1334	B2	□(CH)
	1337-1347	$\square_{s}$(NCN)		1365	A1	$\square_{s}$(NCN)
	1507-1514	$\square_{as}$(HNH)		1551	B2	$\square_{as}$(HNH)
	1567-1581	$\square_{s}$(HNH)		1619	A1	$\square_{s}$(HNH)
	1704-1726	$\square_{as}$(NCN)		1743	B2	$\square_{as}$(NCN)
	3092-3099	□(C-H)		3145	A1	□(CH)
	3032-3078	□(N-H3)		3417	B2	$\square_{s\text{-}as}(NH_2)$
	3164-3181	□(N-H1)		3431	A1	$\square_{s\text{-}s}(NH_2)$

	3243-3277	ν_s(N-H4)		3532	B2	$\nu_{as\text{-}as}(NH_2)$
	3308-3332	ν(N-H2)		3534	A1	$\nu_{as\text{-}s}(NH_2)$