DETECTION OF THE NEAR-INFRARED SPECTRUM OF CH_2^+

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The molecular ion CH_2^+ is of special interest because of its quasilinearity (resulting from a small barrier to linearity, 1089 cm^{-1}) and the strong interaction of its ground and first excited states due to the Renner-Teller effect. At linearity the ground state is a doubly degenerate $^2\Pi_u$ state that splits into $\widetilde{X}^2A_1$ and $\widetilde{A}^2B_1$ states as the molecule bends. Although in the ground state the molecule is a near-prolate asymmetric rotor ($\angle$HCH=140°), the excited state equilibrium geometry is linear. Both the initial detection of the infrared spectrum of the ν_3 band[a,b] and a more recent PFI-ZEKE study[c] confirm the bent nature of CH_2^+ in the ground state. This work presents the first experimental spectroscopic characterization of the $\widetilde{A}^2B_1$ state.

Using a Ti:sapphire laser, we have observed four new absorption bands in the near-infrared region (11,000-13,000 cm^{-1}). The comparison between spectra recorded in He/CH_4 and He/CH_4/H_2 liquid-nitrogen cooled positive column discharges was used to identify these transitions, the strongest of which had a signal-to-noise ratio of ~100. A least-squares fit of 57 transitions from the $\widetilde{A}(0,3,0)^1 \leftarrow \widetilde{X}(0,0,0)^0$ band has given preliminary values for the excited state molecular constants B=7.140(22) and D_N=-0.00034(16). The fit of 46 lines from the $\widetilde{A}(0,4,0)^0 \leftarrow \widetilde{X}(0,0,0)^1$ band resulted in the following excited state constants: B=6.796(56) and D_N=-0.00170(42). Recent *ab initio* predictions[d] of the rovibronic spectra of CH_2^+ show good agreement with the observed spectrum ($\triangle\nu_{o-c}$=-53 cm^{-1} for the $\widetilde{A}(0,3,0)^1 \leftarrow \widetilde{X}(0,0,0)^0$ band and $\triangle\nu_{o-c}$=-18 cm^{-1} for the $\widetilde{A}(0,4,0)^0 \leftarrow \widetilde{X}(0,0,0)^1$ band). Assignment of the $\widetilde{A}(0,3,0)^2 \leftarrow \widetilde{X}(0,0,0)^1$ and $\widetilde{A}(0,3,0)^3 \leftarrow \widetilde{X}(0,0,0)^2$ bands is underway.

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