THE NEAR ULTRAVIOLET BAND SYSTEM OF SINGLET METHYLENE

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In a classic paper entitled "The spectrum and structure of singlet CH_2" by G. Herzberg and J. W. C. Johns (*Proc. Roy. Soc.* **A295**, 107-128 (1966)) the analysis of the $\tilde{b}\ ^1B_1 \leftarrow \tilde{a}\ ^1A_1$ red absorption band system of CH_2 is discussed in detail for the first time. In addition to that band system the observation of a fragment of a weak near ultraviolet absorption band system is reported. The three observed bands of the system could not be vibrationally assigned or rotationally analyzed but it was pointed out that they probably involve absorption into the second excited singlet state, $\tilde{c}\ ^1A_1$. We show this supposition to be true here by simulation. In order to simulate the spectrum we have calculated *ab initio* the $\tilde{c}$-$\tilde{a}$ and $\tilde{c}$-$\tilde{b}$ transition moment surfaces, and used the MORBID and RENNER program systems with previously determined potential energy surfaces for the $\tilde{a}$, $\tilde{b}$ and $\tilde{c}$ states in a calculation of the energy levels and wavefunctions. We find that the three bands seen by Herzberg and Johns are part of the $\tilde{c} \leftarrow (\tilde{a}/\tilde{b})$ system but that all of the bands of the system above about 31 000 cm^{-1} are missing as a result of $\tilde{c}$ state predissociation. We can vibrationally assign the bands, but the weakness of the spectrum, and the presence of perturbations, make it impossible for us to assign all the rotational structure. It would be worthwhile to record this spectrum again using a more sensitive modern laser based technique in order to probe singlet state CH_2 at these energies.