

## INFRARED SPECTRUM OF THE Ar-HNH<sup>+</sup> IONIC COMPLEX

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Rotationally resolved infrared spectra of the  $\nu_1$  and  $\nu_3$  N-H stretching vibrations of the Ar-HNH<sup>+</sup> radical ionic complex have been observed by means of photodissociation spectroscopy.<sup>a</sup> 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<sup>+</sup> characterized by an intermolecular center of mass separation of 3.085 Å. The origins of the  $\nu_1$  and  $\nu_3$  bands were determined as 2803.65(2) and 3287.36(2) cm<sup>-1</sup>, and the frequency of the intermolecular stretch vibration,  $\nu_s$ , as 170.4(6) cm<sup>-1</sup>. Ab initio calculations performed at the UMP2 level of theory confirm that the quasi-linearity and the diradical character of HNH<sup>+</sup> 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<sup>-1</sup>,  $R_{Ar-H}\sim 2.01$  Å,  $\nu_s\sim 185$  cm<sup>-1</sup>) and the predicted complexation induced frequency shifts for  $\nu_1$  and  $\nu_3$  are in good agreement with the experimental results.

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<sup>a</sup>O. Dopfer, S. A. Nizkorodov, R. V. Olkhov, J. P. Maier, and K. Harada, *J. Phys. Chem.* **A102**, 10017 (1998).