

Addition complex and insertion isomers on the potential energy surface of the reaction of indium dimer with water studied with relativistic ECP.

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Streszczenie

Stationary points on the lowest singlet and triplet $\text{In}_2 + \text{H}_2\text{O}$ potential energy surfaces (PESs) have been explored using the coupled cluster method, including single and double excitations with perturbative triples (CCSD(T)), and the density functional theory (DFT), employing the effective core potential (ECP) for indium (In), which accounts for scalar relativistic effects, with the triple-zeta quality basis set. The CCSD(T) calculated binding energy and anharmonic ν_2 -bending mode frequency for the triplet ground-state addition complex, $\text{In}_2 \cdots \text{OH}_2(^3\text{B}_1)$, are consistent with the complex detected in the matrix isolation infrared (IR) spectroscopic study under the thermal conditions. The two minimum energy crossing points between the triplet and the singlet PESs that have been located between the structures of $\text{In}_2 \cdots \text{OH}_2$ and the transition state for the O–H bond breakage are not likely to be thermally accessible under the low-temperature matrix conditions. With the CCSD(T)-calculated $\text{In}_2 + \text{H}_2\text{O}$ reaction profile and anharmonic vibrational frequencies for several $\text{In}_2(\text{H})(\text{OH})$ insertion product isomers, we support the IR matrix isolation detection (by two experimental groups) of the lowest energy singlet double-bridged $\text{In}(\mu\text{-H})(\mu\text{-OH})\text{In}$ isomer. For the proposed two-step mechanism of H_2 elimination from the $\text{In}_2(\text{H})(\text{OH})$ species, the estimated energy barriers are also compatible with experiment.

Słowa kluczowe

$\text{In}_2\text{-OH}_2$ complex, $\text{In}_2(\text{H})(\text{OH})$ isomers, anharmonic frequencies, singlet and triplet PESs crossing, CCSD(T)/aug-cc-pVTZ

Adres publiczny

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