VIBRATIONAL SPECTROSCOPY AND THEORY OF $Fe_x{}^+(CH_4)_n$ (x =2,3) (n = 1–3)

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Vibrational spectra are measured for $Fe_x{}^+(CH_4)_n$ (x =2,3) (n = 1–3) in the C–H stretching region (2650–3100 cm^{-1}) using photofragment spectroscopy, by monitoring the loss of CH_4. All of the spectra exhibit an intense peak corresponding to the symmetric C–H stretch around 2800 cm^{-1}, which is red shifted by about 100 cm^{-1} from free methane. The presence of a single peak suggests a nearly equivalent interaction between the methane ligands and the iron center. The peak becomes slightly less red shifted as the number of methane ligands increases. Density functional theory calculations, B3LYP and BPW91, are used to identify possible structures and predict the spectra. Results suggest that the methane(s) bind in a terminal configuration and that the $Fe_2{}^+$complexes are in the octet spin state while the $Fe_3{}^+$ complexes are in the dectet spin state. Lower C-H stretching frequencies are observed for $Fe_3{}^+$ complexes, indicating that the CH_4 interacts more strongly with $Fe_3{}^+$ than $Fe_2{}^+$.