A comparative study of the lattice dynamics of alkali titanium hexahalides

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Abstract

This file contains supplementary figures and tables for the main article.

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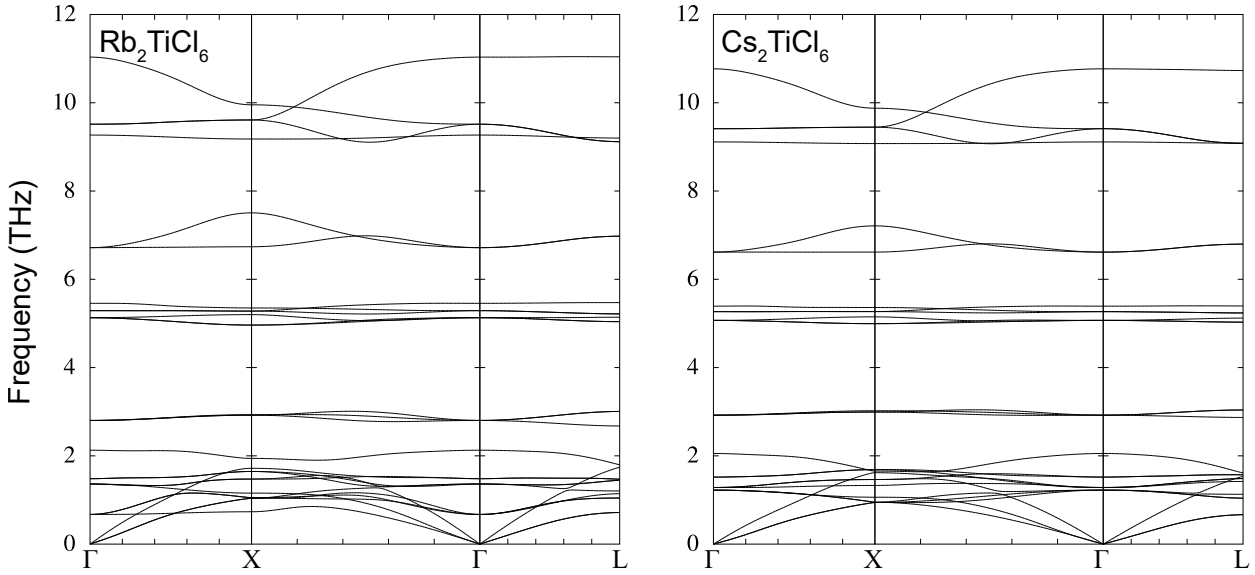

FIG. S1: Phonon dispersion curves of Rb_2TiCl_6 (left) and Cs_2TiCl_6 (right) in the space group of $Fm\bar{3}m$. The wave vectors lables are Γ = [0, 0, 0], X = [0, 0, 1] and L = [1/2, 1/2, 1/2].

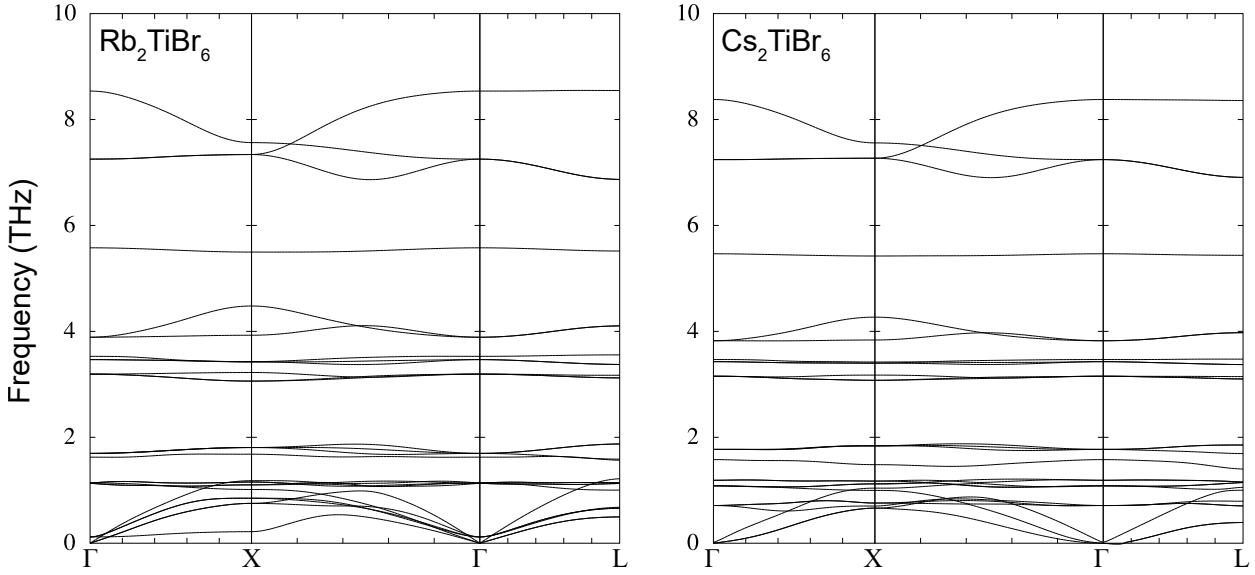

FIG. S2: Phonon dispersion curves of Rb_2TiBr_6 (left) and Cs_2TiBr_6 (right) in the space group of $Fm\bar{3}m$. The wave vectors lables are Γ = [0, 0, 0], X = [0, 0, 1] and L = [1/2, 1/2, 1/2].

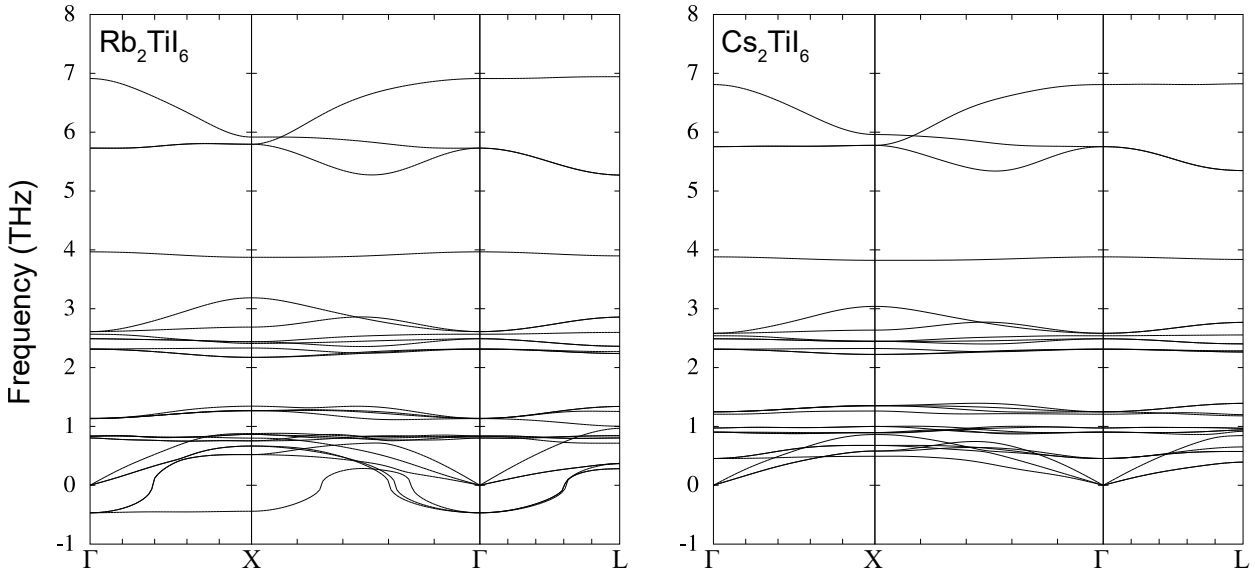

FIG. S3: Phonon dispersion curves of Rb_2TiI_6 (left) and Cs_2TiI_6 (right) in the space group of $Fm\bar{3}m$. The wave vectors lables are Γ = [0, 0, 0], X = [0, 0, 1] and L = [1/2, 1/2, 1/2]. Negative values indicate imaginary values, from the fact that the calculated frequency-squared values are negative.

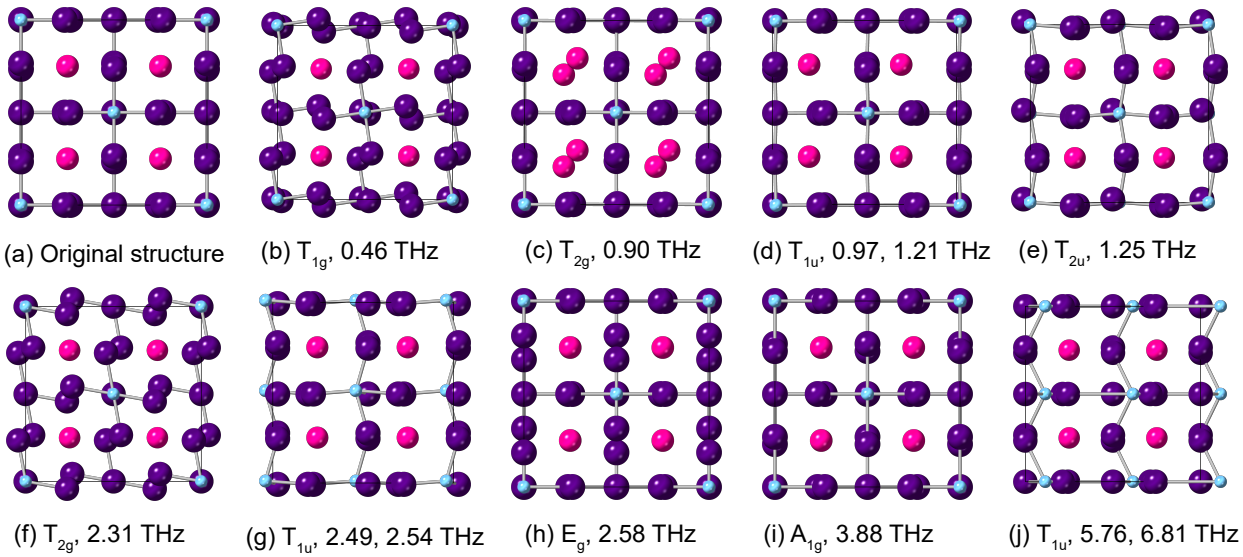

FIG. S4: Representations of mode eigenvectors and corresponding frequencies at zero wave vector for Cs_2TiI_6. Pink, blue and purple spheres denote Cs, Ti and I elements, respectively, and the silver rods denote the Ti–I bonds. (a) shows the original crystal structure viewed from the $[1, 0, 0]$ direction. (b) shows the external mode involving rotations of the TiI_6 octahedra. (c, d) show the external modes involving displacements of the Cs cations and whole-body displacements of the TiI_6 octahedra. (e, f, g) show the three different types of internal modes with bending of the bonds within the TiI_6 octahedra. (h, i) show the internal nodes with stretching of the Ti–I bonds in a way that preserves the octahedral centre of symmetry, with (i) showing the totally-symmetric stretch mode. (j) shows the asymmetric-stretch internal mode in which the Ti cation is displaced from the centre of the TiI_6 octahedra and stretches and contracts the two Ti–I bond in the direction of the displacement.

TABLE S1: Calculated frequencies in units of THz for double perovskites A_2TiX_6 at zero wave vector, where modes are labelled by their irreducible representation. For each mode we indicate the type of motion: rot means whole-body rotations of the TiX_6 octahedra; d means whole body displacements of the TiX_6 octahedra and A cations, where the two cases correspond to motions that either break or preserve the centre of symmetry; b denotes bending of bonds within the TiX_6 octahedra, with only small (or none in the case of the T_{2u} mode) displacements of the cations; ss denotes stretching modes in which the centre of symmetry is preserved because the displacements are symmetric along the linear X–Ti–X connections; and as denotes stretching modes involving the loss of the centre of symmetry because the displacements are antisymmetric along the linear X–Ti–X connections. The two imaginary values represent the fact that the calculated values of the squared frequencies are negative.

Mode	Motion	Rb_2TiF_6	Rb_2TiCl_6	Rb_2TiBr_6	Rb_2TiI_6	Cs_2TiF_6	Cs_2TiCl_6	Cs_2TiBr_6	Cs_2TiI_6
T_{1g}	rot	0.85i	0.67	0.12	0.47i	1.00	1.28	0.71	0.46
T_{2g}	d	1.89	1.36	1.14	0.84	1.55	1.22	1.08	0.90
T_{1u}	d	1.99, 3.34	1.48, 2.13	1.13, 1.62	0.80, 1.14	1.89, 3.05	1.52, 2.05	1.19, 1.58	0.97, 1.21
T_{2u}	b	4.14	2.80	1.70	1.13	4.27	2.92	1.77	1.25
T_{2g}	b	8.13	5.13	3.20	2.32	8.01	5.07	3.16	2.31
T_{1u}	b	8.15, 8.59	5.29, 5.46	3.47, 3.53	2.49, 2.57	8.12, 8.51	5.27, 5.40	3.43, 3.47	2.49, 2.54
E_g	ss	13.48	6.72	3.89	2.61	13.27	6.62	3.83	2.58
A_{1g}	ss	17.15	9.27	5.58	3.97	16.96	9.12	5.47	3.88
T_{1u}	as	16.57, 18.77	9.52, 11.04	7.26, 8.54	5.73, 6.92	16.33, 18.24	9.42, 10.78	7.25, 8.38	5.76, 6.81