SPECTROSCOPIC STUDIES OF SMALL POLYATOMIC MOLECULES NEAR ION-PAIR DISSOCIATION THRESHOLDS

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At high vibrational quantum numbers, ion-pair states (A^+–B^-) behave like high Rydberg states. Their level structure can be approximately described by Rydberg's formula after replacing the Rydberg constant R_∞ by the appropriate mass-scaled value $R_{IP} = R_\infty \frac{\mu_{A^+-B^-}}{m_e}$.[a]

We present the results of spectroscopic investigations of high-lying excited ion-pair states of small polyatomic molecules in the vicinity of ion-pair dissociation thresholds. Such states have been extensively characterized in diatomic molecules (see ref. [a,b] and references therein) and are at the heart of the technique of threshold ion-pair production spectroscopy.[c] Only few studies have been carried out on polyatomic molecules.[d,e] Polyatomic molecules exhibit denser series of ion-pair dissociation thresholds corresponding to the different rovibrational levels of the positively and negatively charged fragments. We will present the results of our investigations of OCS and H_2S in the vicinity of their lowest ion-pair dissociation thresholds. The experiments are carried out using cold samples in skimmed supersonic expansions. The region of the lowest ion-pair dissociation threshold is reached by single-photon excitation from the neutral ground state using narrow-band VUV radiation. The experiments provide access to the ion-pair dissociation energies from which the level structure of the ionic fragments can be determined as well as other thermochemical data such as electron affinities, ionization and dissociation energies.

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