NEW POTENTIAL ENERGY SURFACES FOR THE $\tilde{X}$ AND $\tilde{A}$ STATES OF CH_2^+

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We report new *ab initio* calculations of the three-dimensional potential energy surfaces for the Renner-effect coupled $\tilde{X}\,^2A_1$ ground electronic state and $\tilde{A}\,^2B_1$ first excited electronic state of the CH_2^+ molecule. We also make an *ab initio* calculation of the spin-orbit coupling surface $A_{\rm SO}(r_{12}, r_{32}, \rho)$ between these states. Using these *ab initio* surfaces, and our previously obtained[b] *ab initio* dipole moment and transition moment surfaces, in our computer program RENNER, we calculate term values and absorption line intensities. We compare with recently observed high resolution spectra. Adjusting two parameters in the potential surfaces we are able to achieve satisfactory agreement with the experimental results except for those that involve the $\tilde{A}$ state ($v_2^{\rm linear}$ = 8, l = 1) vibronic level. The implication of this disagreement is discussed.

Apart from having the facility of using dipole moment and transition moment surfaces so that absolute intensity calculations can be made, our RENNER computer program has the second unique feature of being able to calculate the energies of high lying rotational states because it is based on the Hougen-Bunker-Johns Hamiltonian. This has made it possible to study the phenomenon of rotational energy level clustering in Renner molecules. A recent study for PH_2 exemplifies this aspect of our work[c]

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[b] G. Osmann, P. R. Bunker, P. Jensen, and W. P. Kraemer, *Chem. Phys.* **225,** 33-54 (1997).

[c] S. N. Yurchenko, W. Thiel, P. Jensen, and P. R. Bunker, *J. Mol. Spectrosc.* **239,** 160-173 (2006).