Theoretical spectroscopy of the diacetylene cation in the ground $X \, ^2\Pi_g$ and low-lying excited electronic states

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Polyacetylenes in their neutral and ionic forms have been recognized as transient species in plasma and combustion reactions, in planetary atmospheres, and in interstellar medium. The radical cation of diacetylene, HCCCCH$^+$, is a reactive linear molecule being an open-shell $\pi$-electron system that has been considered as a precursor to larger hydrocarbons in interstellar environment and also as a potential carrier of Diffuse Interstellar Bands (DIBs). Thus, good knowledge of its spectral properties is very important for the detection in laboratory, plasmas and interstellar environments [1-5]. HCCCCH$^+$ molecule is particularly interesting because in its ground $X \, ^2\Pi_g$ and several low-lying doublet and quartet electronic states exhibits the Renner-Teller effect, which along with the spin-orbit coupling may complicate its vibrational spectrum.

This study is motivated by the recent high-resolution photoelectron spectroscopy measurements which were aimed to study the spin-orbit interaction and Renner-Teller effect in HCCCCH$^+$ and DCCCCD$^+$ [5], and also by earlier experimental studies [1-3]. We report here the results of $ab$ initio calculations of geometry, vertical electronic spectrum, excitation energies, bending potential curves, and spin-orbit interactions in the low-lying doublet and quartet electronic states of HCCCCH$^+$, HCCCCD$^+$ and DCCCCD$^+$ by means of coupled-cluster singles-and-doubles with perturbative inclusion of triples [CCSD(T)], complete active space self-consistent (CASSCF) and multi-reference configuration-interaction with Davidson corrections (MRCI+Q) methods, in the aug-cc-pVTZ basis set.

Vibronic energy levels of the $X \, ^2\Pi_g$ and $A \, ^2\Pi_u$ electronic states will be variationally calculated via a simple model for $ab$ initio handling of the Renner-Teller effect (and spin-orbit coupling) in molecules with linear equilibrium geometry and with arbitrary number of nuclei [6, 7]. The program for the variational treatment of Renner-Teller effect in six-atomic molecules is written in the Python programming language using Numpy package.