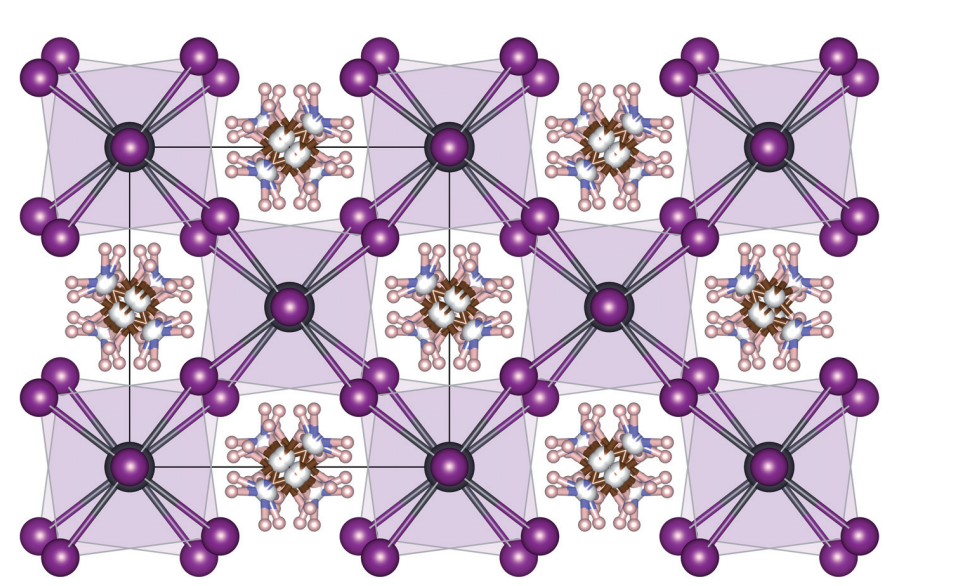


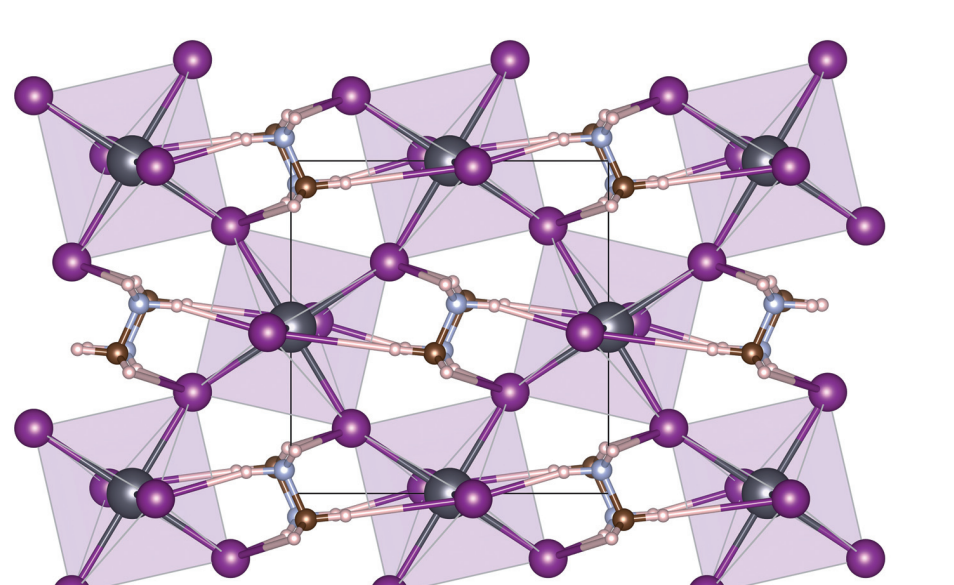
# Influence of chloride substitution on the rotational dynamics of methylammonium in $\text{MAPbI}_{3-x}\text{Cl}_x$ perovskites

## Hydrogen bond layers and rotational jump models

**Tetragonal  $I4/mcm$**   
**162 K**



**Orthorhombic  $Pnma$**   
**161 K**



Schuck et al. [1]

FTIR investigations [1] indicate that in the orthorhombic phase ( $T < 161$  K) the iodide is more strongly influenced by hydrogen bonding than the chloride.

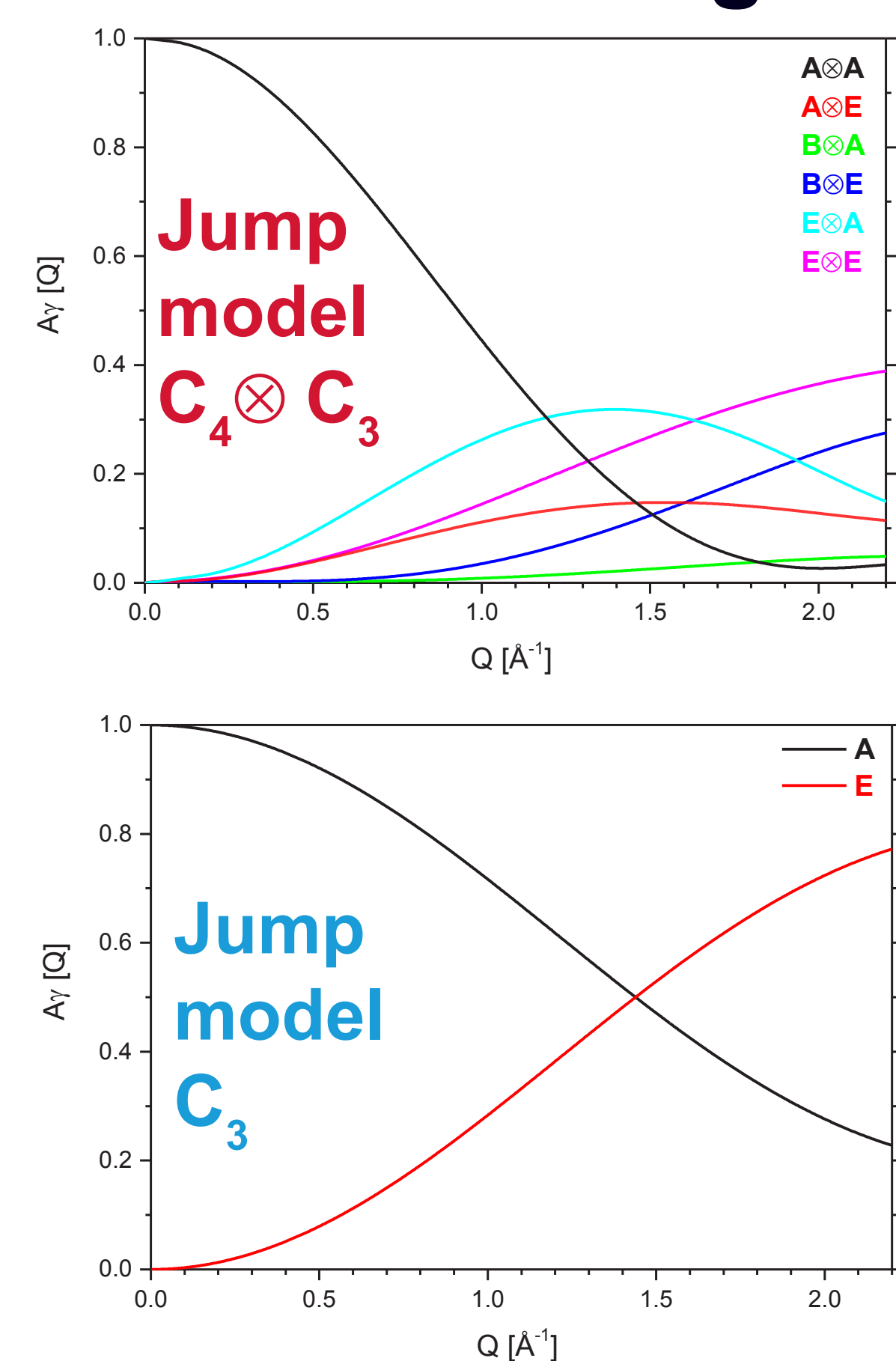
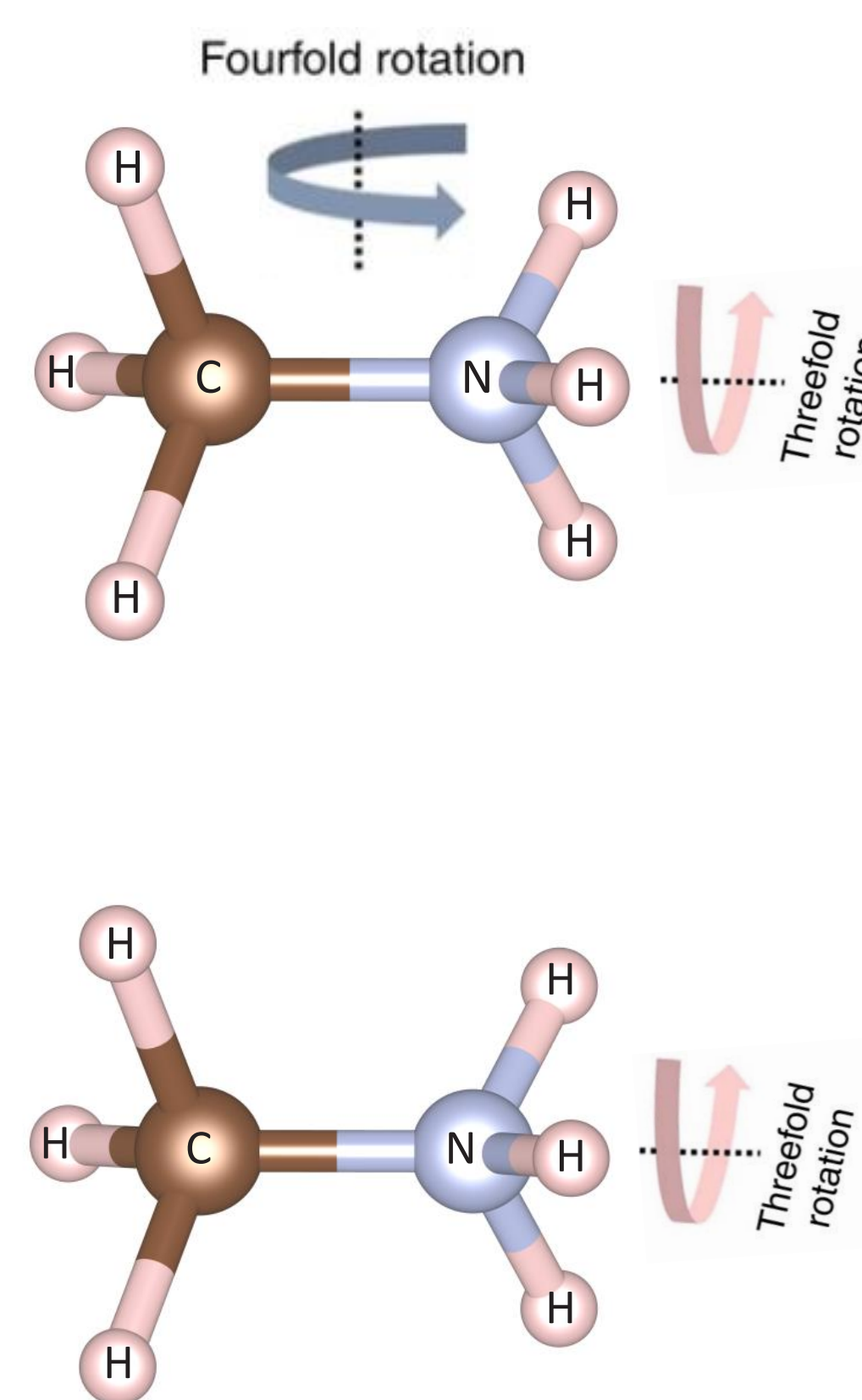
Chen et al. [2] suggested that for quasi-elastic neutron scattering (QENS) of  $\text{MAPbI}_3$  in the tetragonal (161 K to 327 K) phase, the  $\text{CH}_3\text{NH}_3^+$  ions exhibit four-fold rotational symmetry of the C-N axis ( $C_4$ ) along with three-fold jump rotation around the C-N axis ( $C_3$ ) (rotational jump model  $C_4 \otimes C_3$ ). The  $C_4 \otimes C_3$  model includes one elastic component  $A \otimes A$  and five quasi-elastic components (each with quasi-elastic structure factors QISF), convolution products ( $\otimes$ ) of the  $C_3$  and  $C_4$  models components:  $A \otimes E$ ,  $B \otimes A$ ,  $B \otimes E$ ,  $E \otimes A$ , and  $E \otimes E$  (corresponding to five Lorentzian functions).

In the orthorhombic phase ( $T < 161$  K) only  $C_3$  jump rotation is present (rotational jump model  $C_3$ ).

$$S_{\text{theo}(C_3)}(\mathbf{Q}, \omega) = \text{EISF}_{C_3}(\mathbf{Q}) \cdot \delta(\omega) + \text{QISF}_{C_3}(\mathbf{Q}) \cdot L_{C_3}(\Gamma_{C_3}, \omega)$$

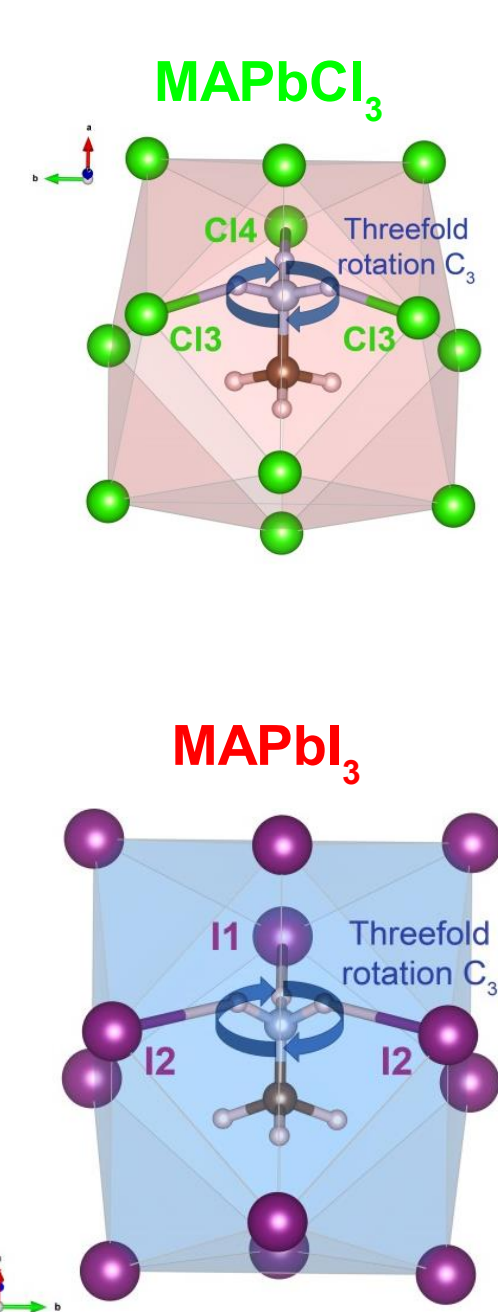
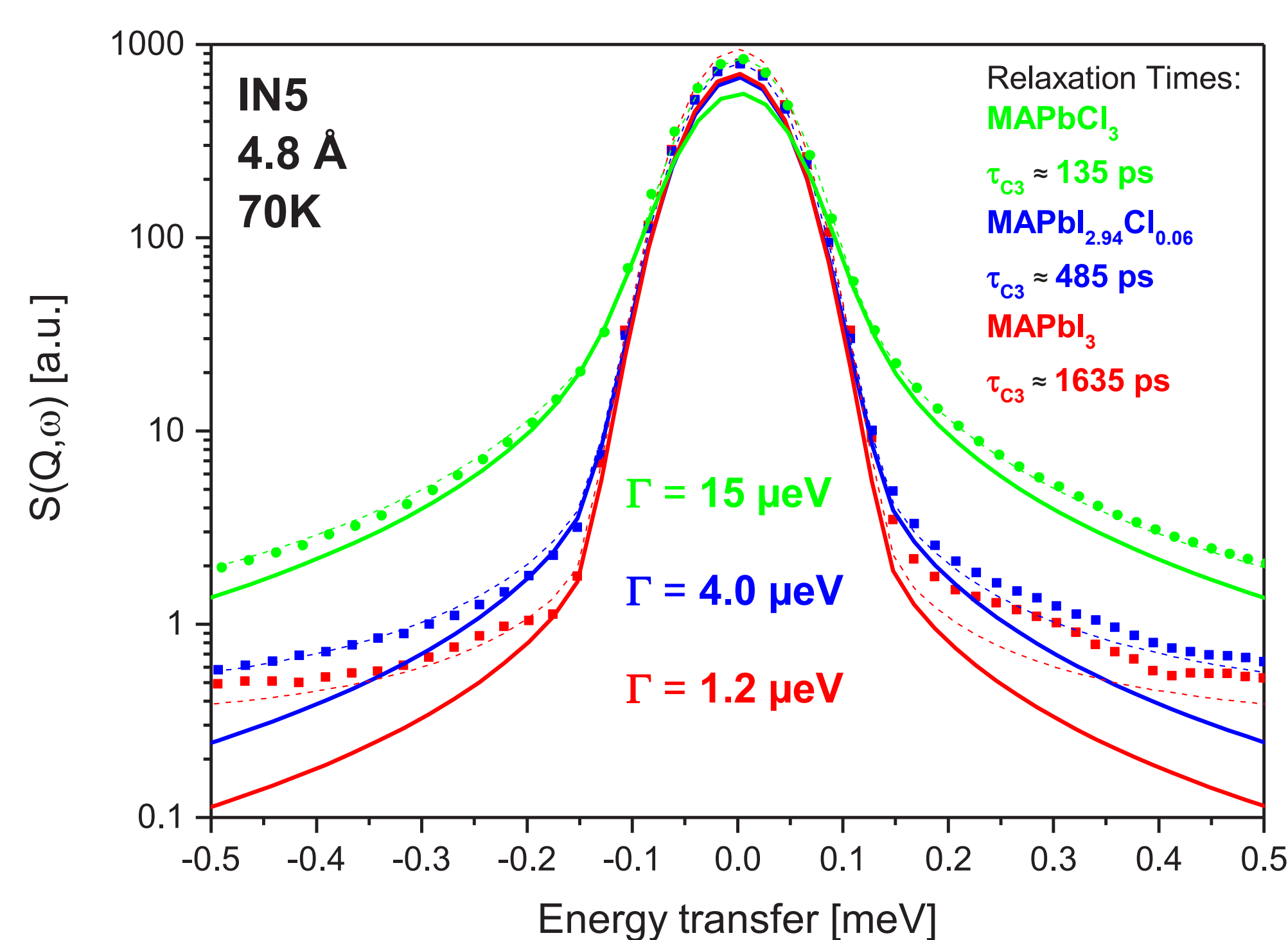
$$\text{QISF}_{C_3} = 2/3[1 - j_0(Qd_{\text{H-H}})]$$

## Quasi-elastic neutron scattering



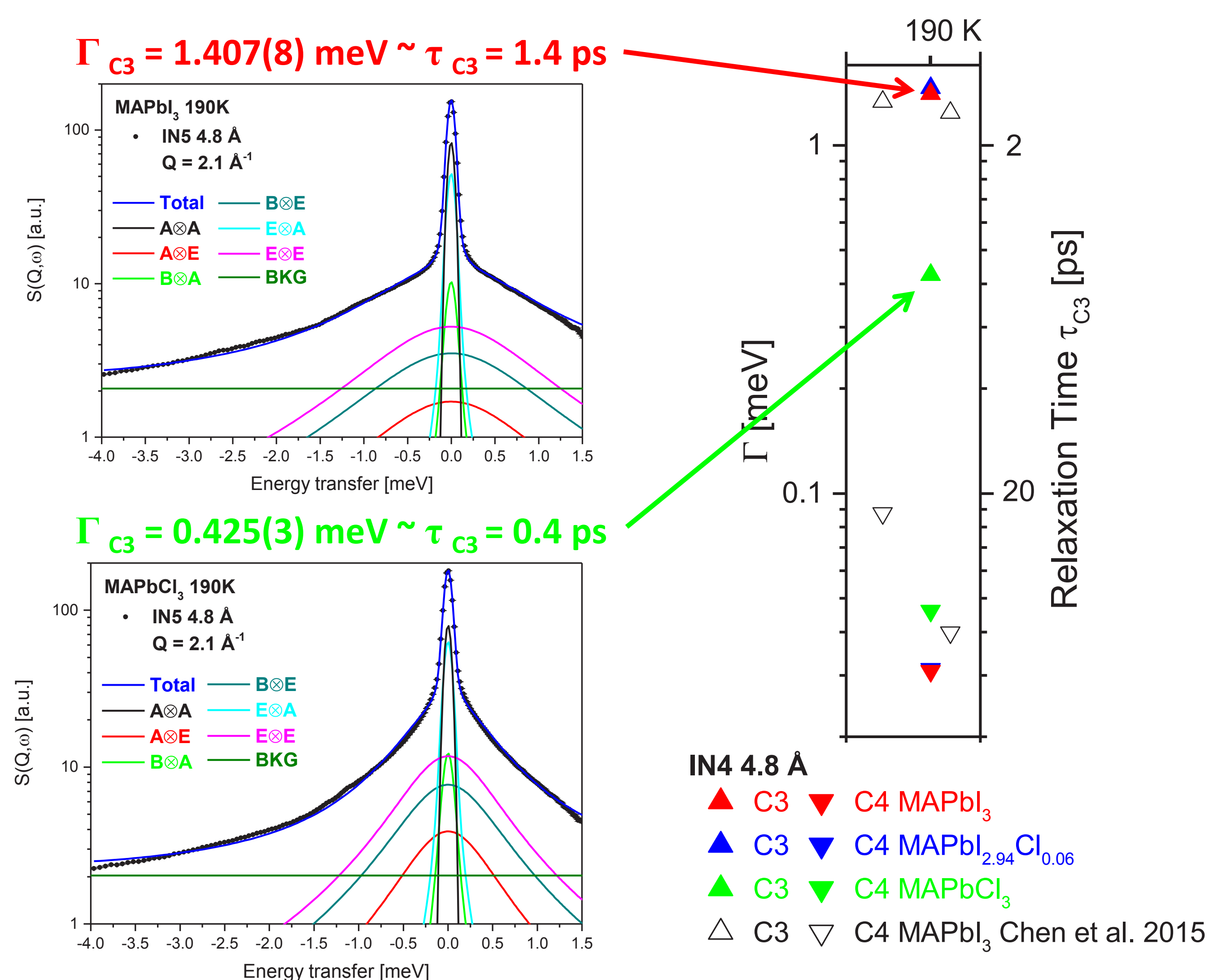
## Analysis of quasi-elastic neutron scattering

### Orthorhombic phase at 70 K

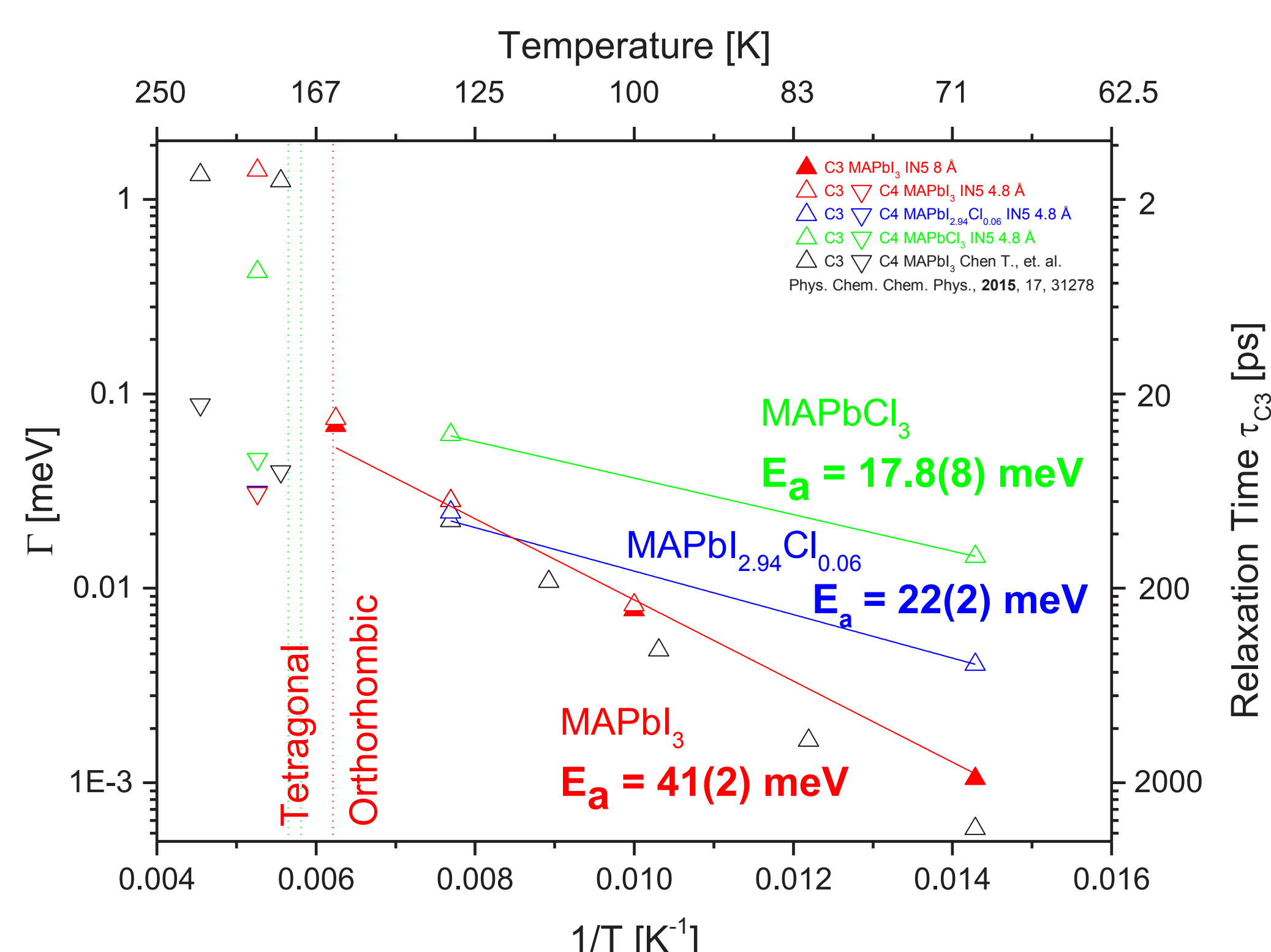


Our results [3] show that chlorine substitution in the orthorhombic phase leads to a weakening of the hydrogen bridge bonds since the characteristic relaxation times of  $C_3$  rotation at 70 K in  $\text{MAPbCl}_3$  (135 ps) and  $\text{MAPbI}_{2.94}\text{Cl}_{0.06}$  (485 ps) are much shorter than in  $\text{MAPbI}_3$  (1635 ps).

### Tetragonal phase at 190 K



## Activation energies



In the tetragonal phase the  $C_3$  component of the MA molecule jump rotation is faster in  $\text{MAPbI}_3$  than in  $\text{MAPbCl}_3$ . This would mean that the influence of the hydrogen bonds in the disordered tetragonal phase of  $\text{MAPbI}_3$  is weaker than in  $\text{MAPbCl}_3$ .

From the temperature-dependent behavior of the experimentally determined HWHM  $\Gamma_{C_3}$ , the activation energies  $E_a$  in the orthorhombic phase for the three halides can be determined according to the Arrhenius law. First of all, the results indicate that the activation energy of  $E_a = 41(2)$  meV determined for  $\text{MAPbI}_3$  is in the range of the  $E_a$  value reported by Chen et al. (48(3) meV) [2]. The activation energies of  $\text{MAPbI}_{2.94}\text{Cl}_{0.06}$   $E_a = 22(2)$  meV and  $\text{MAPbCl}_3$   $E_a = 17.8(8)$  meV are significantly lower compared to  $\text{MAPbI}_3$ . This shows the direct influence of chlorine on the dynamics of the MA jumping rotation. Even small amounts of chlorine obviously weaken the hydrogen bond in the orthorhombic phase so that a faster MA dynamic is possible.

## REFERENCES

- [1] G. Schuck, D. M. Töbrens, M. Koch-Müller, I. Efthimiopoulos, and S. Schorr, J. Phys. Chem. C, **122** (2018) 5227  
 [2] T. Chen, B. J. Foley, B. Ipek, M. Tyagi, J. R. D. Copley, C. M. Brown, J. J. Choi and S.-H. Lee, Phys.Chem.Chem.Phys., **17** (2015) 31278  
 [3] G. Schuck, F. Lehmann, J. Ollivier, H. Mutka, S. Schorr, J. Phys. Chem. C, **123** (2019) 11436