THE SPECTRUM OF SINGLET SILYLENE

S. N. YURCHENKO and P. R. BUNKER, *Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6*; W. P. KRAEMER, *Max Planck Institut für Astrophysik, Karl-Schwarzschild-Strasse 1, Postfach 1523, D-85740 Garching, Germany*; PER JENSEN, *Theoretische Chemie, Fachbereich 9, Bergische Universität, D–42097 Wuppertal, Germany*.

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.