Theoretical predictions of bound and continuum states in cyanopolyyne anions

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We present a theoretical study of electronic structure of four cyanopolyyne anions. Our main focus are low-lying excited states which are metastable with respect to electron detachment. These are electronic resonances embedded in the detachment continuum. Unbound nature of electronic resonances makes them particularly challenging for theoretical ab initio investigations with high and controllable accuracy [1]. Yet, such metastable states often are the only (semi)-discrete features of anions electronic spectra, therefore they play a central role in their characterization by means of photoelectron or ultrafast spectroscopy. Here we employ equation-of-motion coupled-cluster (EOM–CCSD) method augmented with complex absorbing potential [2] to study bound and continuum states of four cyanopolyyne anions $C_{2n+1}N^-$, $n = 0 - 3$. These specific molecules belong to the family of anions recently discovered in the interstellar medium [3]. We show that already in CN^-, the smallest anion in the family, there are several low-lying metastable states of both singlet and triplet spin symmetry. As the carbon chain length increases, these resonances gradually stabilize and finally turn into stable valence bound states. We analyze the identified resonances in terms of their dominant Dyson orbitals and natural transition orbitals. Further, we show how the Hückel model can be employed to rationalize trends in energetics of the transitions leading to both resonance and stable excited states. Finally, we propose how the identified resonances can manifest themselves in experimental observables such as photodetachment cross sections or absorption spectra, and suggest what implications the electronic resonances might have for the anions formation process in space.

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