INFRARED SPECTRUM OF THE Ar-HNH$^+$ IONIC COMPLEX


Rotationally resolved infrared spectra of the $\nu_1$ and $\nu_2$ N-H stretching vibrations of the Ar-HNH$^+$ radical ionic complex have been observed by means of photodissociation spectroscopy. The analysis of the rotational structure shows that the complex has a $^3\Sigma^-$ ground electronic state with a linear or quasi-linear proton-bound structure Ar-H-N-H$^+$ characterized by an intermolecular center of mass separation of 3.085 Å. The origins of the $\nu_1$ and $\nu_2$ bands were determined as 2803.65(2) and 3287.36(2) cm$^{-1}$, and the frequency of the intermolecular stretch vibration, $\nu_{s}$, as 170.4(6) cm$^{-1}$. Ab initio calculations performed at the UMP2 level of theory confirm that the quasi-linearity and the diradical character of HNH$^+$ in its electronic ground state are not changed upon Ar complexation. The calculated properties of the intermolecular bond of the complex (D$e$=1773 cm$^{-1}$, $R_{Ar-H}\sim$2.01 Å, $\nu_{s}\sim$185 cm$^{-1}$) and the predicted complexation induced frequency shifts for $\nu_1$ and $\nu_2$ are in good agreement with the experimental results.