Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Controlling the H to T′ Structural Phase Transition via Chalcogen Substitution in $MoTe_2$ Monolayers

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Table S1. Lattice parameters (in A) of fully relaxed $MoTe_2$ monolayers in the H, T', and T phase and a 6-atom unit cell. The energy is taken with reference to the total energy of the H phase and normalized to the number of formula units.

phase	a (Å)	b (Å)	ΔE (eV/f.u.)
H	3.560	6.166	0
T'	3.463	6.382	0.032
T	3.511	6.082	0.511

Table S2. Formation energy (E_F, in units of eV) of each alloy at a defect concentration of 4.17% under Te-rich and Te-poor conditions.

Dopant	Phase	E_F (eV), Te-rich	E_F (eV), Te-poor	E_{fill} (eV)
N	H	1.745	0.499	-0.113
	T'	2.965	1.734	0.022
P	H	0.554	-0.692	-0.200
	T'	0.345	-0.884	-0.171
Sb	H	0.955	-0.291	-0.171
	T'	0.596	-0.634	-0.152
F	H	0.011	-1.235	-0.240
	T'	-0.833	-2.063	-0.257
Br	H	1.521	0.275	-0.129
	T'	0.505	-0.726	-0.159
I	H	1.855	0.608	-0.105
	T'	0.815	-0.431	-0.136
Se	H	-0.493	-1.740	-0.277
	T'	-0.202	-1.432	-0.211

Table S3. Formation energy (E_F, in units of eV) of each alloy at a defect concentration of 2.08% under Te-rich and Te-poor conditions.

Dopant	Phase	E_F (eV), Te-rich	E_F (eV), Te-poor	E_{fill} (eV)
N	H	1.742	0.495	-0.106
	T'	2.744	1.514	0.012
P	H	0.547	-0.699	-0.194
	T'	0.291	-0.939	-0.168
Sb	H	0.947	-0.287	-0.164
	T'	0.574	-0.656	-0.147
F	H	0.013	-1.234	-0.234
	T'	-0.955	-2.185	-0.259
Br	H	1.473	0.226	-0.126
	T'	0.482	-0.748	-0.154
I	H	1.842	0.595	-0.099
	T'	0.796	-0.449	-0.131
Se	H	-0.493	-1.739	-0.271
	T'	-0.201	-1.431	-0.204

Figure S1. Computational supercells used for a concentration of (a) 4.17% in the H phase, (b) 4.17% in the T' phase, (c) 12.5% in the H phase, and (d) 12.5% in the T' phase. The dopant atom is shown in blue.

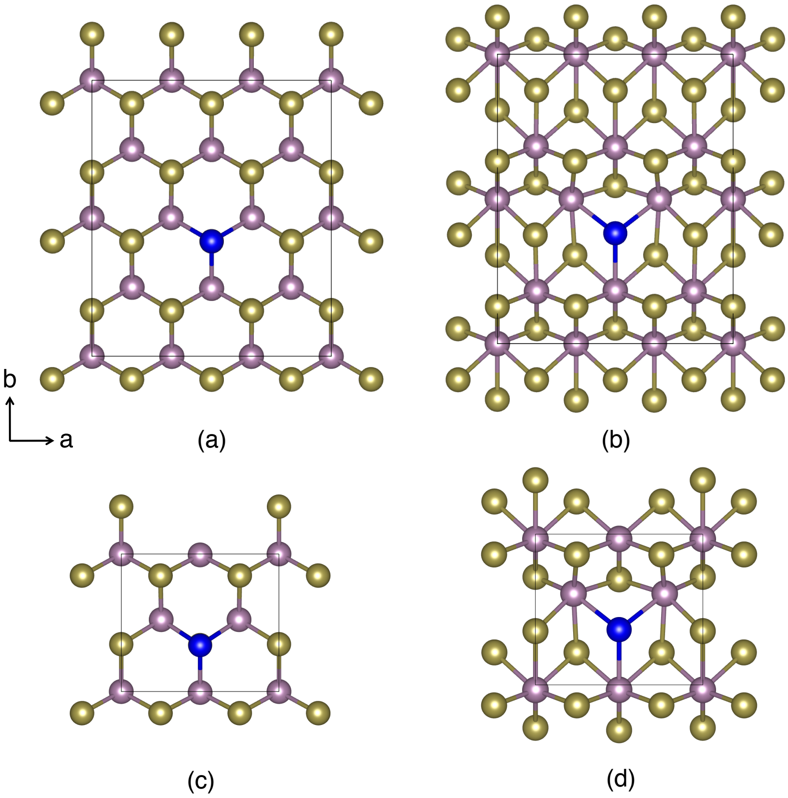


Figure S2. Phonon band structures of MoTe$_{1.75}X_{0.25}$ alloy monolayers in the (a) H phase and (b) T' phase. A lack of negative phonon frequencies indicates that all of these alloys are dynamically stable in both phases.

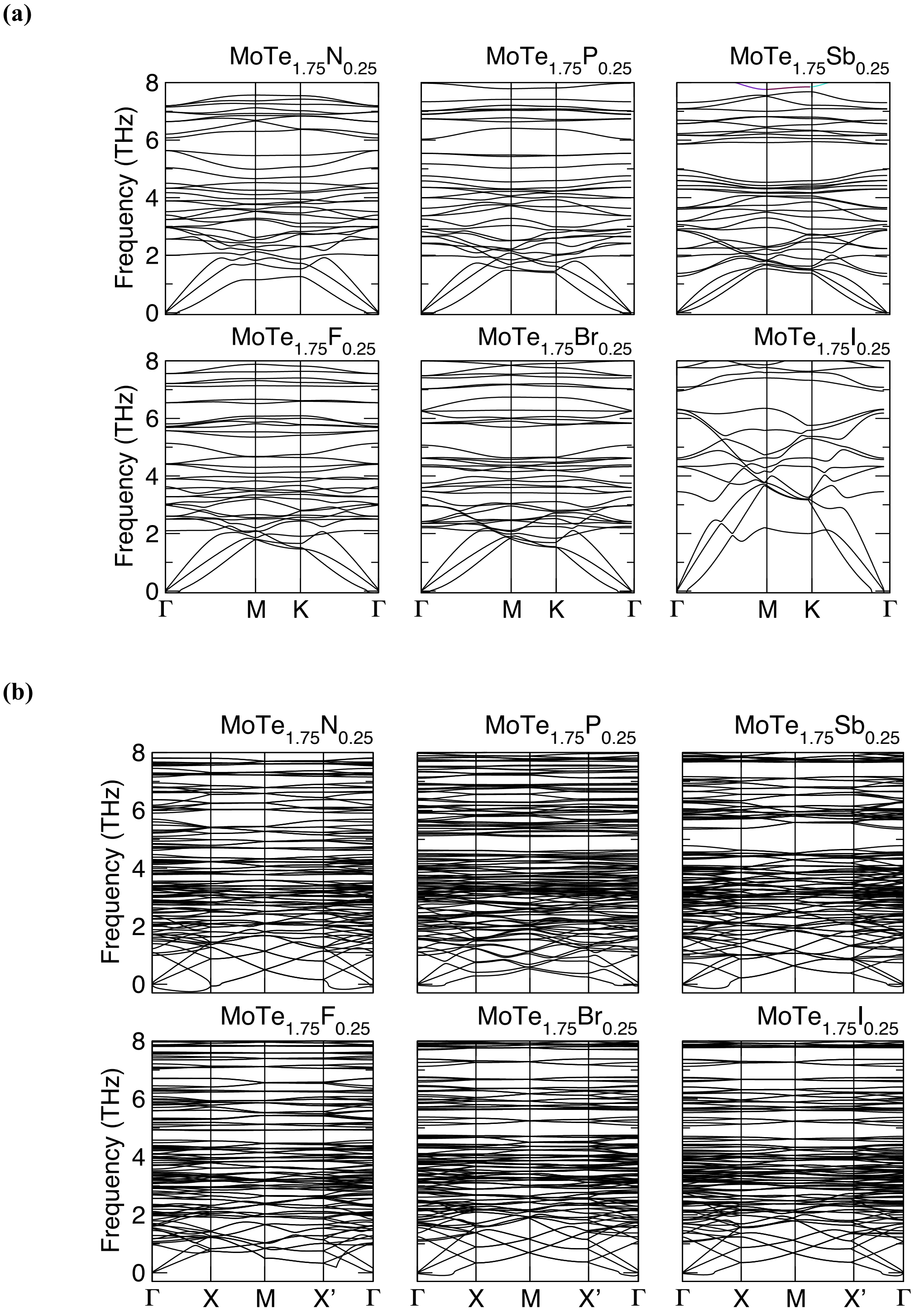


Figure S3. Electronic band structure of $\mathrm{MoTe}_{1.75}X_{0.25}$ alloy monolayers in the H phase. The Fermi level is set to 0 eV.

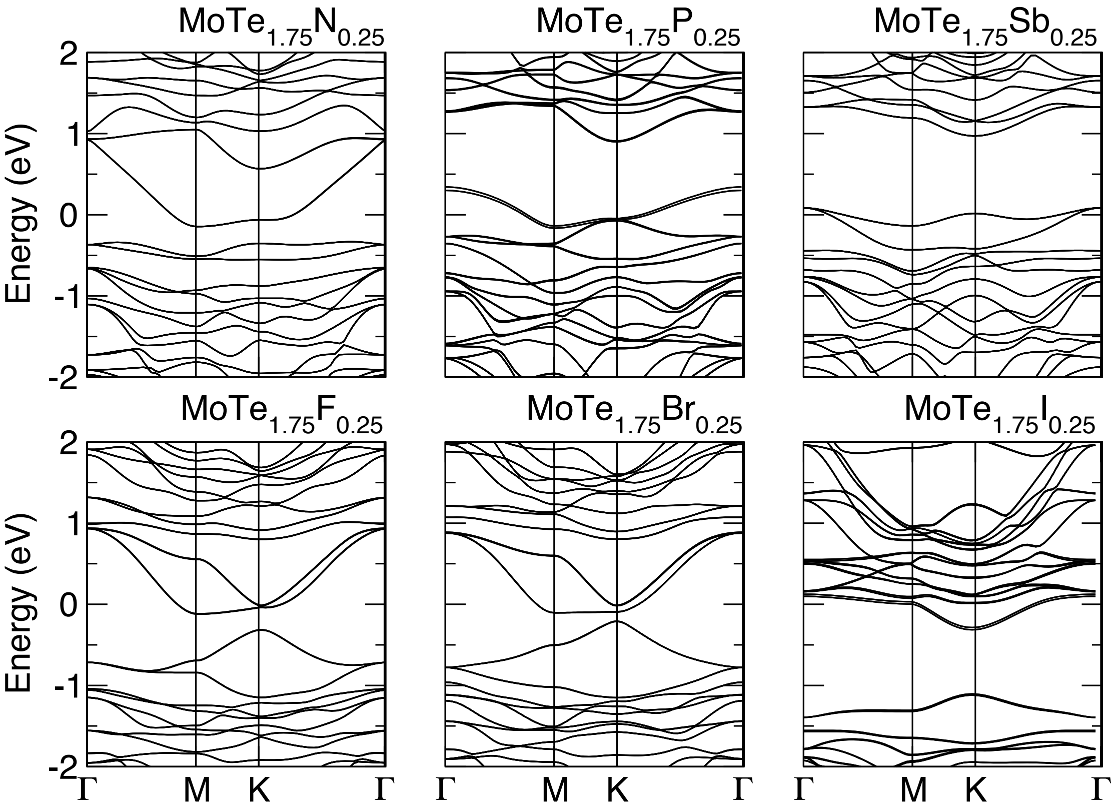


Figure S4. Electronic band structure of the T' phase of (a) $\mathrm{MoTe}_{1.75}X_{0.25}$ and (b) $\mathrm{MoTe}_{1.917}X_{0.083}$ alloy monolayers. The Fermi level is set to 0 eV.

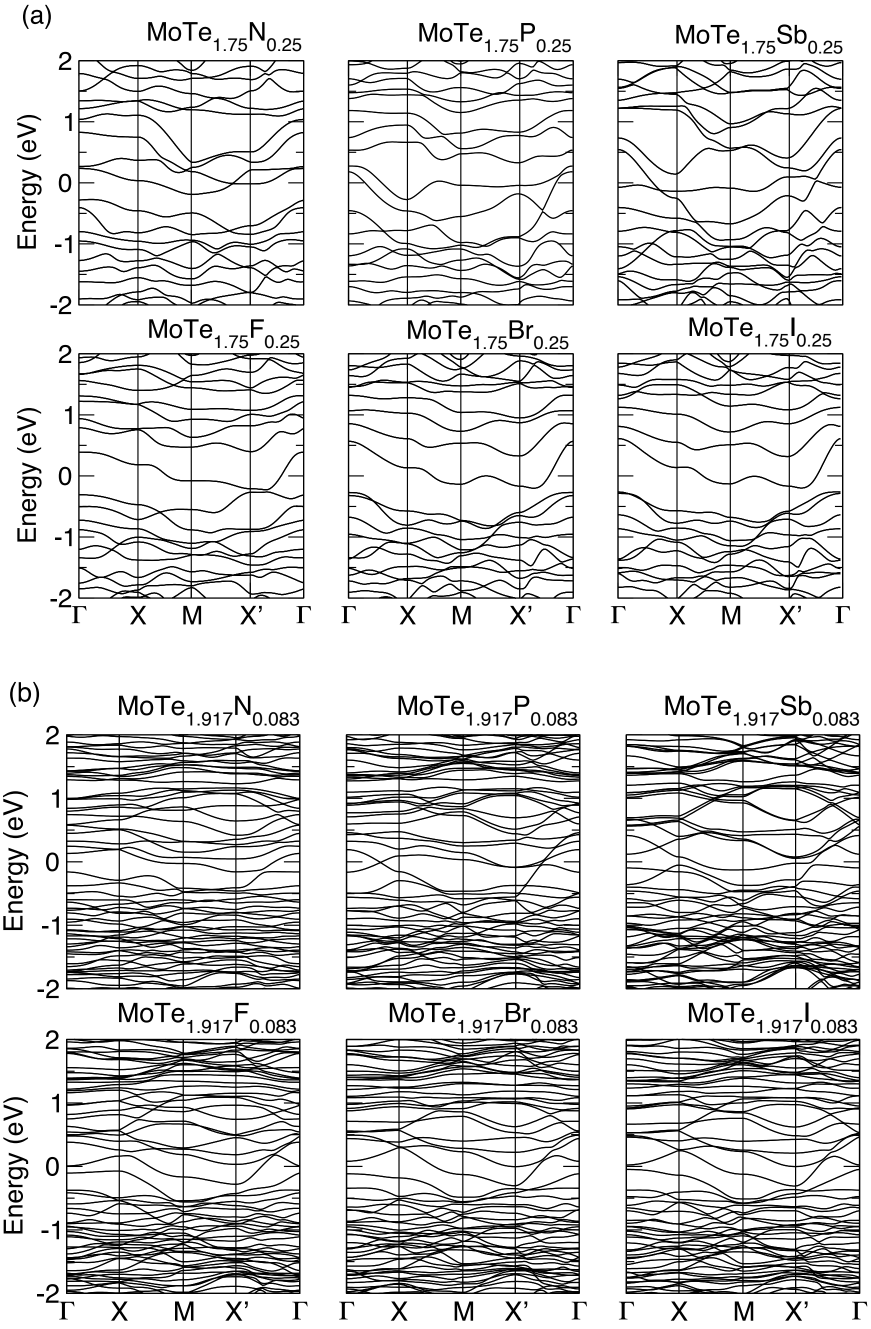
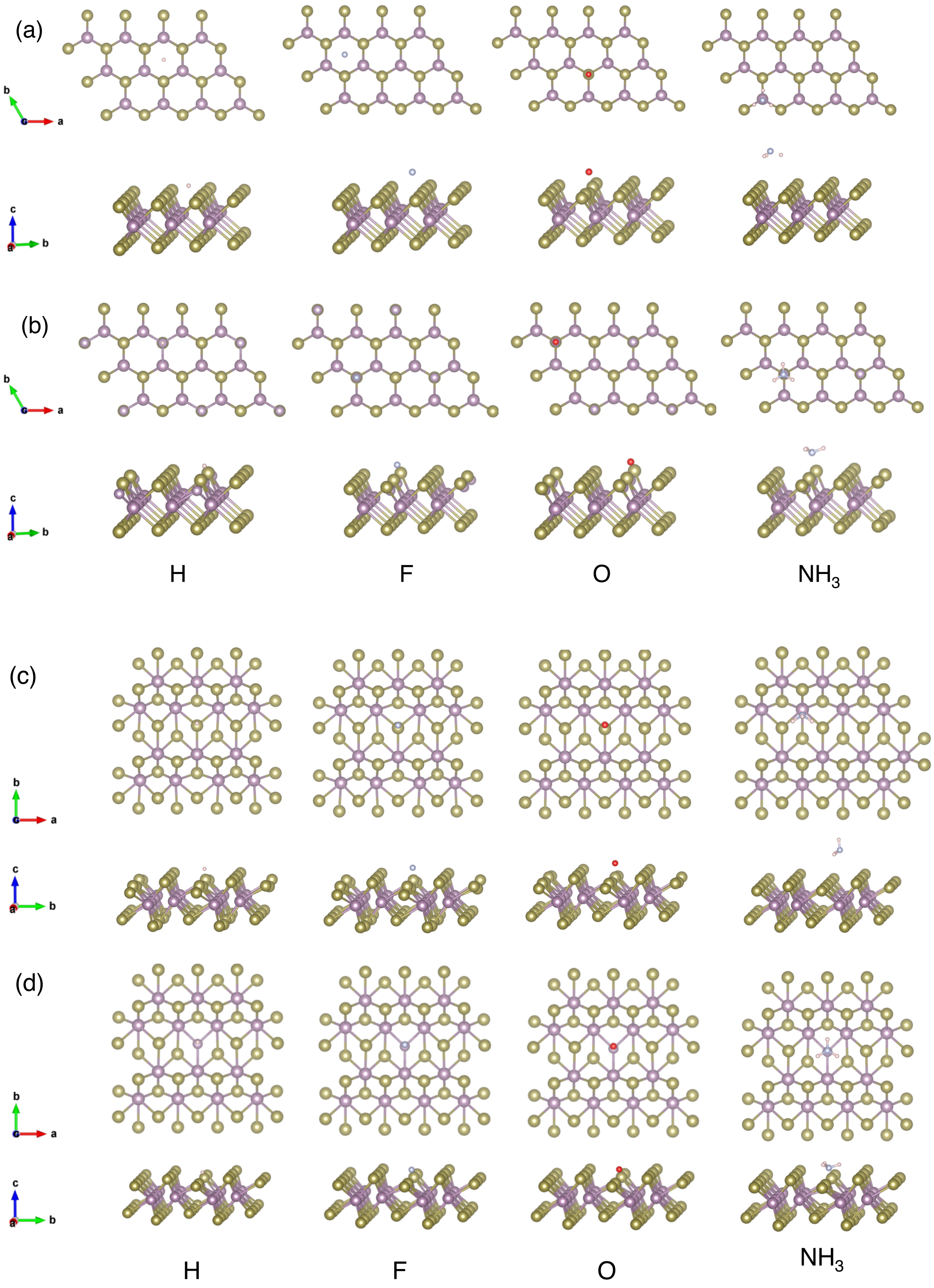


Figure S5. Preferred adsorption sites of H, F, O, and NH_3 adatoms on the (a) H-phase of $MoTe_2$, (b) H-phase of $MoTe_{2-x}P_x$, (c) T'-phase of $MoTe_2$, and (d) T'-phase of $MoTe_{2-x}P_x$ monolayers.



Supplemental Note 1. Detailed description of Δv parameter.

We defined the parameter Δv in equation (3) of the main text, which captures the contribution of electron or hole doping to the change in the energy difference between the H and T' phases of the monolayer alloys. Here, we more clearly describe the physical meaning underlying this quantity. The numerator is the absolute number of electrons or holes introduced to the system upon substitution of a Te atom with an alloying atom X, given by v_{Te} - v_X, where v_{Te} and v_X are the number of electrons in the outermost shell of the neutral atom (e.g., $v_{Te} = 6$, $v_N = 5$, etc.). The denominator is the number of electrons needed to reach a half-filled 4d subshell in the Mo^{4+} cation. Nominally, Mo^{4+} has a $4d^2$ valence electron configuration, so 3 electrons are needed to half-fill the shell (hence the added 3). Upon hole doping (i.e., $v_{Te} - v_X = 1$), 4 electrons are needed to half-fill the 4d subshell, so the denominator becomes 4; upon electron doping (i.e., $v_{Te} - v_X = -1$), the denominator becomes 2. This term was added to equation 5 to account for the fact that both electron *and* hole doping stabilizes the T' phase. This is due to the fact that it is more energetically favorable to add or remove electrons from the states near the Fermi level present in the T' phase than it is to the states in the conduction band of the H phase. A more detailed description of this can be found in Ref. 25 in the main text.