

On the structures and spectroscopic fingerprints of $(\text{H/D})_n\text{Rg}_m^+$ complexes (Rg = He, Ne, Ar)

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The first members of H_nRg_m^+ complexes (with rare-gas atoms Rg = He, Ne, Ar) are rare-gas-solvated proton ($n = 1$), H_2^+ ($n = 2$), and H_3^+ ($n = 3$). Due to different bonding arrangements these complexes exhibit interesting and diverse structures and complex rovibrational spectra.

The molecular structures, the (ro)vibrational energy levels, and the spectroscopic fingerprints of the complexes HHe_n^+ , corresponding to He-solvated proton, have been investigated experimentally [via mass and low- and high-resolution molecular spectroscopy]¹⁻³ and at high levels of electronic-structure theory.³⁻⁶ The MS measurements reveal interesting trends about the stability of the starting members of the HHe_n^+ family. The computations and the low- and high-resolution rovibrational spectroscopy experiments^{1,2} establish that the basically linear, strongly bound, symmetric triatomic molecular ion $\text{He}(\text{H}^+)\text{He}$, with an experimentally determined equilibrium H–He distance of 0.924 Å, is the molecular core of all of the $n \geq 3$ complexes. Definitive quantum-chemical results are obtained for a number of these complexes. A useful notation, $[k-l-m]\text{-HHe}_n^+$, is introduced to characterise qualitatively the three possible belts around the He–H⁺–He core in HHe_n^+ ($n \geq 3$), where l denotes the number of He atoms in the central belt and $k \geq m$ denote the number of He atoms in the top and bottom belts. Capping He atoms attached to the belts can be indicated by sub- and superscripts.

Experimental as well as computational results have also been obtained for the $(\text{H/D})_2\text{He}^+$ system.^{3,4} The band origins obtained experimentally are fully explained by accurate variational computations of the bound and resonance⁶ rovibrational states of H_2He^+ and D_2He^+ based on the three-dimensional potential energy surface.

Similar results obtained for rare-gas atoms other than He are also discussed in the talk. The structures of the $\text{HRg}_2^+\text{Rg}'$ complexes are characterized by significant nuclear delocalization. Large shifts of the in-plane and out-of-plane bends, as well as of the symmetric and antisymmetric stretches of the chromophores of these complexes are observed.

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⁴ Papp, D.; Szidarovszky, T.; Császár, A. G.. A general variational approach for computing rovibrational resonances of polyatomic molecules. Application to the weakly bound H_2He^+ and H_2CO systems. *J. Chem. Phys.* **2017**, *147*, 094106.

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