Spectroscopic Studies of H_2S and D_2S Near Ion-Pair Dissociation Thresholds

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We present the results of spectroscopic investigations of ion-pair states of small polyatomic molecules near ion-pair thresholds. These states are bound states of an attractive Coulomb potential between the positively and negatively charged fragments. They are analogous to high Rydberg states of atoms and molecules, but with a much larger reduced mass. They are therefore called heavy Rydberg states. Such heavy Rydberg states are well characterized in diatomic molecules [1, 2] but have not been observed yet in many polyatomic molecules [3, 4] so that many of their characteristics are not well understood. Accurate threshold energies give access to thermochemical properties such as bond energies. We are currently investigating triatomic systems, in particular H_2S and D_2S. The sample of interest is cooled down in a supersonic expansion. The cold gas cloud passes a skimmer before it is excited via a one-photon transition with narrow-band VUV laser radiation to high-lying heavy Rydberg states with principal quantum numbers $n \approx 10000$. After delayed pulsed-field dissociation, the molecular fragments are extracted in a photoion/photoelectron time-of-flight spectrometer. We determined the ion-pair formation energy for the two lowest thresholds of the SH^- X $^1\Sigma^+(v^- = 0, 1) + H^+$ ion-pair channel to be $E_{IP}^{H_2S}(v^- = 0,\ N^- = 0) = 122460 \pm 2\,cm^{-1}$ and $E_{IP}^{H_2S}(v^- = 1,\ N^- = 0) = 124997 \pm 5\ cm^{-1}$, respectively. For the SD^- X $^1\Sigma^+(v^- = 0) + D^+$ channel we found $E_{IP}^{D_2S}(v^- = 0,\ N^- = 0) = 123035 \pm 5\,cm^{-1}$. With this values, we can improve the bond energy (D_0(HS-H) and D_0(DS-D)) of the neutral species of both molecules.

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