THE INFRARED SPECTRUM OF CH_2^+ REVISITED

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The first reported spectrum of CH_2^+ was the $K_a = 0$ series of the ν_3 fundamental, recorded by our group in 1991.[a] Subsequently, the $K_a = 1$ series was observed in 1993 and later analyzed by Jensen et al.[b] These spectra were recorded in liquid-nitrogen-cooled positive-column discharges of CH_4, H_2, and He. In the 1993 spectrum, absorption lines from CH_2^+ were discriminated from those of CH_3^+ by recording the spectrum of a discharge without H_2. In the absence of H_2, the CH_2^+ lines grew stronger and the CH_3^+ lines weakened. In the 1993 spectrum, weak lines attributed to CH_2^+ with $K_a = 2$ were observed. The $K_a = 2$ lines were significantly weaker than the $K_a = 1$ lines because of a reduced Boltzman factor ($A \approx 67\ \mathrm{cm}^{-1}$). The assignment of these lines was stalled because of their low intensity, the complicated spectral pattern of CH_2^+ (due to the combined effects of quasi-linearity and the Renner-Teller effect), and interfering absorption lines of CH_3^+, $C_2H_2^+$, and $C_2H_3^+$.

Two new developments have led us to revisit the infrared spectrum of CH_2^+, with the goal of assigning $K_a \geq 2$ lines. The first development is the observation of the $\tilde{A}(0,3,0)^3 \leftarrow \tilde{X}(0,0,0)^2$ electronic band of CH_2^+.[c,d] This band provides combination differences that can be directly compared with the ν_3 fundamental. The second development is the discovery of a new plasma chemistry — allene and He in a water-cooled positive-column discharge — that appears to be selective for CH_2^+. This new chemistry allows us to confirm CH_2^+ as the carrier of previously observed lines. This paper will discuss progress made in the assignment of the infrared spectrum of CH_2^+ in light of these new developments.

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[a] M. Rösslein, C. M. Gabrys, M.-F. Jagod, and T. Oka, *J. Mol. Spectrosc.* **153**, 738 (1992).
[b] P. Jensen, M. Brumm, W. P. Kraemer, and P. R. Bunker*J. Mol. Spectrosc.* **172**, 194 (1995).
[c] J. L. Gottfried and T. Oka, *J. Chem. Phys.* **121**, 11527 (2004).
[d] See talk entitled "The Near-Infrared Spectrum of CH_2^+."