Calculation of highly accurate *ab initio* potential energy surfaces (PESs) and study of rovibrational spectra for cyanogen isomers and isotopologues

/Workplan of Leonid Shirkov/

The astrochemistry of the interstellar medium (ISM) is crucial in our understanding of such processes as star, planet and comet formation, and ultimately, the origin of life. Recent advances in radio telescope astronomy as well as microwave and infrared spectroscopy have allowed for the discovery of complex molecular species, including long chain molecules such as cyanopolyynes up to $HC_{11}N$. [1-2] The interstellar molecular formation mechanism suggests the existence of other linear molecular classes such as polyynes and dicyanopolyynes. Thus, the theoretical description and computational modeling of spectroscopic processes involving linear organic compounds is very important.

The objective of this STSM is the study of four linear cyanogen isomers – NCCN, CNCN, CNNC and NNCC via methods of modern quantum chemistry and theoretical spectroscopy. In the first step, accurate equilibrium structures and harmonic frequency analysis will be carried out for these species with different variants of the coupled cluster method, conventional CCSD(T) and explicitly correlated CCSD(T)-f12. The second step will include the determination of the full dimensional *ab initio* PES for two symmetric isomers, NCCN and CNNC, with the CCSD(T)-f12 method. The PES for linear tetratomic molecules includes 3 stretching and 3 angle coordinates, and therefore, construction of the full PES requires *ab initio* calculations of at least a few hundred single point geometries, which will be fitted to the analytical form of the potential. The third step will include calculations of the quartic force field constants from the determined analytical PESs. Finally, Nielsen second order vibrational perturbation theory (VPT2) will be applied and the rovibrational constants, such as χ_{rs}, χ_{ll}, α_s and q_t, will be found. [3-4] The results obtained are expected to improve the existing theoretical ones reported previously only for the NCCN isomer. [3]

The constructed PESs will also be applicable for more accurate variational calculations with RVIB4 and WAVR4 codes based on FBR and DVR techniques, and with the new code being developed. [5-7] This will allow for the determination of transition line lists.

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