Observation of Ultrafast NH₃ (Å) State Relaxation Dynamics using a Combination of Time-resolved Photoelectron Spectroscopy and Photoproduction Detection

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Electronic Supplementary Information

SM.1 INTRODUCTION

Contained in this supplementary material is a close-up of the ν₂’ = 2 photoelectron spectrum and a complete set of transient profiles obtained after UV (197 – 208 nm) excitation of the ν₂’ = 2 - 5 levels of NH₃ (Å). Results from time-resolved photoelectron spectroscopy (TRPES; SM.2), time-resolved ion yield (TRIY; SM.3), and time-resolved photofragment translation spectroscopy (TRPTS; SM.4) experiments are presented in the same sequence as in the main document. Details of data acquisition and production of transient profiles from the raw data are contained in the main document. These plots are omitted from the main text as they appear nearly identical to the plots contained therein. Results from plots in this supplementary material section are reported in Table 2 of the main text and are used to analyze the photophysics of ammonia. Description of each plot is given in the caption.
Figure 1. Photoelectron binding energy spectrum obtained after 208.5 nm excitation of NH$_3$ (Å) $\nu_2' = 2$. This close-up view of Fig. 3(a) in the main document is meant to highlight the presence of peaks iii ($1^12^2$) and iv ($1^02^6$).
Figure 2. Photoelectron transients obtained after 208.5 nm excitation of NH$_3$ (Å) $v_2' = 2$. Data (circles) and fits (solid lines) are shown for two peaks in the photoelectron spectrum. Fit function is an exponential decay convoluted with the Gaussian instrument response function (IRF) of fixed width (230 fs).
**Figure 3.** Photoelectron transients obtained after 204.6 nm excitation of NH$_3$ (Å) $v_2'$ = 3. Data (circles) and fits (solid lines) are shown for four peaks in the photoelectron spectrum. Fit function is an exponential decay convoluted with the IRF. Data for peak i are presented in the main paper as Figure 4, with individual contributions from the decay and IRF clearly identified.
Figure 4. Photoelectron transients obtained after 200.8 nm excitation of NH$_3$ ($\tilde{\nu}$) $\nu_2' = 4$. Data (circles) and fits (solid lines) are shown for four peaks in the photoelectron spectrum. Fit function is an exponential decay convoluted with the IRF.
Figure 5. Photoelectron transients obtained after 197.1 nm excitation of NH$_3$ (Å) $v_2'$ = 5. Data (circles) and fits (solid lines) are shown for four peaks in the photoelectron spectrum. Fit function is an exponential decay convoluted with the IRF.
SM.3 TIME-RESOLVED ION YIELD

Figure 6. Transient profiles obtained from TRIY experiments on $v_2' = 2$ - 5 (a – d) levels of NH$_3$ (Å). Data (circles) and fits (solid lines) for NH$_3^+$, NH$_2^+$, and H$^+$ are shown top to bottom, respectively, in each panel. Panel (c) is presented in Section 3.2 of the main document. For NH$_3^+$, the fit function is an exponential decay convoluted with the IRF. For H$^+$, the fit function is an exponential rise convoluted with the IRF, and the extracted rise constant, $\tau_R$, measures the H-atom emission timescale. For NH$_2^+$, the fit function is the combination of exponential decay and rise convoluted with the IRF. Within each $v_2'$ level, $\tau_R$ is fixed to the value obtained in fitting of the H$^+$ transient, and $\tau_D$ is fit. $\tau_D$ obtains as the same value as the NH$_3^+$ decay time and is therefore associated with the NH$_3$ (Å) state.
Figure 7. H-ion transients obtained after 208.5 nm excitation of NH$_3$ (Å) $\nu_2' = 2$. Data (circles) and fits (solid lines) are shown for six regions of the H-atom energy distribution. H and NH$_2$ are co-fragments of NH$_3$ dissociation, and the NH$_2$ internal energy can be inferred from the measurement of H-atom kinetic energy (KE). Labels in each panel refer to quanta in the bend vibrational mode of the NH$_2$ ground state. Fit function is an exponential rise convoluted with the IRF. Extracted decay constants, $\tau_R$, measure the dissociation timescale. Notice the elongation of $\tau_R$ as $\nu_2$ increases.
Figure 8. H-ion transients obtained after 204.6 nm excitation of NH$_3$ (Å) $v_2' = 3$. Data (circles) and fits (solid lines) are shown for six regions of the H-atom energy distribution. The $v_2 = 4$, 8, and 8 transient data are presented in Section 3.3 of the main document. H and NH$_2$ are co-fragments of NH$_3$ dissociation, and the NH$_2$ internal energy can be inferred from the measurement of H-atom kinetic energy (KE). Labels in each panel refer to quanta in the bend vibrational mode of the NH$_2$ ground state. Fit function is an exponential rise convoluted with the IRF. Extracted decay constants, $\tau_R$, measure the dissociation timescale. Notice the elongation of $\tau_R$ as $v_2$ increases.
Figure 9. H-ion transients obtained after 200.8 nm excitation of NH$_3$ (Å) $v_2' = 4$. Data (circles) and fits (solid lines) are shown for seven regions of the H-atom energy distribution. H and NH$_2$ are co-fragments of NH$_3$ dissociation, and the NH$_2$ internal energy can be inferred from the measurement of H-atom kinetic energy (KE). Labels in each panel refer to quanta in the bend vibrational mode of the NH$_2$ ground state. The $v_2 = 9$ level is accessible at this initial excitation energy. Fit function is an exponential rise convoluted with the IRF. Extracted decay constants, $\tau_R$, measure the dissociation timescale. Notice the elongation of $\tau_R$ as $v_2$ increases.
Figure 10. H-ion transients obtained after 197.1 nm excitation of NH₃ (Å) ν₂' = 5. Data (circles) and fits (solid lines) are shown for seven regions of the H-atom energy distribution. H and NH₂ are co-fragments of NH₃ dissociation, and the NH₂ internal energy can be inferred from the measurement of H-atom kinetic energy (KE). Labels in each panel refer to quanta in the bend vibrational mode of the NH₂ ground state. The ν₂ = 9 level is accessible at this initial excitation energy. Fit function is an exponential rise convoluted with the IRF. Extracted decay constants, τₐ, measure the dissociation timescale. Notice the elongation of τₐ as ν₂ increases.