Observation of Ultrafast NH_3 (Ã) State Relaxation Dynamics using a Combination of Time-resolved Photoelectron Spectroscopy and Photoproduct Detection

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Electronic Supplementary Information

SM.1 INTRODUCTION

Contained in this supplememtatry material is a close-up of the ν_2' = 2 photoelectron spectrum and a complete set of transient profiles obtained after UV (197 – 208 nm) excitation of the ν_2' = 2 - 5 levels of NH_3 (Ã). 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.

SM.2 TIME-RESOLVED PHOTOELECTRON SPECTRA

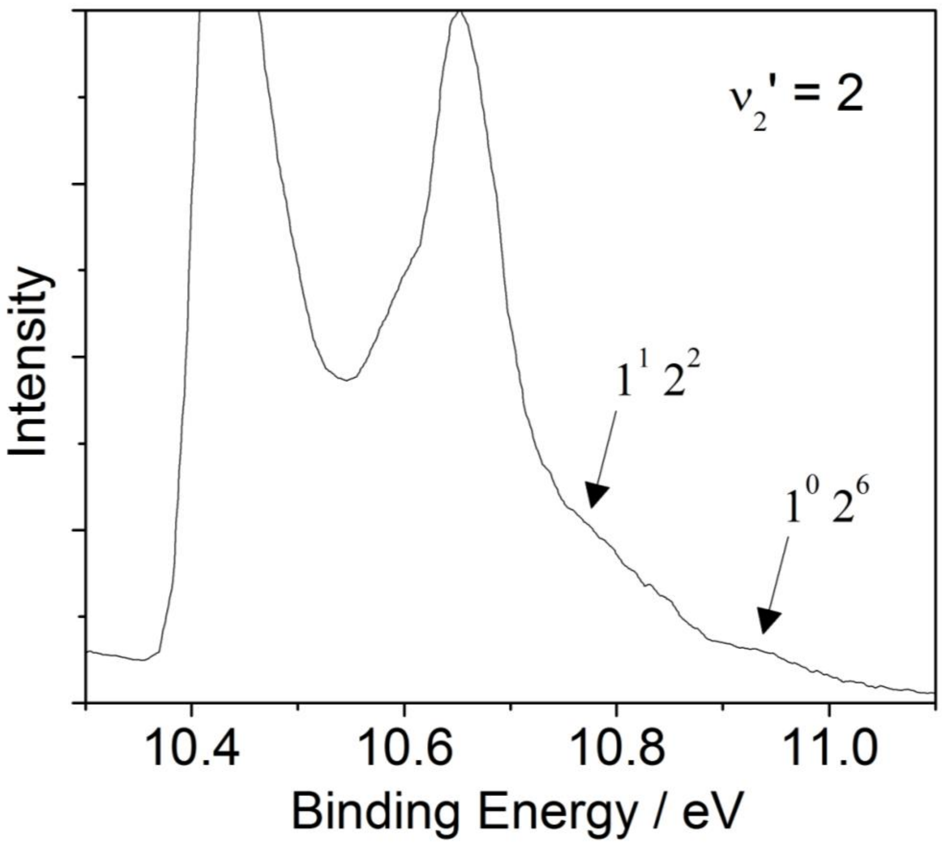

Figure 1. Photoelectron binding energy spectrum obtained after 208.5 nm excitation of NH_3 (Ã) $\nu_2' = 2$. This close-up view of Fig. 3(a) in the main document is meant to highlight the presence of peaks iii ($1^1 2^2$) and iv ($1^0 2^6$).

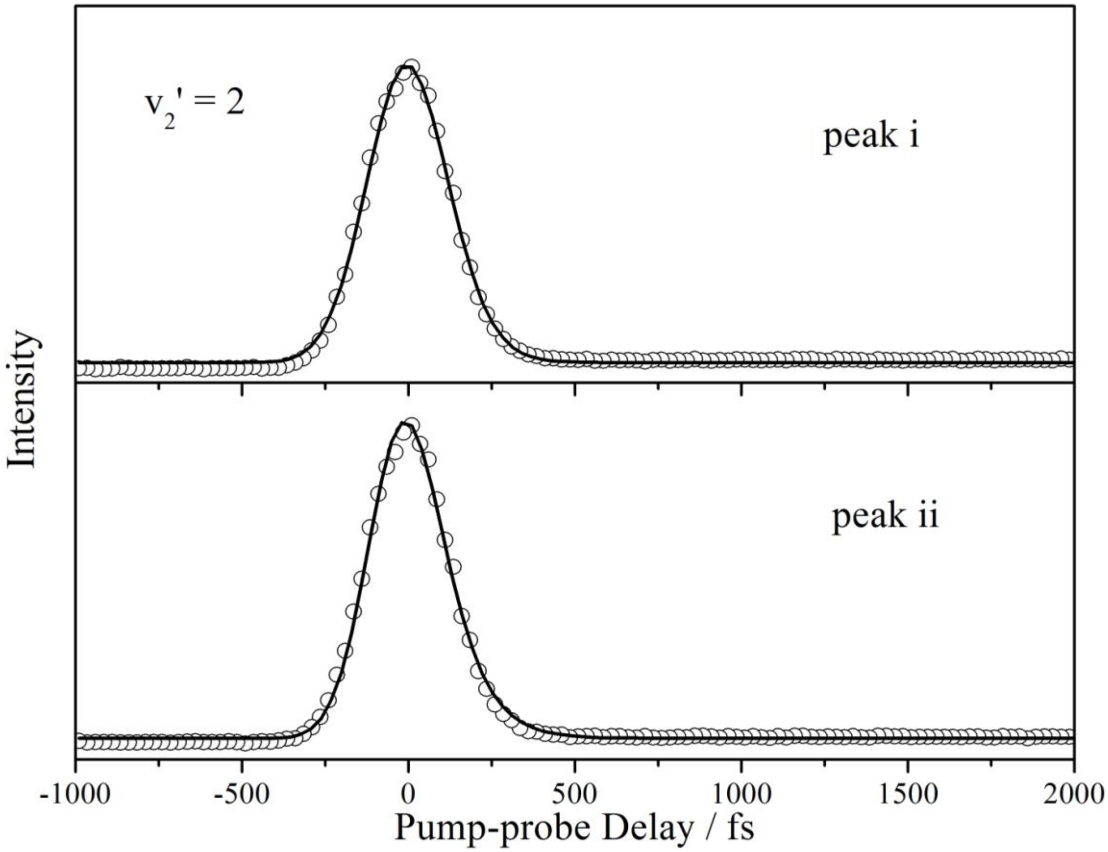

Figure 2. Photoelectron transients obtained after 208.5 nm excitation of NH_3 (Ã) ν_2’ = 2. Data (circles) and fits (solid lines) are shown for two peaks in the photoelectron spectrum. Fit function is an exponential decay convoluted with the Gaussian instrument response function (IRF) of fixed width (230 fs).

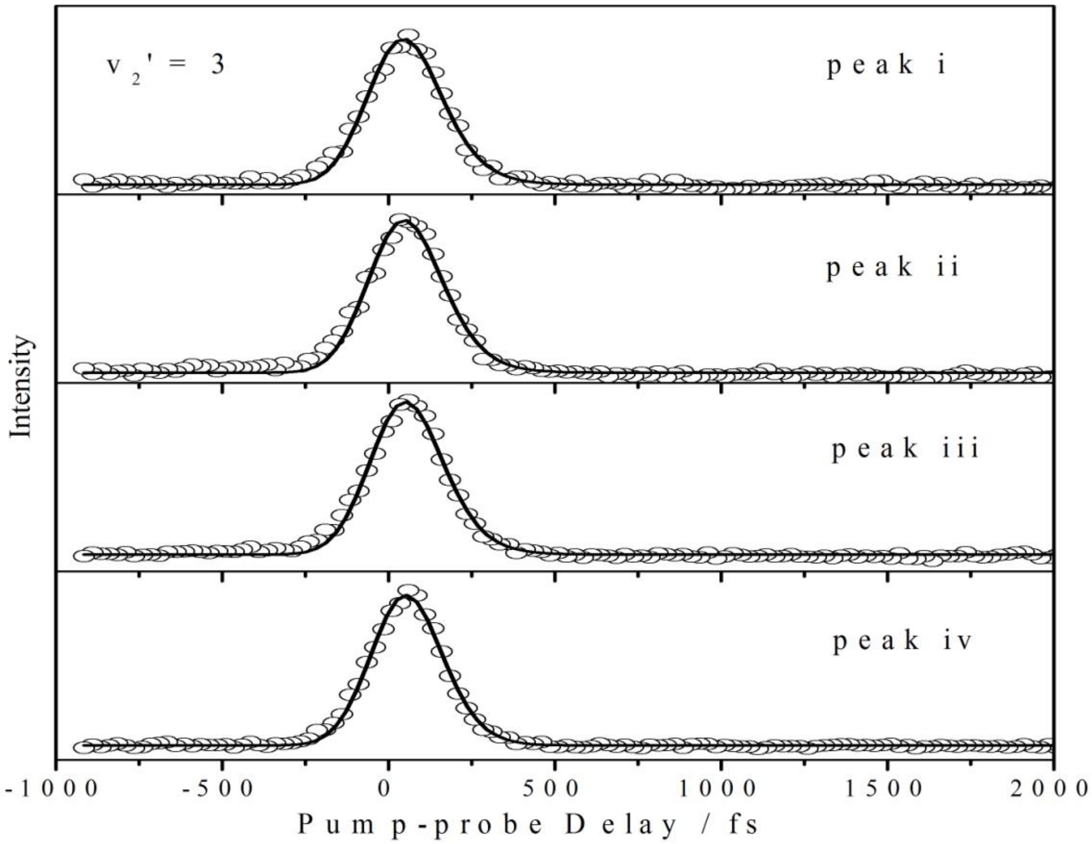

Figure 3. Photoelectron transients obtained after 204.6 nm excitation of NH_3 (Ã) ν_2' = 3. Data (circles) and fits (solid lines) are shown for four peaks in the photoelectron spectrum. Fit function is an exponential decay convoluted with the IRF. Data for peak i are presented in the main paper as Figure 4, with individual contributions from the decay and IRF clearly identified.

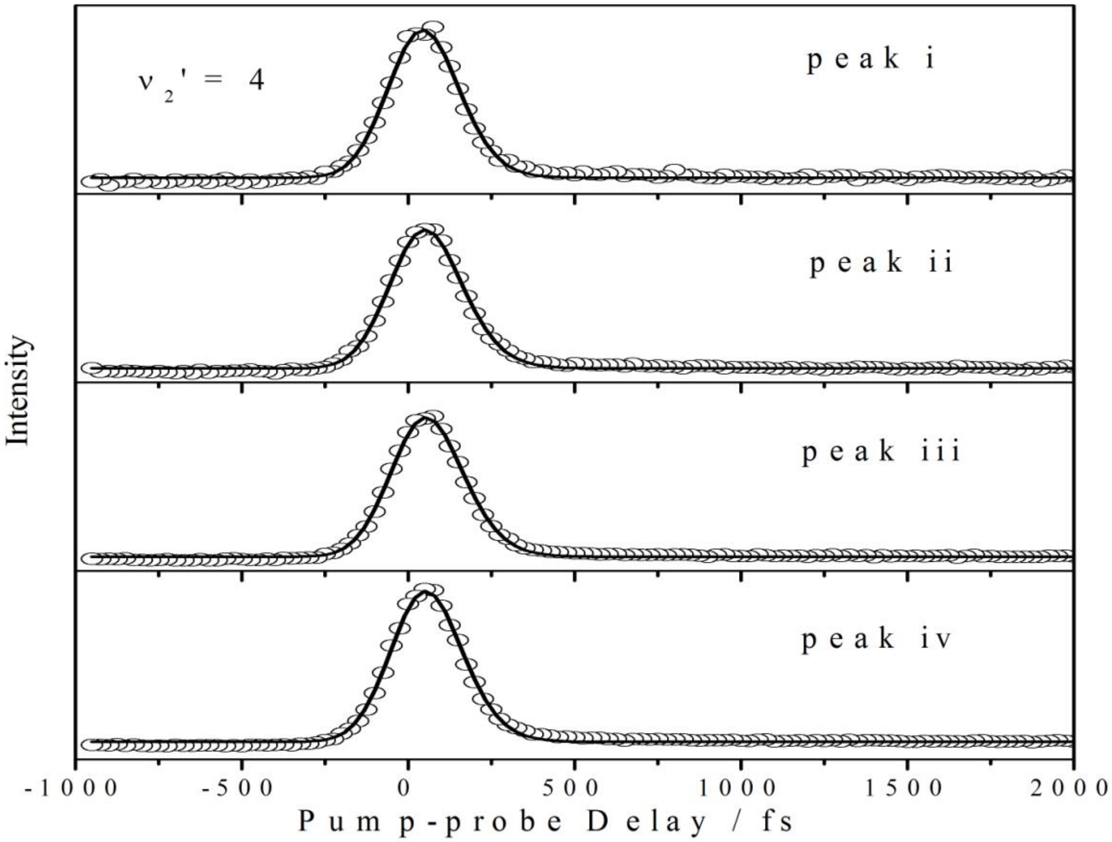

Figure 4. Photoelectron transients obtained after 200.8 nm excitation of NH_3 (Ã) ν_2' = 4. Data (circles) and fits (solid lines) are shown for four peaks in the photoelectron spectrum. Fit function is an exponential decay convoluted with the IRF.

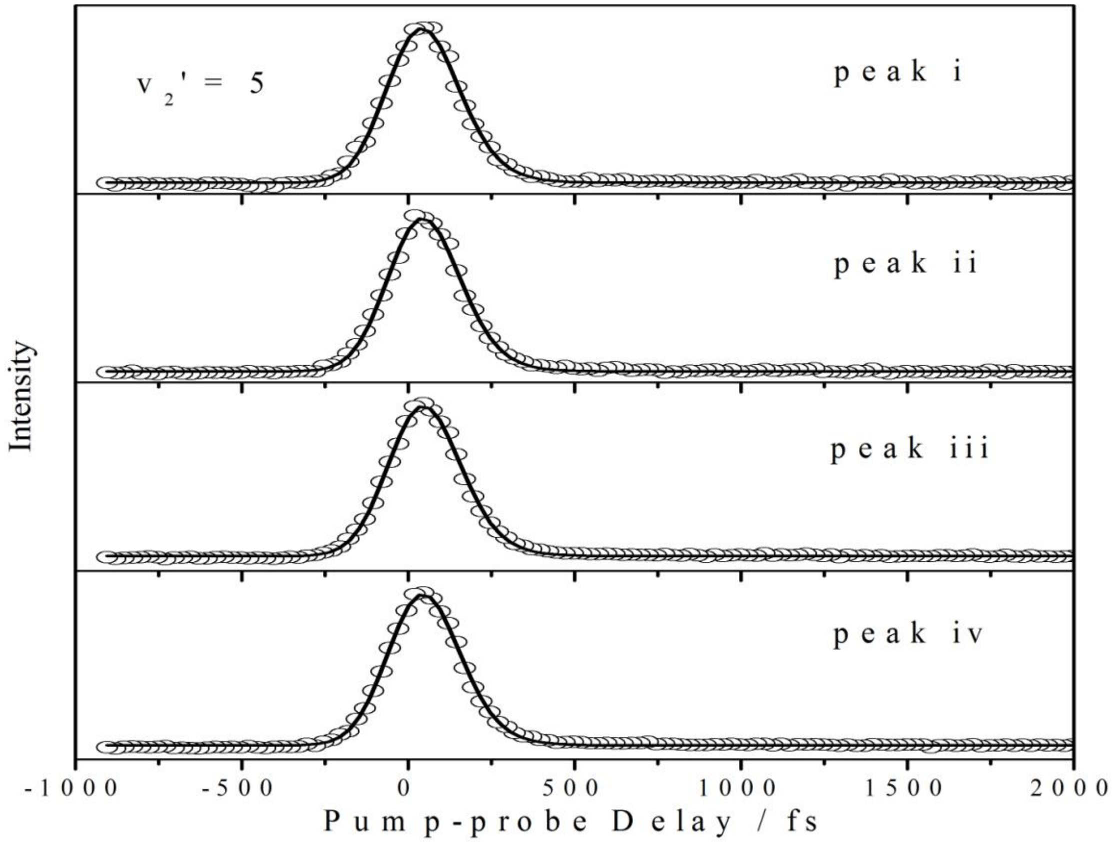

Figure 5. Photoelectron transients obtained after 197.1 nm excitation of NH_3 (Ã) ν_2’ = 5. Data (circles) and fits (solid lines) are shown for four peaks in the photoelectron spectrum. Fit function is an exponential decay convoluted with the IRF.

SM.3 TIME-RESOLVED ION YIELD

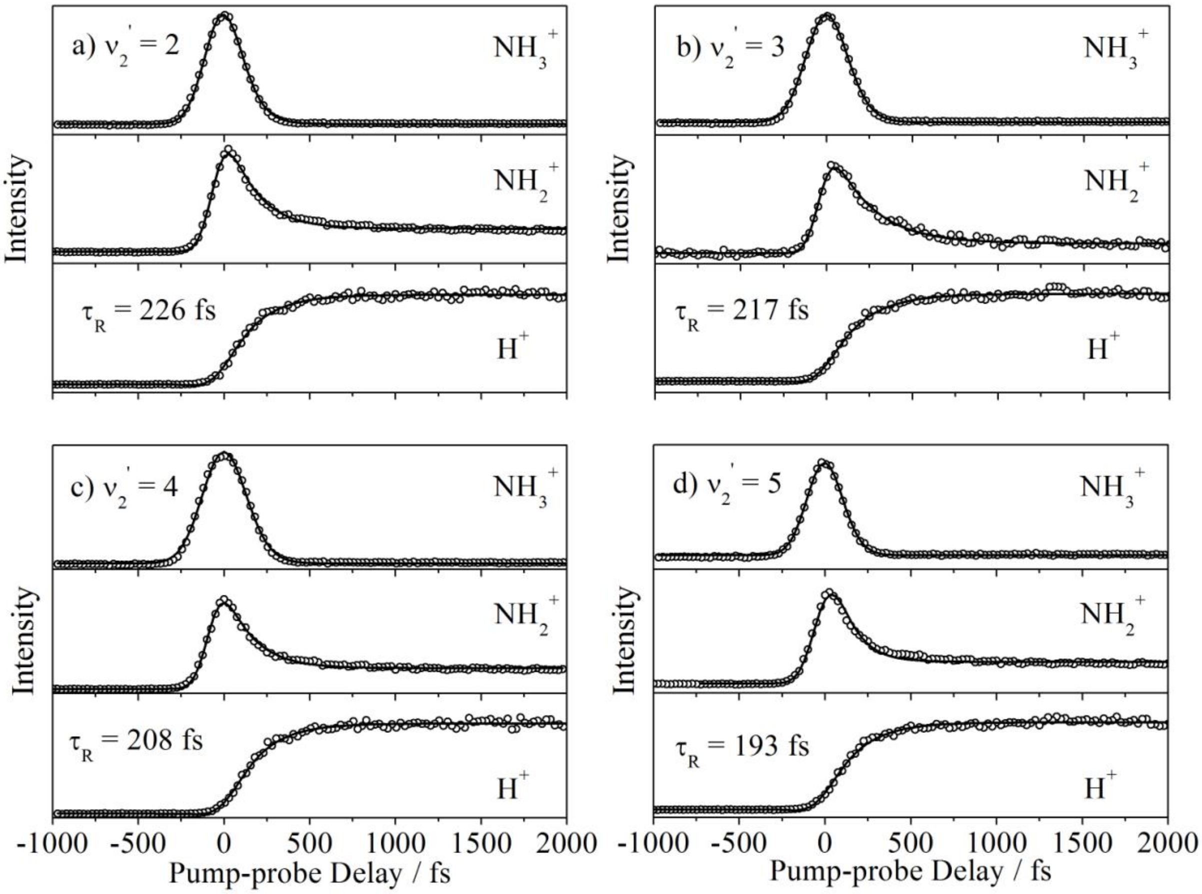

Figure 6. Transient profiles obtained from TRIY experiments on ν_2’ = 2 - 5 (a – d) levels of NH_3 (Ã). Data (circles) and fits (solid lines) for NH_3^+, NH_2^+, and H^+ are shown top to bottom, respectively, in each panel. Panel (c) is presented in Section 3.2 of the main document. For NH_3^+, the fit 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, τ_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 ν_2’ level, τ_R is fixed to the value obtained in fitting of the H^+ transient, and τ_D is fit. τ_D obtains as the same value as the NH_3^+ decay time and is therefore associated with the NH_3 (Ã) state.

SM.3 TIME-RESOLVED PHOTOFRAGMENT TRANSLATION SPECTRA

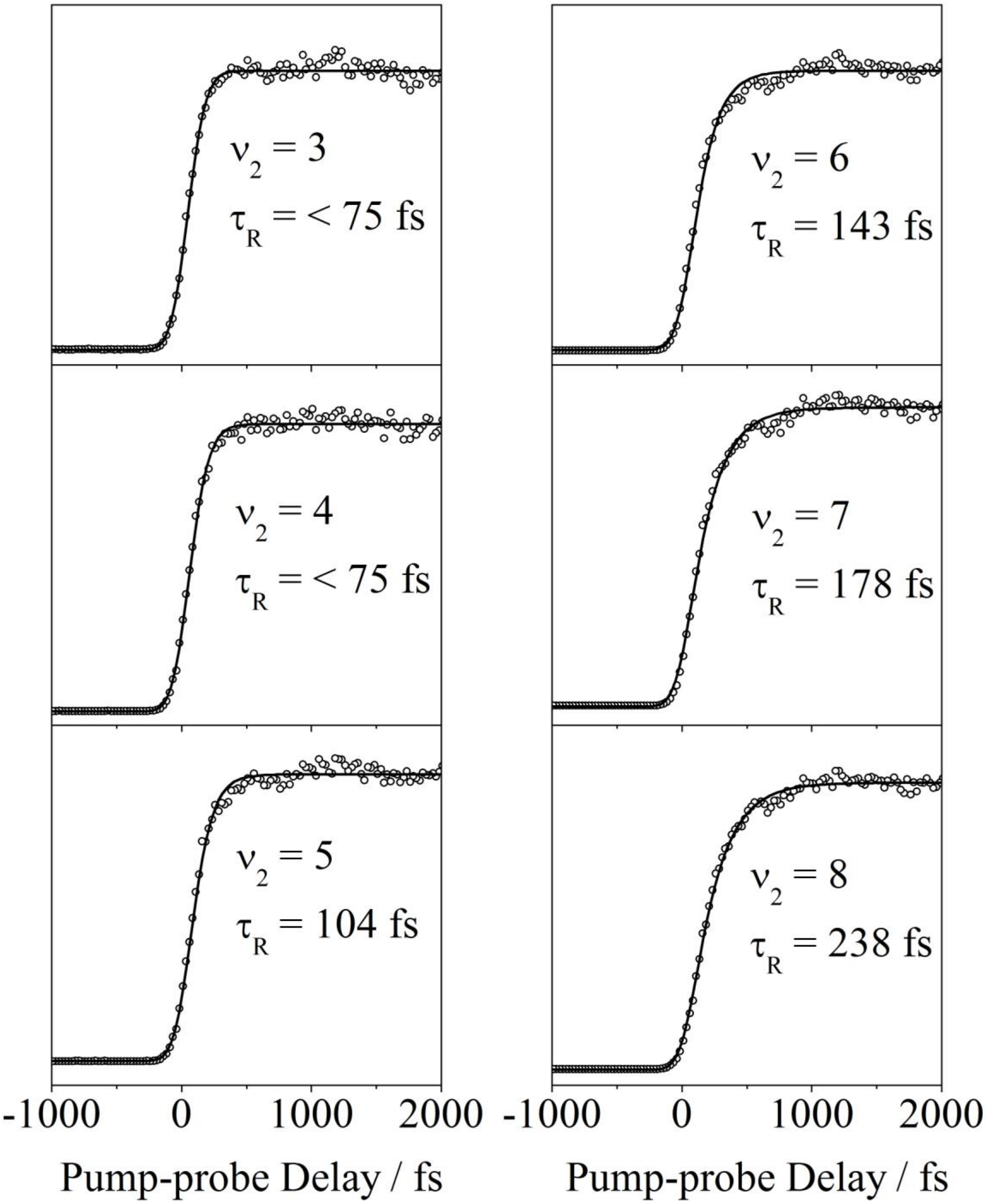

Figure 7. H-ion transients obtained after 208.5 nm excitation of NH_3 (Ã) ν_2’ = 2. Data (circles) and fits (solid lines) are shown for six regions of the H-atom energy distribution. H and NH_2 are co-fragments of NH_3 dissociation, and the NH_2 internal energy can be inferred from the measurement of 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, τ_R, measure the dissociation timescale. Notice the elongation of τ_R as ν_2 increases.

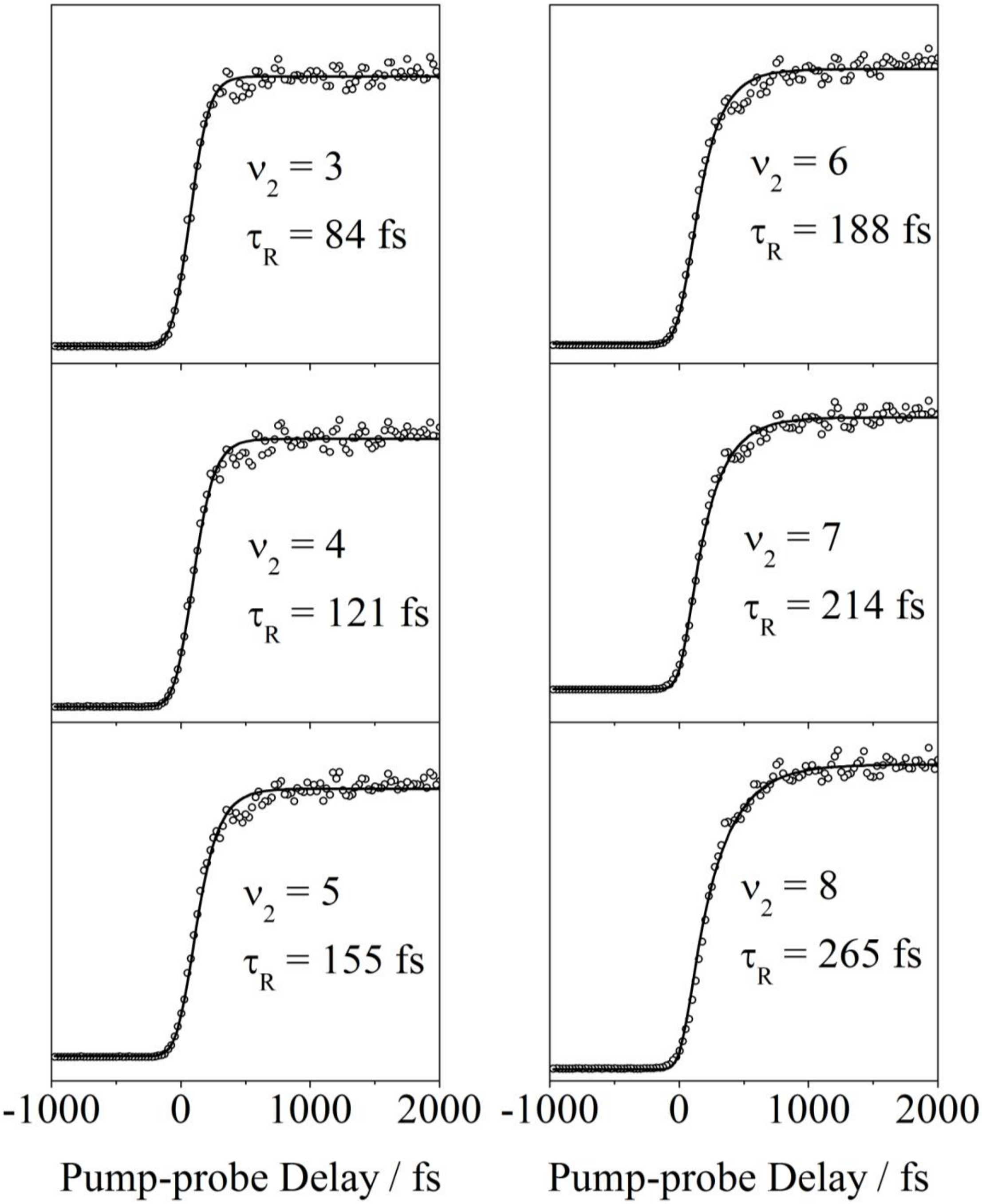

Figure 8. H-ion transients obtained after 204.6 nm excitation of NH_3 ($\tilde{A}$) ν_2' = 3. Data (circles) and fits (solid lines) are shown for six regions of the H-atom energy distribution. The ν_2 = 4, 8, and 8 transient data are presented in Section 3.3 of the main document. H and NH_2 are co-fragments 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, τ_R, measure the dissociation timescale. Notice the elongation of τ_R as ν_2 increases.

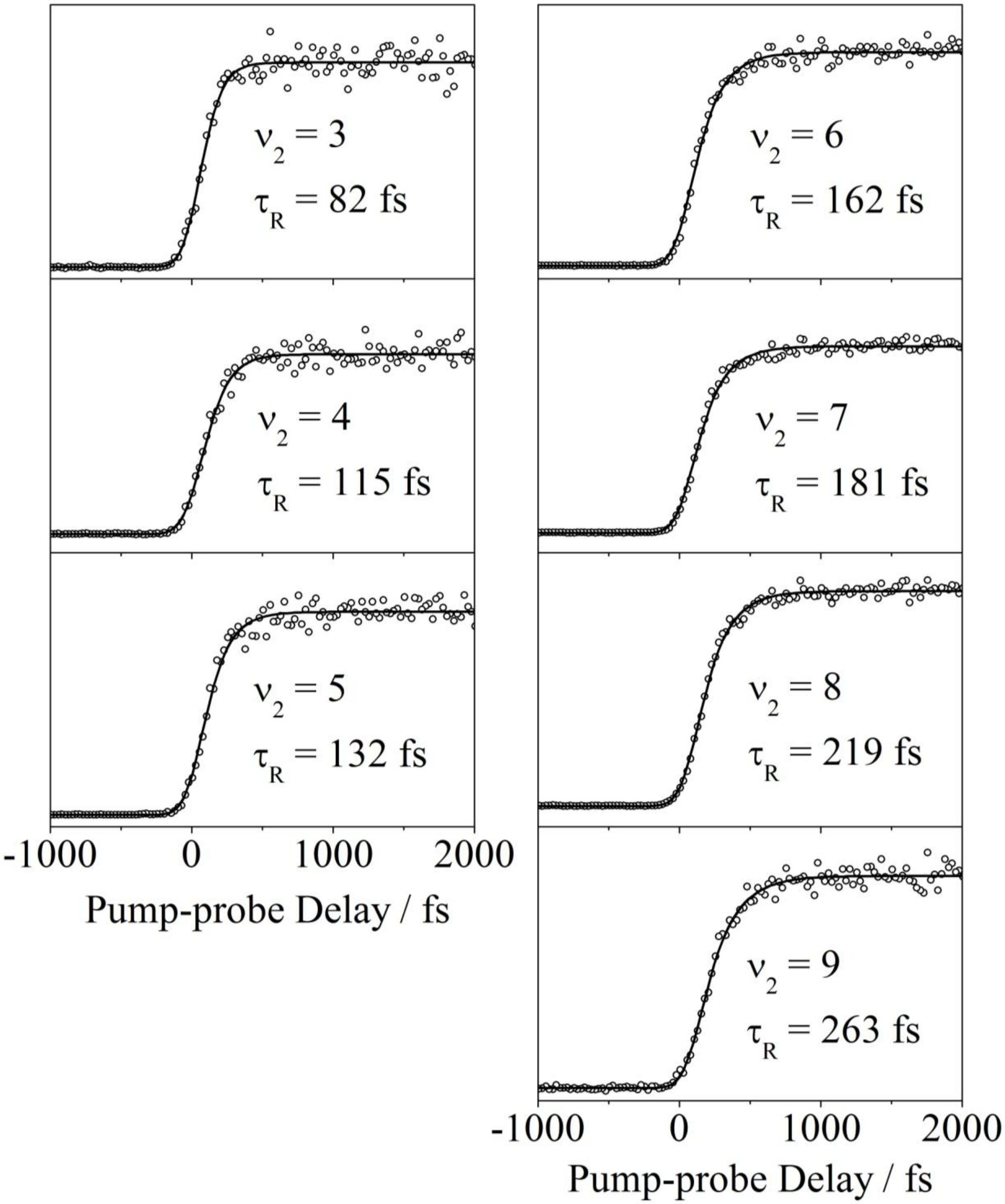

Figure 9. H-ion transients obtained after 200.8 nm excitation of NH_3 (Ã) ν_2' = 4. Data (circles) and fits (solid lines) are shown for seven regions of the H-atom energy distribution. H and NH_2 are co-fragments of NH_3 dissociation, and the NH_2 internal energy can be inferred from the measurement 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 ν_2 = 9 level is accessible at this initial excitation energy. Fit function is an exponential rise convoluted with the IRF. Extracted decay constants, τ_R, measure the dissociation timescale. Notice the elongation of τ_R as ν_2 increases.

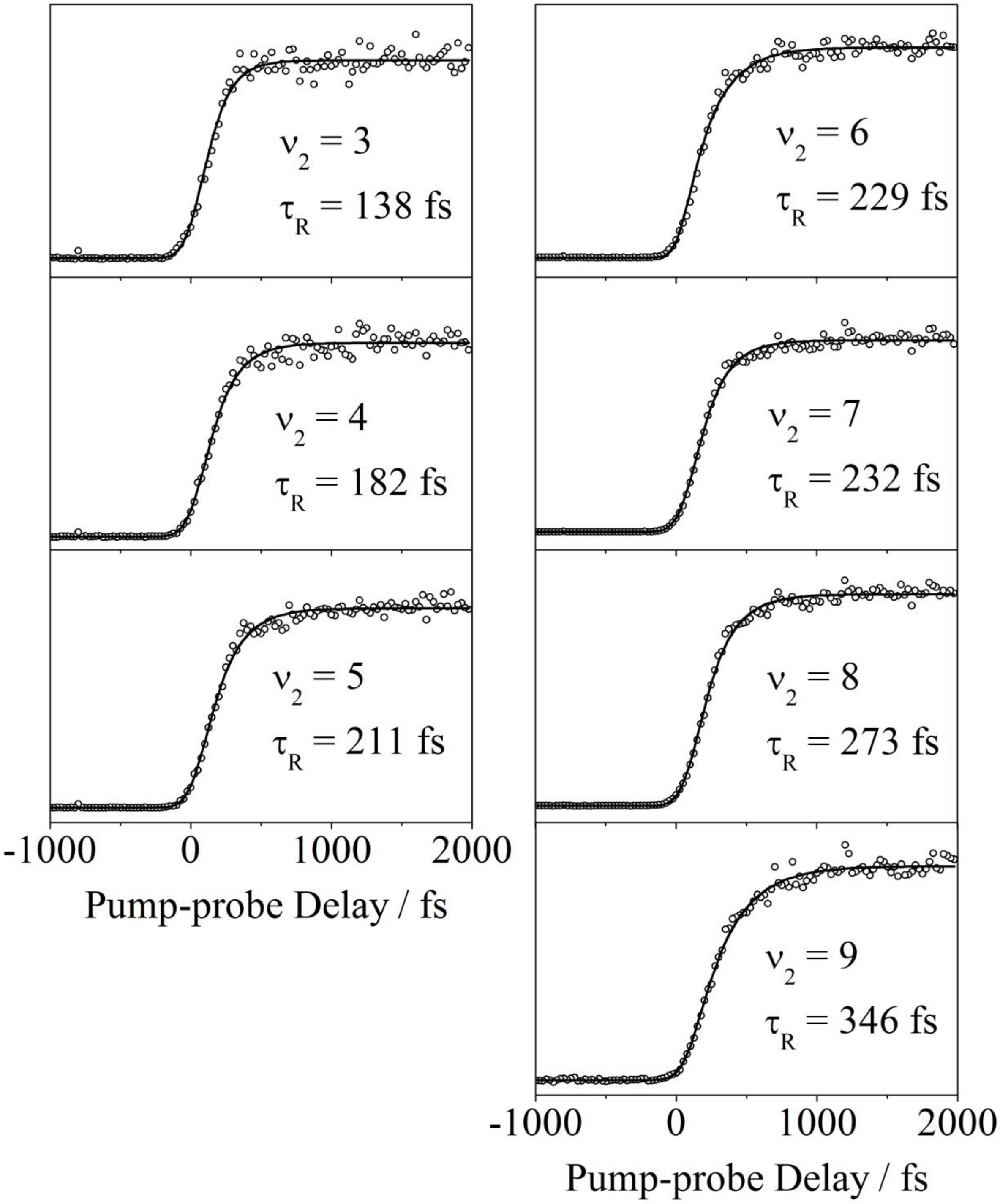

Figure 10. H-ion transients obtained after 197.1 nm excitation of NH_3 ($\tilde{A}$) $\nu_2' = 5$. Data (circles) and fits (solid lines) are shown for seven regions of the H-atom energy distribution. H and NH_2 are co-fragments of NH_3 dissociation, and the NH_2 internal energy can be inferred from the 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 $\nu_2 = 9$ level is accessible at this initial excitation energy. Fit function is an exponential rise convoluted with the IRF. Extracted decay constants, τ_R, measure the dissociation timescale. Notice the elongation of τ_R as ν_2 increases.