

THE INFRARED SPECTRUM OF CH₂⁺ REVISITED

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The first reported spectrum of CH₂⁺ 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 CH₄, H₂, and He. In the 1993 spectrum, absorption lines from CH₂⁺ were discriminated from those of CH₃⁺ by recording the spectrum of a discharge without H₂. In the absence of H₂, the CH₂⁺ lines grew stronger and the CH₃⁺ lines weakened. In the 1993 spectrum, weak lines attributed to CH₂⁺ with $K_a = 2$ were observed. The $K_a = 2$ lines were significantly weaker than the $K_a = 1$ lines because of a reduced Boltzmann factor ($A \approx 67 \text{ cm}^{-1}$). The assignment of these lines was stalled because of their low intensity, the complicated spectral pattern of CH₂⁺ (due to the combined effects of quasi-linearity and the Renner-Teller effect), and interfering absorption lines of CH₃⁺, C₂H₂⁺, and C₂H₃⁺.

Two new developments have led us to revisit the infrared spectrum of CH₂⁺, 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 CH₂⁺.^{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 CH₂⁺. This new chemistry allows us to confirm CH₂⁺ as the carrier of previously observed lines. This paper will discuss progress made in the assignment of the infrared spectrum of CH₂⁺ in light of these new developments.

^aM. Rösslein, C. M. Gabrys, M.-F. Jagod, and T. Oka, *J. Mol. Spectrosc.* **153**, 738 (1992).

^bP. Jensen, M. Brumm, W. P. Kraemer, and P. R. Bunker, *J. Mol. Spectrosc.* **172**, 194 (1995).

^cJ. L. Gottfried and T. Oka, *J. Chem. Phys.* **121**, 11527 (2004).

^dSee talk entitled “The Near-Infrared Spectrum of CH₂⁺.”