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 \( v_3 \) 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 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 CH$_2^+$ (due to the combined effects of quasi-linearity and the Renner-Teller effect), and interfering absorption lines of CH$_3^+$, C$_2$H$_5^+$, and C$_2$H$_4^+$.

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 \( A(0, 3, 0) \leftarrow X(0, 0, 0) \) electronic band of CH$_2^+$\(^c\).\(^d\) This band provides combination differences that can be directly compared with the \( v_3 \) 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.

\(^d\)See talk entitled “The Near-Infrared Spectrum of CH$_2^+$.”