

One-photon mass-analyzed threshold ionization (MATI) spectroscopy of
thietane cation

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Thietane as a four-membered heterocyclic ring compound is prototypical molecule for studying on equilibrium configuration of the neutral and the cation. We have measured the high-resolution vibrational spectrum of thietane (trimethylene sulfide) cation in the gas phase by employing the vacuum ultraviolet mass-analyzed threshold ionization (VUV-MATI) technique. The measured VUV-MATI spectrum featured complicatedly in the low frequency region, which demonstrated notably the twin peaks separated by 17 cm^{-1} with the FWHM of $\sim 8\text{ cm}^{-1}$ as the lowest frequency bands. Peaks in the low frequency region of the observed spectrum of thietane cation could be successfully reproduced by solving the Schrodinger equation with one-dimensional (1D) symmetric double-well potentials along the ring puckering coordinates on both the S_0 and D_0 states of thietane, respectively, which revealed as a progression of the ring puckering vibrational mode. The values of the interconversion barrier and the ring puckering angle on the S_0 state, the parameters used for the quantum chemical calculations, were assumed to be 274 cm^{-1} and 26° . The barrier and the angle on the D_0 state, however, are found to be 48.0 cm^{-1} and 18.2° , respectively, where such small barrier height and puckering angle for the cation suggest that the conformation of thietane cation on the D_0 state should be more planar than that of the thietane neutral. Then, the accurate ionization energy of thietane was determined to be $69,762 \pm 3\text{ cm}^{-1}$ ($8.6493 \pm 0.0004\text{ eV}$) under the zero field limit.