

Tunneling Dynamics of the NH_3 ($\tilde{\text{A}}$) State Observed by Time-resolved Photoelectron and H-atom Kinetic Energy Spectroscopies

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Supporting Information

SI.1 INTRODUCTION

Contained in this supplementary information are results from time-resolved photoelectron spectroscopy (TR-PES; SI.2) and time-resolved total kinetic energy release spectroscopy (TR-TKER; SI.3) experiments on the first electronic excited state of ammonia, $\text{NH}_3(\tilde{\text{A}})$. Presented here is a complete set of transient profiles obtained after UV (204 – 216 nm) excitation of the $\nu_2' = 0 - 3$ levels of $\text{NH}_3(\tilde{\text{A}})$. Details of transient profile production from the raw data and of least-squares fits are contained in the main document. Fit results from plots in this supplementary information section are reported in Tables 2 and 3 of the main text and are used to analyze the photophysics of ammonia. See each figure caption for detailed description.

SI.2 TIME-RESOLVED PHOTOELECTRON SPECTRA

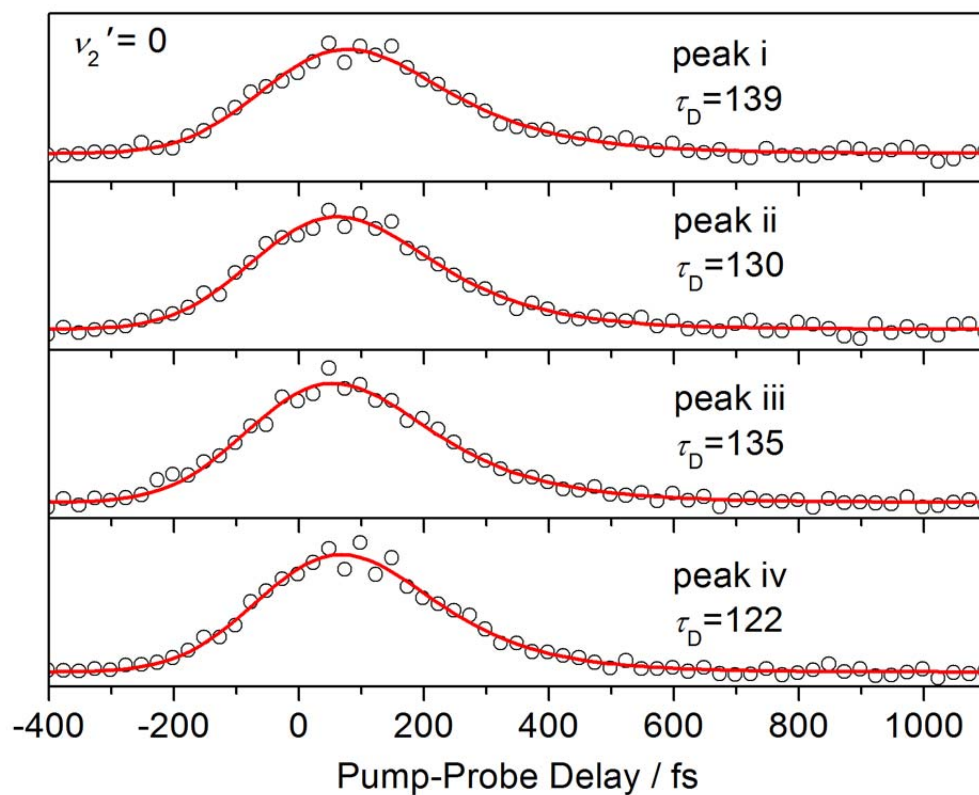


Figure 1. Photoelectron transients obtained after 216.4 nm excitation of NH_3 ($\tilde{\text{A}}$) $\nu_2' = 0$. Data (circles) and fits (red lines) are shown for four peaks as labeled in Fig. 2 of the main document.

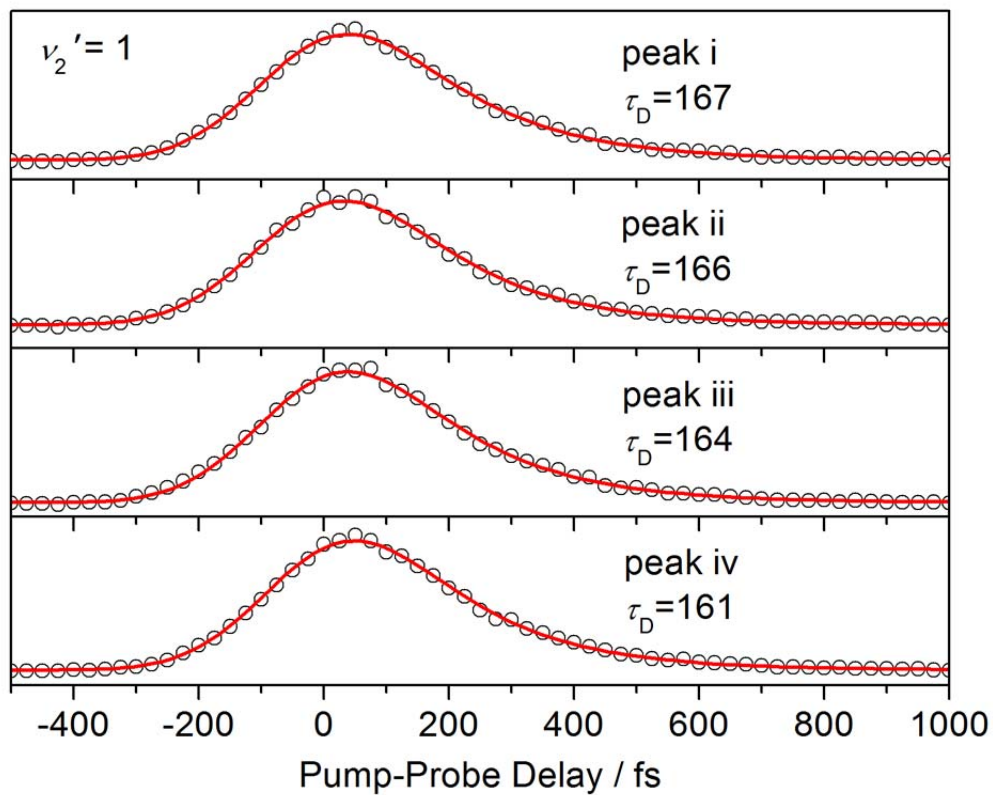


Figure 2. Photoelectron transients obtained after 212.6 nm excitation of NH_3 ($\tilde{\text{A}}$) $\nu_2' = 1$. Data (circles) and fits (red lines) are shown for four peaks as labeled in Fig. 2 of the main document.

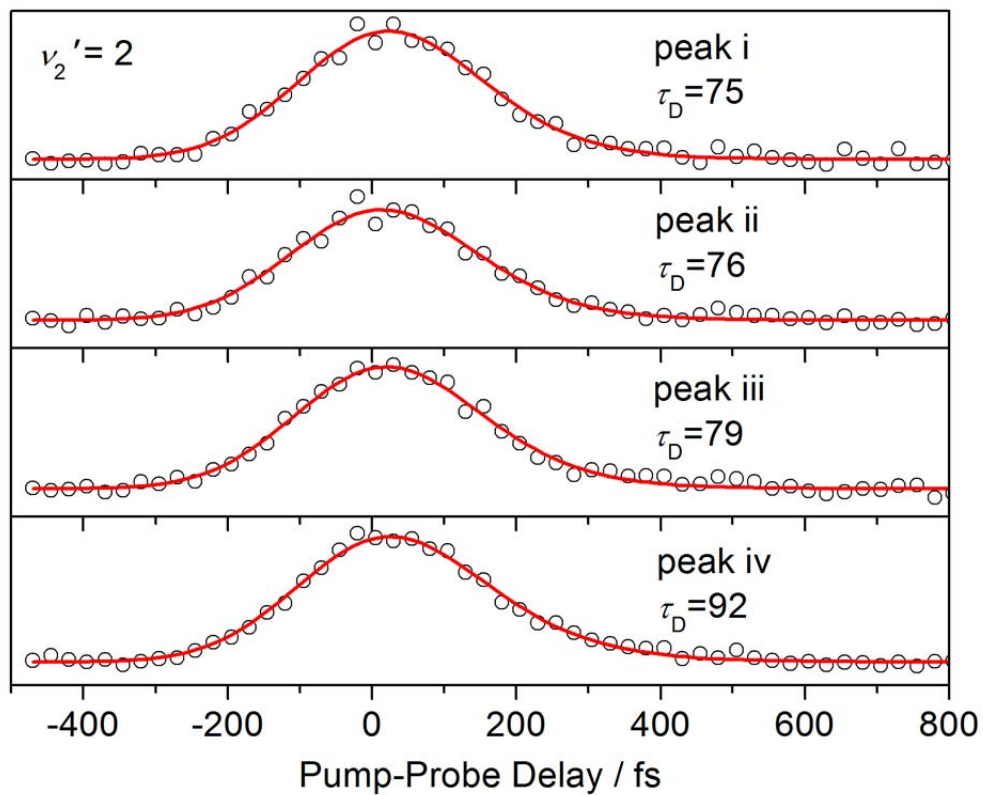


Figure 3. Photoelectron transients obtained after 208.5 nm excitation of NH_3 ($\tilde{\text{A}}$) $\nu_2' = 2$. Data (circles) and fits (red lines) are shown for four peaks as labeled in Fig. 2 of the main document.

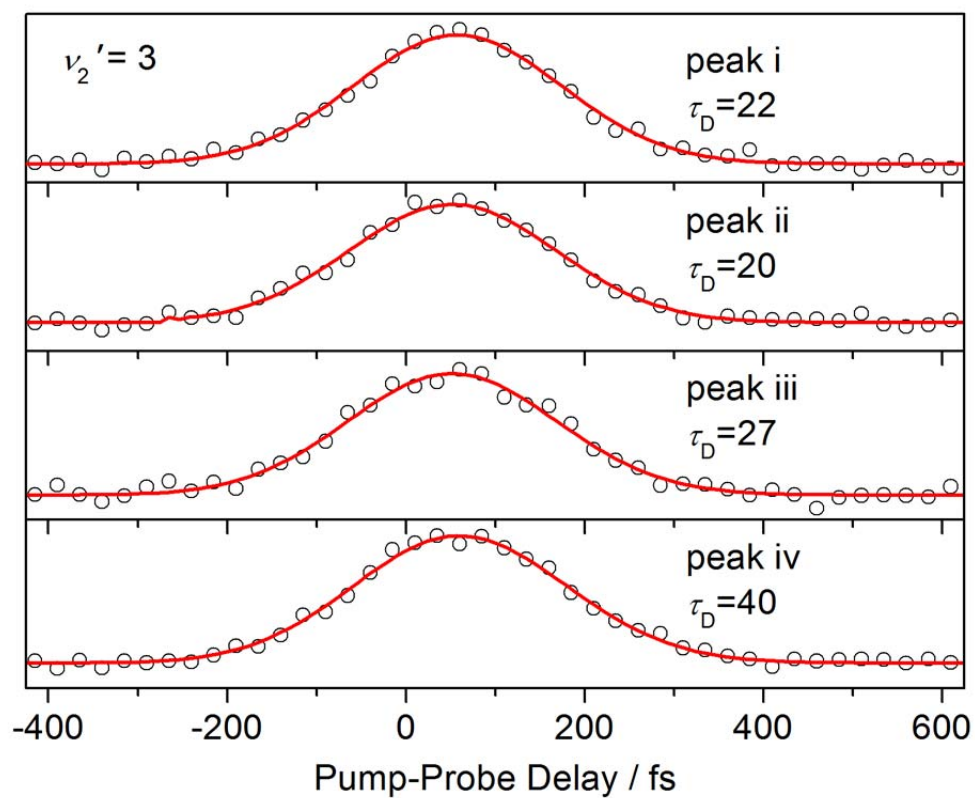


Figure 4. Photoelectron transients obtained after 204.6 nm excitation of NH_3 ($\tilde{\text{A}}$) $\nu_2' = 3$. Data (circles) and fits (red lines) are shown for four peaks as labeled in Fig. 2 of the main document.

SI.3 TIME-RESOLVED NH₂ INTERNAL ENERGY SPECTRA

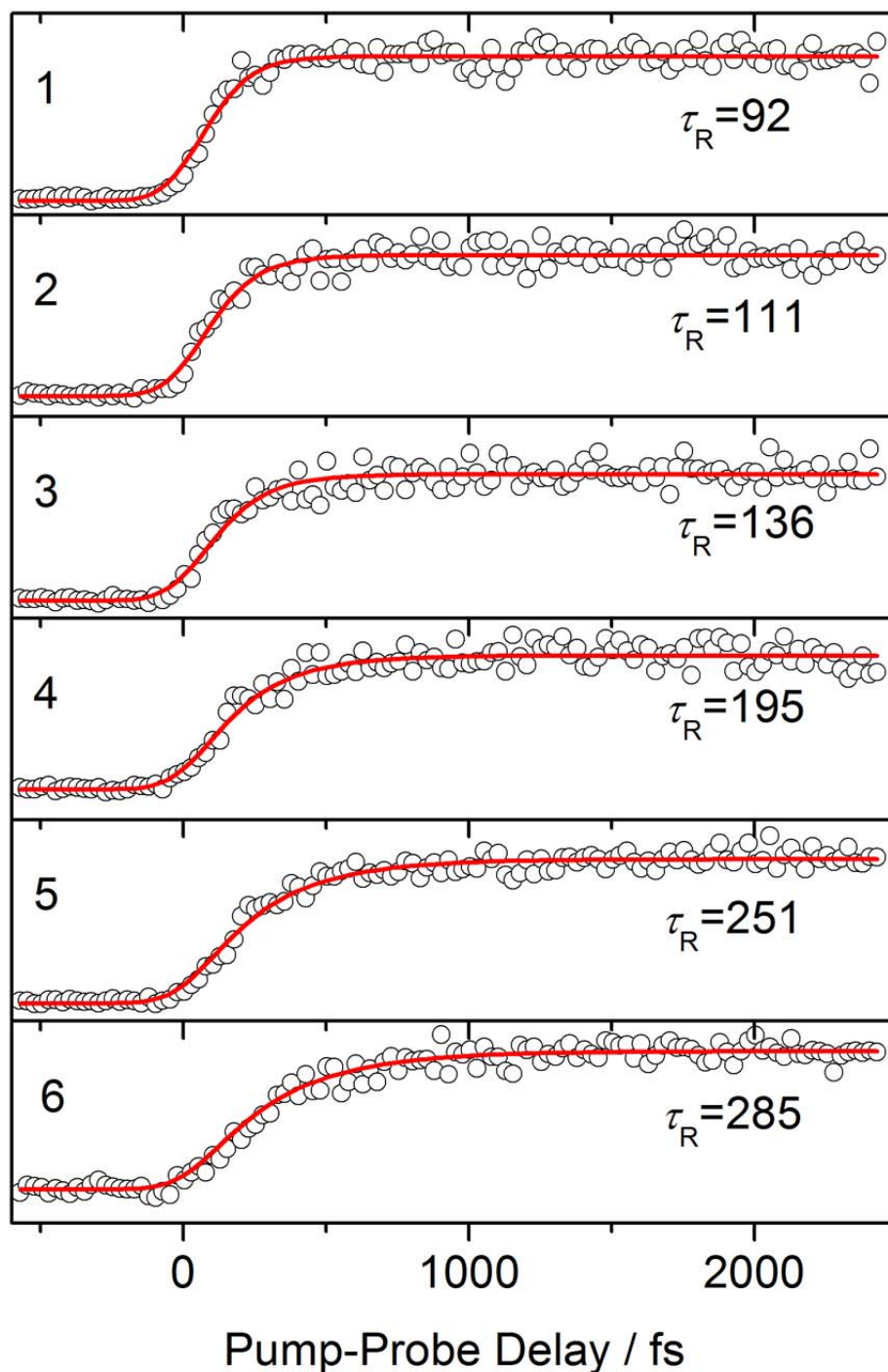


Figure 5. Transients obtained after 216.4 nm excitation of NH₃ (\tilde{A}) $\nu_2' = 0$. Data (circles) and fits (red lines) are shown for six regions of the NH₂ internal energy distribution displayed in Fig. 5 of the main document with integration boundaries defined in Table 3. The fit function is an exponential rise convoluted with the IRF and extracted rise constants, τ_R , measure the dissociation timescale.

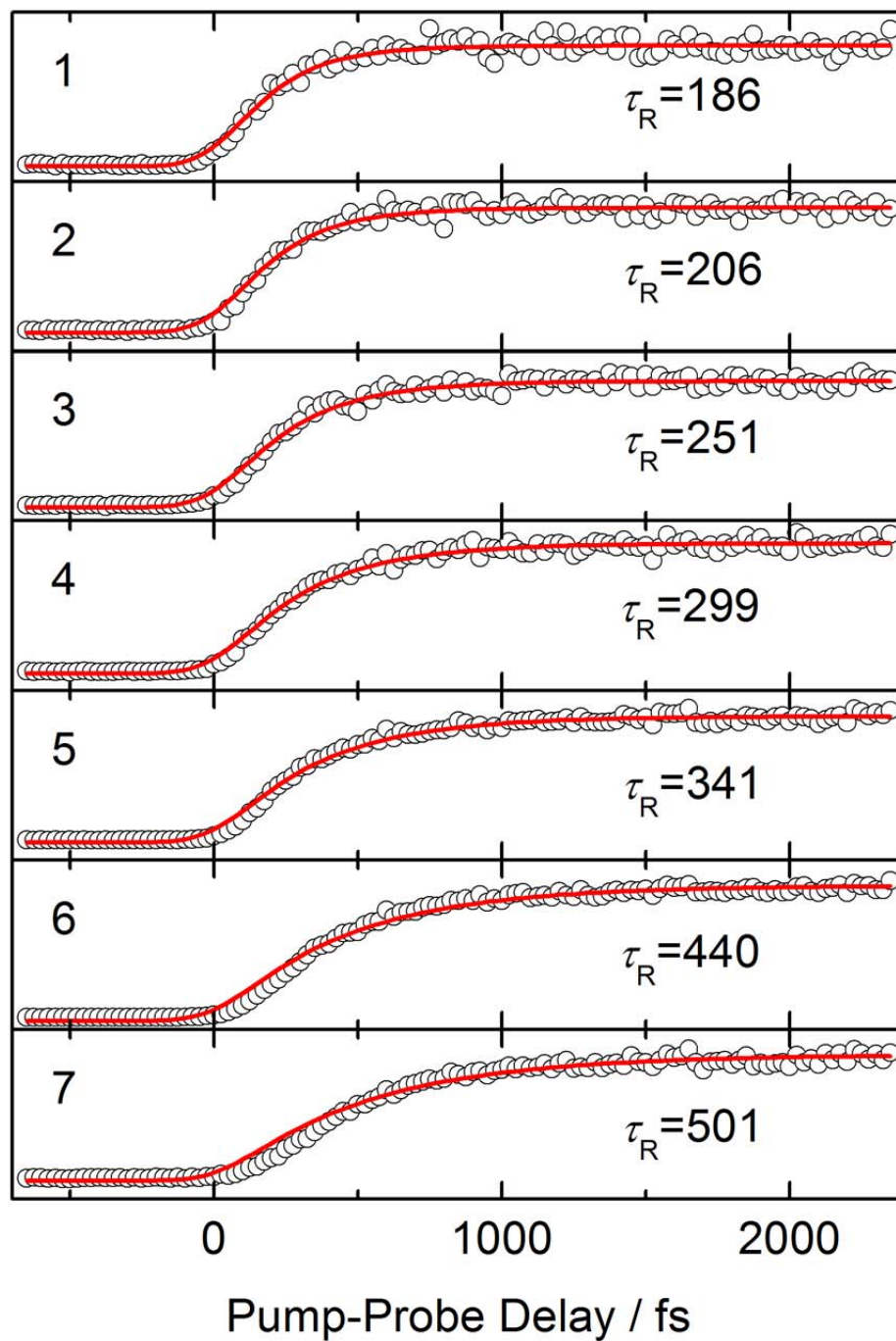


Figure 6. Transients obtained after 212.6 nm excitation of NH_3 ($\tilde{\text{A}}$) $\nu_2' = 1$. Data (circles) and fits (red lines) are shown for seven regions of the NH_2 internal energy distribution with integration boundaries defined in Table 3. The fit function is an exponential rise convoluted with the IRF. Extracted rise constants, τ_R , measure the dissociation timescale.

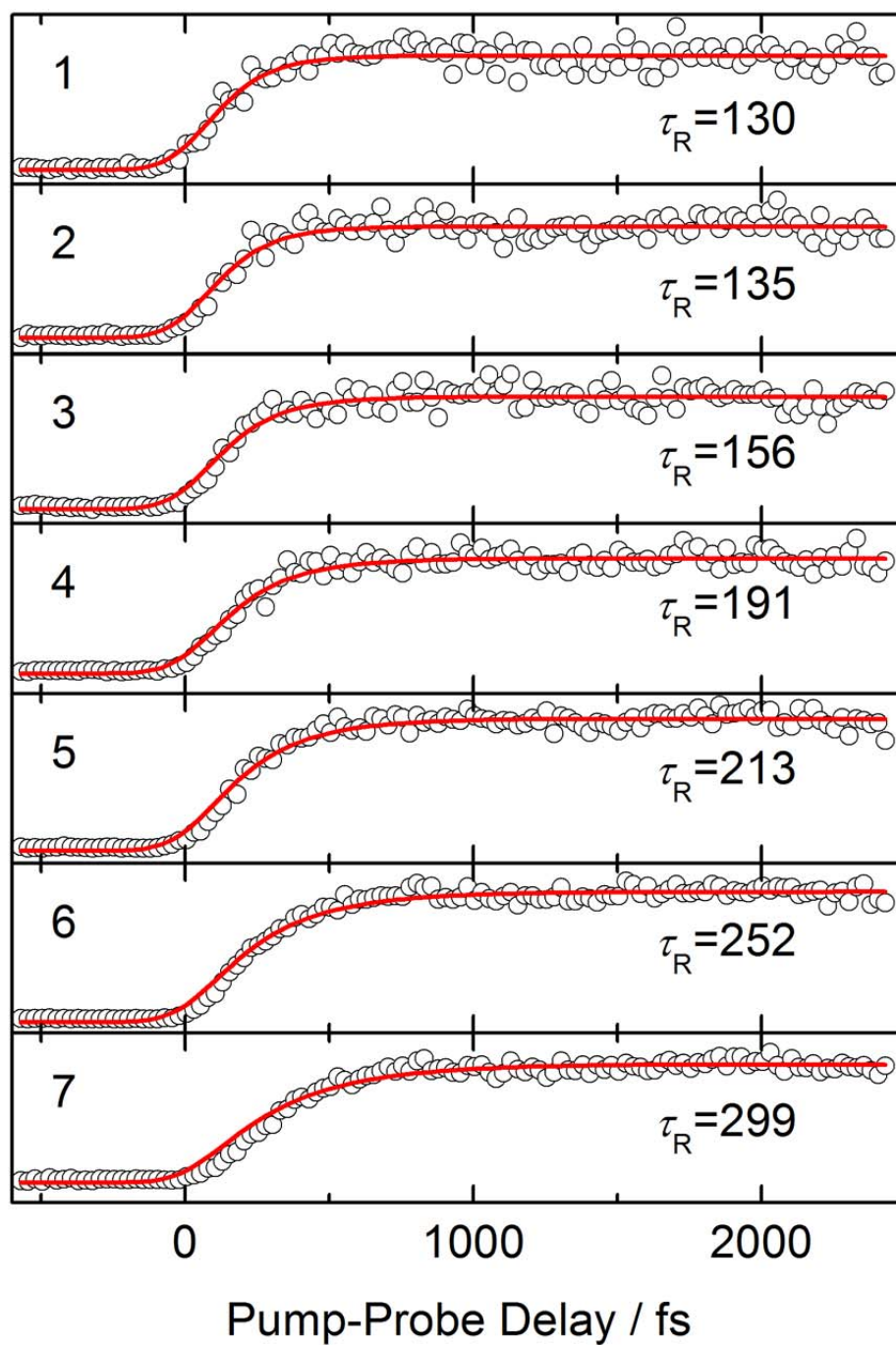


Figure 7. Transients obtained after 208.5 nm excitation of NH_3 ($\tilde{\text{A}}$) $\nu_2' = 2$. Data (circles) and fits (red lines) are shown for seven regions of the NH_2 internal energy distribution with integration boundaries defined in Table 3. Fit function is an exponential rise convoluted with the IRF. Extracted rise constants, τ_R , measure the dissociation timescale.

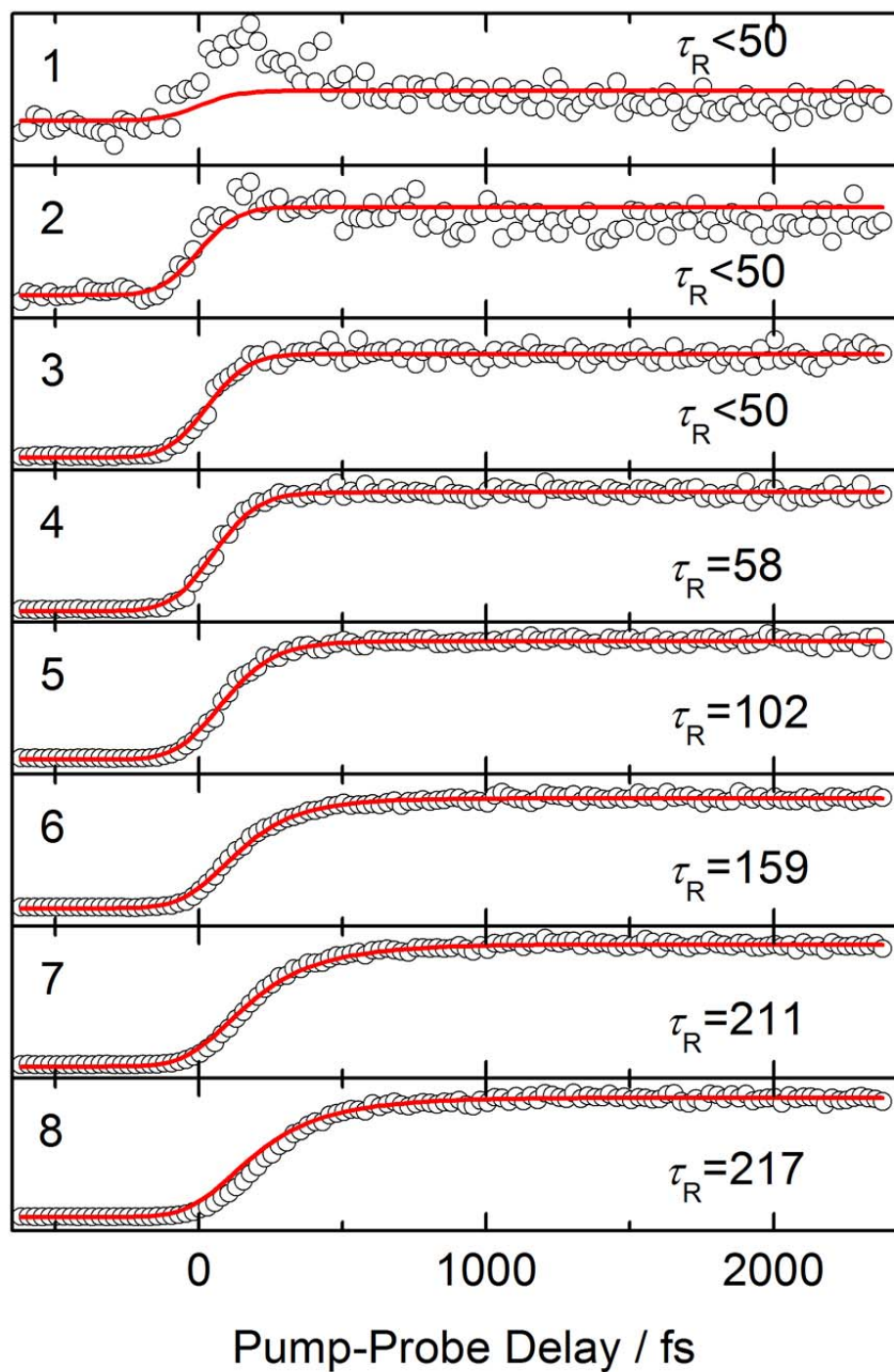


Figure 8. Transients obtained after 204.6 nm excitation of NH_3 ($\tilde{\text{A}}$) $\nu_2' = 3$. Data (circles) and fits (red lines) are shown for seven regions of the NH_2 internal energy distribution with integration boundaries defined in Table 3. Fit function is an exponential rise convoluted with the IRF. Extracted rise constants, τ_R , measure the dissociation timescale.