An ab initio calculation of BH_2^- rovibronic energies: a very small singlet-triplet splitting

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For each of the $\widetilde{X}^3B_1$, $\widetilde{a}^1A_1$, and $\widetilde{b}^1B_1$ electronic states of the BH_2^- molecular ion we have calculated over 50 ab initio points on the potential energy surfaces using the MRD-CI method for all eight electrons. Analytical functions were fitted through the points for each state, and the functions for the $\widetilde{a}$ and $\widetilde{b}$ states were such that the surfaces remain degenerate at all linear configurations. For the $\widetilde{X}$ state the rotation-vibration energies were calculated from the surface using the MORBID[a] Hamiltonian, and for the $\widetilde{a}$ and $\widetilde{b}$ states the rovibronic energies were calculated using the RENNER[b] Hamiltonian. For the $\widetilde{X}$ state we obtain $r_e = 1.2034$ Å, $\alpha_e = 129.5°$ and a barrier to linearity of 2226 cm^{-1}. The vibrational wavenumbers are determined to be $\nu_1 = 2353$ cm^{-1}, $\nu_2 = 883$ cm^{-1} and $\nu_3 = 2498$ cm^{-1}. For the $\widetilde{a}$-state we determine $r_e = 1.2369$ Å, $\alpha_e = 105.7°$, a barrier height to linearity of 6071 cm^{-1} and the vibrational wavenumbers $\nu_1 = 2070$ cm^{-1}, $\nu_2 = 986$ cm^{-1}, and $\nu_3 = 2059$ cm^{-1}. For the $\widetilde{b}$-state we determine $r_e = 1.1936$ Å, $\alpha_e = 135.9°$, a barrier height to linearity of 1069 cm^{-1} and the vibrational wavenumbers $\nu_1 = 2399$ cm^{-1}, $\nu_2 = 915$ cm^{-1}, and $\nu_3 = 2591$ cm^{-1}. The most interesting result we obtain is that the singlet-triplet splitting T_0 $(\widetilde{a}^1A_1)$ is only 153 cm^{-1} for $^{11}BH_2^-$. Hence singlet-triplet perturbations will significantly affect all levels of the ground state.

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