

HXH⁺ vs X⁺-(H₂) for X = C-Sn: High-level Theoretical Calculations Reveal a Surprisingly High Thermodynamic Stability for the Side-On ²C⁺-(H₂) Complex

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Neutral methylene (HCH) and its heavier group IVA congeners have been the subject of numerous theoretical and spectroscopic studies over the last few decades. In contrast, the few reports concerning the corresponding anions and cations have focused on the derivation of thermodynamic quantities (eg. IEs or EAs via photodetachment or photoionisation), spectroscopic constants or refinement of advanced theoretical methods. Within the literature, there is an implicit (unstated) assumption that the inserted isomers (HXH^{+/-}) are the global minima of the [X,H²]^{+/-} surfaces. While this tenet is well-founded for the anions, it is at least disputable for [X,H₂]⁺, X = Ge, Sn, Pb.

High-level calculations (CCSD(T), B3LYP) will be reported which confirm the side-on isomers X⁺-(H₂), X = C-Ge, are stable with respect to the spin-allowed dissociation ²P X⁺ + ¹Σ_g⁺ H₂; in the case of carbon, ²C⁺-(H₂) is bound by 33 kcal mol⁻¹ according to B3LYP/6-311++G(d,p). Moreover, the results suggest ²B₂ X⁺-(H₂), X = Ge, Sn are the global minima on the respective [X, H₂]⁺ surfaces. Both purely electrostatic (²B₁) and partially covalent (²B₂, see figure) isomers were located, and a decomposition of the bonding in ²B₂ X⁺-(H₂) undertaken. This will be discussed, together with the chemical implications for carbon-containing plasmas.