LARGE AMPLITUDE BENDING MOTION: COMPUTATIONAL MOLECULAR SPECTROSCOPY AND EXPERIMENTS OF TRANSITION-METAL ISOCYANIDE AND CYANIDES

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Computational molecular spectroscopy and experimental spectroscopy have a common aim: understanding of molecular property; one start from theoretical determination of the relevant potential energy surface (PES), and the other ends in the understanding of the PES behind the observed frequencies. Although the methods how to treat the large amplitude bending motion have been proposed almost every decade, geometries derived from experiments without applying these methods have often been reported. We have studied *ab initio* the ground states FeNC,[a] FeCN,[b] CoCN,[c] and NiCN,[d] and computed the ro-vibrationally averaged structures, i.e. r_0 structures, as the expectation values of ro-vibronic wavefunctions based on the *ab initio* PESs obtained at the MR-SDCI+Q+E_{rel}/[Roos ANO (transition metal), aug-cc-pVQZ (C, N)] level of theory. The r_0(C–N)'s, in Å, thus determined *ab initio* (and available experimental values in parentheses) are 1.187 (1.03(8)[e]) for FeNC, 1.172 for FeCN, 1.172 (1.1313(10)[f]) for CoCN, and 1.171 (1.1580(8),[g] and 1.1591(29) ($r_{0,5/2}$)[h]) for NiCN. The discrepancies in all cases can be ascribed to the negligence of averaging over the large amplitude bending motion in the determination of the experimentally derived values.

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