Investigation of the effect of Mg^{2+} incorporation on the structure of $CaCO_3$ clusters by the anharmonic downward distortion following method

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The formation process of $CaCO_3$ polymorphs from aqueous solutions has attracted research for more than a century. Recently, a crystallization pathway through non-classical mechanisms has been put forward as a possible process for early-stage $CaCO_3$ formation [1]. Molecular dynamics simulation studies with accurate force fields have succeeded to provide to a new picture of how $CaCO_3$ growth occurs [2], however this technique cannot be adopted to systems including Mg^{2+}, which is considered to have an influence on $CaCO_3$ polymorph selection, because a Mg^{2+} ion in aqueous solution cannot be released from a tight hydration shell within the time scale of computer simulations.

Therefore in the present study, to investigate the effect of Mg^{2+} incorporation on $CaCO_3$ nucleation, the stable structures of anhydrous additive-free and Mg-containing $CaCO_3$ clusters are derived by using the anharmonic downward distortion following (ADDF) method, which is recently developed to make an automated global exploration for reaction pathways on the quantum chemical potential energy [3-5]. As a result, in the case of the additive-free $CaCO_3$ system, structures similar to calcite appear when four $CaCO_3$ units aggregate into the cluster, while the structure of the Mg-containing $CaCO_3$ tetramer resembles the aragonite structure in the way that CO_3 ions are stacked [6]. These results indicate that Mg^{2+} can play a key role in aragonite formation in the early stages of $CaCO_3$ formation, not only by inhibiting the growth of calcite but also by directly promoting aragonite nucleation.

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