THE SPECTRUM OF SINGLET SILYLENE

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We report the results of *ab initio* and rovibronic energy calculations for the two electronic states of silylene ($SiH_2$), $\tilde{X}^1A_1$ and $\tilde{A}^1B_1$, that become degenerate when the molecule is linear. Potential energy surfaces, and transition dipole moment functions, are calculated using high level *ab initio* methods. The potential function parameters are optimized by fitting to experimental energies, but in the fitting the shapes of the potential surfaces are constrained by the *ab initio* results. The variational RENNER program is used to calculate rotation-vibrational energies, and to simulate the $\tilde{X}^1A_1$–$\tilde{A}^1B_1$ emission spectrum of $SiH_2$. Local mode assignments within the $\tilde{X}$–state polyad blocks are made, and these are important in the fitting process; they are also important for the predictions.