Theoretical spectroscopy of the diacetylene cation in the ground X $^2\Pi_\mathbf{g}$ 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 π-electron system that has been considered as a precursor to larger hydrocarbons in interstallar 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 $^2\Pi_\mathbf{g}$ 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 $^2\Pi_\mathbf{g}$ and A $^2\Pi_\mathbf{u}$ 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.

[1] C. Ramos, P. R. Winter, and T. S. Zwier, J. Chem. Phys. **116**, 4011 (2002).
[2] J. Szczepanski, H. Wang, B. Jones, C. A. Arringtonb, and Martin T. Vala, Phys. Chem. Chem. Phys. **7**, 738 (2005).
[3] R. Raghunandan, F. J. Mazzotti, A. M. Esmail, and J. P. Maier, J. Phys. Chem. A **115**, 9365 (2011).
[4] A. Ghosh, S. N. Reddy, S. R. Reddy, and S. Mahapatra, J. Phys. Chem. A **120**, 7881 (2016).
[5] U. Jacovella and F. Merkt, Phys. Chem. Chem. Phys. **105**, 156 (2017).
[6] M. Perić, Mol. Phys. **105**, 59 (2007).
[7] M. Mitić, R. Ranković, M. Milovanović, S. Jerosimić, M. Perić, Chem. Phys. **464**, 55 (2016).