

# *Ab initio* study of the vibronic spectrum of $X^2\Pi_u$ electronic state of the dicyanoacetylene cation

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Cyanopolyacetylenes are detected in the interstellar medium (ISM) and in planetary atmospheres. For a long time cyanoacetylene  $H(C\equiv C)CN$  has been known as an interstellar molecule and a precursor to biomolecules found in ISM [1]. Dicyanoacetylene  $N\equiv C-C\equiv C-C\equiv N$  is a linear symmetric molecule which cannot be detected in ISM via rotational microwave spectroscopy. However, similar asymmetric molecules such as cyanoacetylene and cyanodiacetylene have been observed in ISM and other astrophysical environments, which makes the existence of dicyanoacetylene a reasonable postulate [2]. Solid dicyanoacetylene has been detected in Titan's atmosphere by infrared spectroscopy but not yet directly observed in a gas phase in Titan [2,3]. Due to various photochemical processes dicyanoacetylene cation ( $C_4N_2^+$ ) could be formed, which along with the neutral dicyanoacetylene influence the chemistry of ISM and planetary atmospheres.

The ground electronic state of dicyanoacetylene cation is  $^2\Pi_u$ . With respect to that, its vibronic structure is affected by the Renner-Teller (R-T) effect and spin-orbit (S-O) coupling. Lamarre *et al.* [3] studied the vibronic structure of  $C_4N_2^+$  cation via high resolution by pulsed-field-ionisation zero-kinetic-energy photoelectron spectroscopy (PFI-ZEKE PES) and *ab initio* calculations. They found disagreement with the first theoretical study of this molecule [4] where model for the R-T effect in six-atomic linear molecules based on a second-order perturbation theory was used and parameters for the model were calculated at the MRCI(11,10)/aug-cc-pVTZ level of theory.

The goal of this study is to more accurately describe R-T and S-O effects in this molecule and to explain the discrepancy between experimental [3] and theoretical [4] work. The equilibrium geometry and harmonic frequencies of the ground state have been calculated with explicitly correlated CCSD(T)-F12/cc-pVTZ-F12 method, using MOLPRO 2012.1 program package. Spin-orbit (S-O) constant is obtained in the framework of quasi-degenerate perturbation theory (QDPT) incorporated in program package ORCA 4.0, with mean-field spin-orbit Hamiltonian and CASSCF(15,14) wave function. R-T parameters are derived from the bending potential energy values for the two components of the  $X^2\Pi_u$  state, computed at the NEVPT2(15,14)/def2-QZVPP level.

The vibronic spectrum of dicyanoacetylene cation is calculated using model for the R-T effect based on variational approach, contrary to the Ref. [4] where perturbation theory was used.

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