STSM Report.

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Host institution: University Paris-Est Marne-la-Vallée, France

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

The objective of this STSM was the study four linear cyanogen isomers (NCCN, CNCN, CNNC and NNCC) using methods of modern quantum chemistry and theoretical spectroscopy.

The first step consisted on calculations of accurate equilibrium structures and harmonic frequencies for all four isomers with standard CCSD(T) approach. It was shown, that the effects of core-valence (CV) correlation are not negligible for the stretching modes, where corrections of ~5 cm^{-1} for v_2 and ~10 cm^{-1} for v_1 and v_3 fundamental modes are observed. Therefore, the inclusion of CV correction is mandatory for calculations of the six-dimensional potential energy surfaces (6D-PESs) of these species.
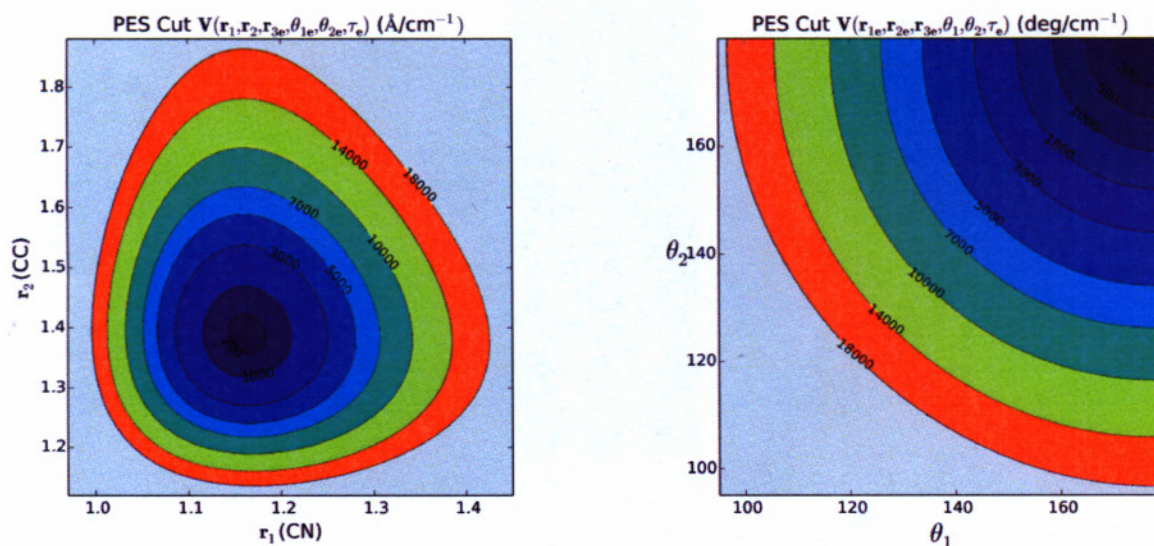

Figure 1: Two contour plots of the NCCN PES computed at the CCSD(T)-F12/avtz level of theory

The next step included calculations of full 6D-PESs with explicitly correlated CCSD(T)-F12 method for NCCN isomer. First, several geometry grids with different increments for valence bond lengths and angles were generated by the program Hsurfita of the host institution. Then, the single energy points of the grids were calculated with Molpro package. These points were then fitted to analytical forms that include up to 5D coupling terms between different coordinates with Hsurfit program (available also at the host institution). The generated potentials were incorporated into RVIB4 variational code (available also at the host institution) for nuclear motion treatments. After comparison to the available IR ad Raman experimental spectra of NCCN, this

allowed to validate the most optimal grid to be chosen. Good agreement is observed between *ab initio* and experimental data (Table 1).

Table 1: Comparison of fundamental anharmonic frequencies with previous theoretical and experimental values for NCCN isomer (in cm^{-1}).

$v_1,v_2,v_3,v_4(l_4),v_5(l_5)$	This work	Prev. theor.[1]	exp.[2]
0,0,0,0(0),1(1)	233.3	233.2	233.7
0,0,0,1(1),0(0)	507.6	493.5	502.8
0,0,1,0(0),0(0)	844.4	850.7	845.6
0,1,0,0(0),0(0)	2154.7	2142.7	2157.8
1,0,0,0(0),0(0)	2335.0	2304.0	2330.5

The further improvement of the 6D-PES will include the following steps.

1. Calculations of 6D-PES at the CCSD(T)/CBS + CV level.
2. Inclusion of triple and quadruple electron excitations corrections (i.e. CCSDT and CCSDT(Q)). This part will be calculated with **CFOUR** package in collaboration with Prof. Christina Puzzarini (U. Bologna, Italy).
3. Calculations of the scalar relativistic correction with the 2nd-order Douglas-Kroll-Hess Hamiltonian.

Once the most accurate 6D-PES is derived for NCCN isomer, similar PESs will be provided for the other three linear isomers and their isotopologues.

[1] M. Hochlaf, J. Mol. Spectrosc, 207, 269(2001)
[2] A. G. Maki, J. Mol. Spectrosc, 269, 166(2011)

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