High accuracy *ab initio* calculations of energy levels of HCN

O. L. Polyansky[a,b], L. Lodi[b], J. Tennyson[b], A. A. Kyuberis[a], and N. F. Zobov[a]

[a] Institute of Applied Physics, Nizhniy Novgorod, Russia, E-mail: zobov@appl.sci-nnov.ru
[b] Department of Physics and Astronomy, University College London, United Kingdom

High accuracy calculations on the rotation-vibration energy levels of HCN are repsorted. These calculations follow our recently reported *ab initio* study on the energy levels of seven water isotopologues which obtained an accuracy of 0.08 cm^{-1} for the levels up to 15000 cm^{-1} [1]. Our goal is to extend this near-experimental accuracy using completely *ab initio* methods to other small astrophysically and atmospherically important molecules with up to about 20 electrons.

Calculations of the vibrational and rovibrational energy levels of 5 HCN isotopologues are presented. In particular multi-reference configuration interaction (MRCI) level electronic structure calculations, performed using the MOLPRO quantum chemistry package, are used with all electron aug-pV5Z and aug-pV6Z basis sets with extrapolation to complete basis set to produce 1050 electronic energy points. These points are fitted to 78 parameters in an analytical potential energy function which reproduces these points to an accuracy of 0.45 cm^{-1}. An adiabatic Born-Oppenheimer Diagonal Correction (BODC) surface together with relativistic surfaces, obtained using the fully relativistic electronic structure program Dirac, were also computed. We use these surfaces to calculate vibration and rotation-vibration energy levels of the isotopologies $H^{12}C^{14}N$, $D^{12}C^{14}N$, $H^{13}C^{14}N$, $D^{13}C^{14}N$ and $H^{12}C^{15}N$. Vibrational J=0 levels of all 5 isotopologues are calculated with an unprecedented accuracy of 0.3 cm^{-1} for energies up to 10000 cm^{-1} above the ground state. Rovibrational levels of the main isotopologue $H^{12}C^{14}N$ with J=9 [2] were calculated with the same accuracy.

[1] O.L. Polyansky, R.I. Ovsyannikov, A.A. Kyuberis, L. Lodi, J. Tennyson, N.F. Zobov, *Phys. Chem. Chem. Phys.* **2013** (in press); dx.doi.org/10.1021/jp312343z

[2] G.C. Mellau, *J. Mol. Spectrosc.* **2011***, 269,* 77.