

A Discharge Flow-Photoionization Mass Spectrometric Study of HNO: Photoionization Efficiency Spectrum, Ionization Energy and Proton Affinity of NO*	U11
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Photoionization efficiency (PIE) spectra of HNO were measured over the wavelength range $\lambda = 110$ to 125 nm and in the ionization threshold region, $\lambda = 118$ to 124 nm, using a discharge flow-photoionization mass spectrometer apparatus. HNO was generated *in situ* by the reaction sequence: $\text{N} + \text{NO} \rightarrow \text{N}_2 + \text{O}$; $\text{O} + \text{C}_2\text{H}_4 \rightarrow \text{CH}_3 + \text{HCO}$; $\text{HCO} + \text{NO} \rightarrow \text{HNO} + \text{CO}$. The PIE spectrum displays step-like behavior near threshold and an HN-O stretching frequency in the cation of $1972 \pm 67 \text{ cm}^{-1}$. A value of $10.184 \pm 0.012 \text{ eV}$ for the adiabatic ionization energy (IE) of HNO was obtained from photoionization thresholds, which correspond to the $\text{HNO}^+(\text{X}^2\text{A}') \leftarrow \text{HNO}(\text{X}^1\text{A}')$ transition. This result is the first PIMS determination of IE(HNO). Also, an *ab initio* molecular orbital calculation (QCISD(T)/aug-cc-pVQZ) was performed that yields a value for IE(HNO) of $10.186 \pm 0.050 \text{ eV}$. There is good agreement between the experimental and the theoretical values for IE(HNO) reported here and that from a recent photoelectron spectroscopy study. The present experimental value for IE(HNO) was employed along with other, known thermodynamic quantities to obtain values for the heat of formation of the HNO cation and the absolute proton affinity of NO: $\Delta_f H_{298}^\circ(\text{HNO}^+) = 1089.73 \pm 1.18 \text{ kJ mol}^{-1}$ ($\Delta_f H_0^\circ(\text{HNO}^+) = 1092.65 \pm 1.18 \text{ kJ mol}^{-1}$); $\text{PA}_{298}(\text{NO}) = 531.55 \pm 1.26 \text{ kJ mol}^{-1}$ ($\text{PA}_0(\text{NO}) = 526.12 \pm 1.26 \text{ kJ mol}^{-1}$).

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