AB INITIO CALCULATION OF BiN SPECTRUM: CAN $^5\Sigma^+$ - $^1\Sigma$ TRANSITIONS BE OBSERVED?

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Potential energy curves of the ground X0$^+$($^1\Sigma^+$) state and a number of the low-lying excited states of BiN are calculated employing the relativistic CI method based on effective core potentials. Fifteen outer electrons of bismuth and five of nitrogen were treated explicitly in the computational procedure. The calculated spectroscopic constants (T_e, r_e, and ω_e) are in good agreement with the available experimental results, as is the ground state D_e value, computed to be 28400 cm^{-1}. The two lowest-lying excited Λ - S states are found to be $a^3\Sigma^+$ and $b^5\Sigma^+$ and have essentially shifted minima with respect to the ground state due to the opening of the π^4 valence shell. The $a_2 0^-$ state is predicted to lie 1740 cm^{-1} higher than $a_1 1$. It is shown that the $b_1 0^+$ state has a strongly perturbed potential curve with a shoulder on its repulsive limb due to an avoided crossing between the $b^5\Sigma^+$ and $^3\Pi$ states. This result explains the increase in its $B_{v'}$ constant with v' found experimentally.[a] A number of other bound states and avoided crossings are indicated in the calculations which may be of relevance in future experimental investigations of this system. The radiative lifetimes are also calculated for electric-dipole-allowed transitions between the states considered and analyzed in terms of Λ - S contributions.

[a] R. Breidohr, K. D. Setzer, O. Shestakov, E. H. Fink, and W. Zyrnicki, *J. Mol. Spectrosc.* **166**, 471 (1994).