PROTONATED ETHYL CYANIDE: QUANTUM CHEMISTRY AND ROTATIONAL SPECTROSCOPY

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Protonated ethyl cyanide, $CH_3CH_2CNH^+$, a likely intermediate in interstellar clouds and in the planetary atmosphere of Titan, has been detected at high spectral resolution by means of Fourier transform microwave spectroscopy at centimeter wavelengths. From 13 a-type rotational transitions between 8 and 44 GHz, the three rotational constants have been determined to better than 0.05%, and two of the leading centrifugal distortion terms to a few percent. Since nitrogen hyperfine structure in the lower rotational transitions is highly compact, only the quadrupole coupling tensor element along the a-inertial axis χ_{aa}(N) could be determined. The agreement between the experimental rotational constants and those calculated theoretically is very good, of order 0.2%, a clear indication that the CCSD(T) level of theory provides an accurate treatment of the electronic structure. By scaling to isoelectronic butyne, even better agreement between the two is achieved ($\ll 0.1\%$). The similarity of the eQq(N) values derived along the C–N bond axis for both protonated vinyl cyanide and protonated ethyl cyanide along with the very small magnitudes of these constants implies a quadruply-bound nitrogen atom and an $H-N^+\equiv C-R$ type structure that is affected little by protonation. Closely spaced torsional doublets in one $K_a = 0$ line and three $K_a = +1$ lines allow an estimate of the threefold barrier to internal rotation of $V_3 = 2.50 \pm 0.09$ kcal mol^{-1}, which is within 4% of that calculated theoretically. Ethyl cyanide has a high proton affinity and is abundant in rich astronomical molecular sources, implying its protonated variant is a good candidate for astronomical detection, particularly since this species is calculated to possess a sizable dipole moment along the a-inertial axis (2.91 D).