Supplementary Information
Unravelling the Full Relaxation Dynamics of Superexcited Helium Nanodroplets

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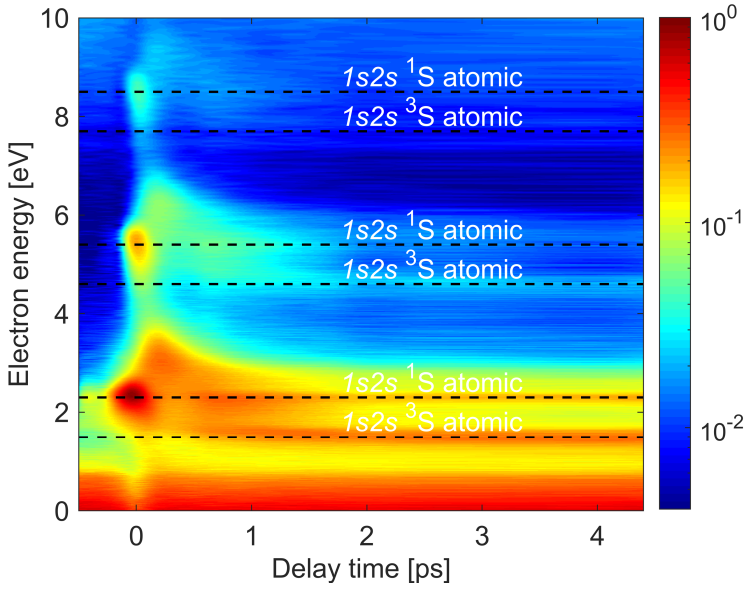


Supplementary Fig. 1: Same electron spectra of He nanodroplets as shown in Fig. 2 of the main text. Only the intensity scale now is logarithmic, the delay axis is constrained to short delays and the electron energy scale is extended to higher energies.

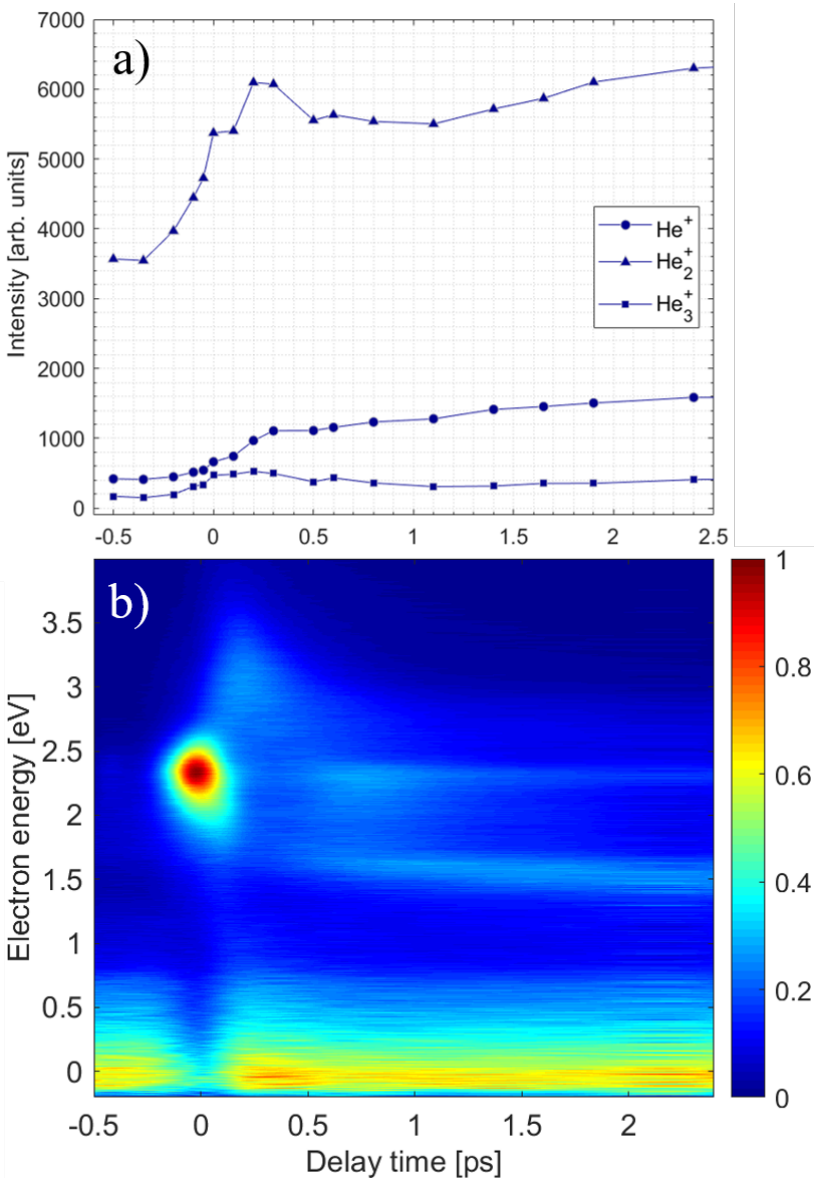
In this Supplementary Information (SI) we present a broader overview of the experimental results obtained at the same experimental conditions as those discussed in the main text and at different conditions. For the latter, both the intensities of pump and probe pulses, as well as the mean He droplet size were varied.

Supplementary Fig. 1 shows the same electron spectra as those presented in Fig. 2 of the main text. We clearly see two replicas of the main features present at electron energies below 4 eV, only shifted up in energy by multiples of the probe-pulse photon energy (3.16 eV) and with dropping intensity. These additional features are due to above-threshold ionization (ATI) of the excited He droplets by 2-4 probe photons, as discussed in Ref. [1]. The presence of ATI features in the spectra clearly shows that multiphoton ionization is efficient in this experiment. Thus, the assignment of the two main prominent lines at electron energies 1.6 eV and 2.4 eV to the $1s2s\,^{1,3}S$ excited states of He being ionized by two-photon absorption is well justified.

Supplementary Fig. 2 shows delay-dependent ion yields in a) and electron spectra in b) for similar experimental conditions as those used when recording the data shown in Figs. 1 and 2 of the main text. He droplets ($\langle N\rangle = 41,000$) were excited by the same pump pulses ($I_{\mathrm{pump}} = 1.7 \times 10^{10}$ Wcm^{-2}) and ionized by slightly weaker probe pulses ($I_{\mathrm{probe}} = 2.6 \times 10^{11}$ Wcm^{-2}). Both the delay-dependent ion yields and the electron spectra closely resemble those shown in Figs. 1 and 2 of the main text, showing the high reproducibility of the measurements.

In Supplementary Fig. 3, both the pump and the probe pulse intensities are increased. Most notably in a), the relative yield of He^+ atomic ions is significantly higher due to more efficient photoionization of the ejected He^* excited atoms. Accordingly, in b) the electron band corresponding to the 2s ^1S atomic state is much brighter than in all other time-resolved spectra. Besides, at this higher probe intensity, the low-energy electrons due to droplet autoionization are more efficiently depleted around zero delay.

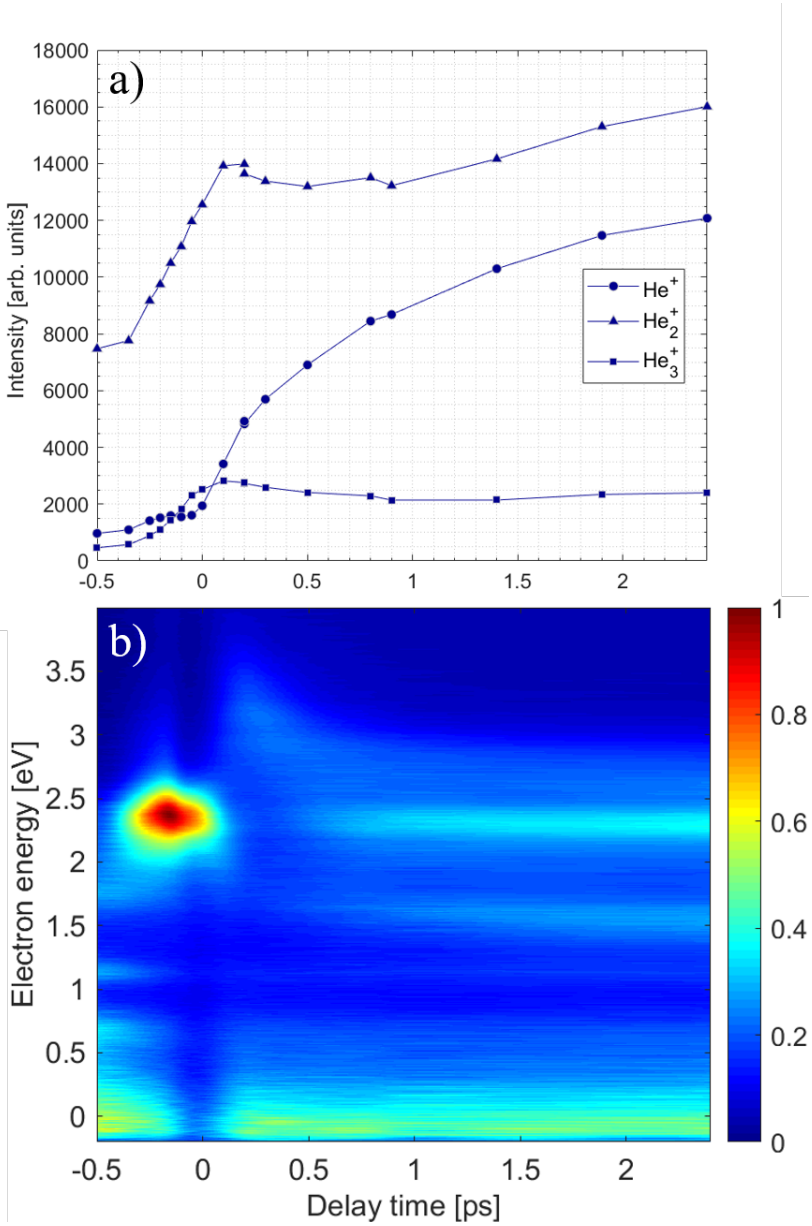
Supplementary Fig. 4 shows ion yields and electron spectra recorded for larger droplets ($\langle N\rangle = 1.7 \times 10^5$) at the standard pulse intensities. Clearly, the bands in the electron spectra are significantly broadened. However, the relaxation dynamics remains nearly unchanged. Similar line broadening for increasing droplet size was observed in our previous experiment where the droplets were resonantly excited into the lower absorption band [2]. The line



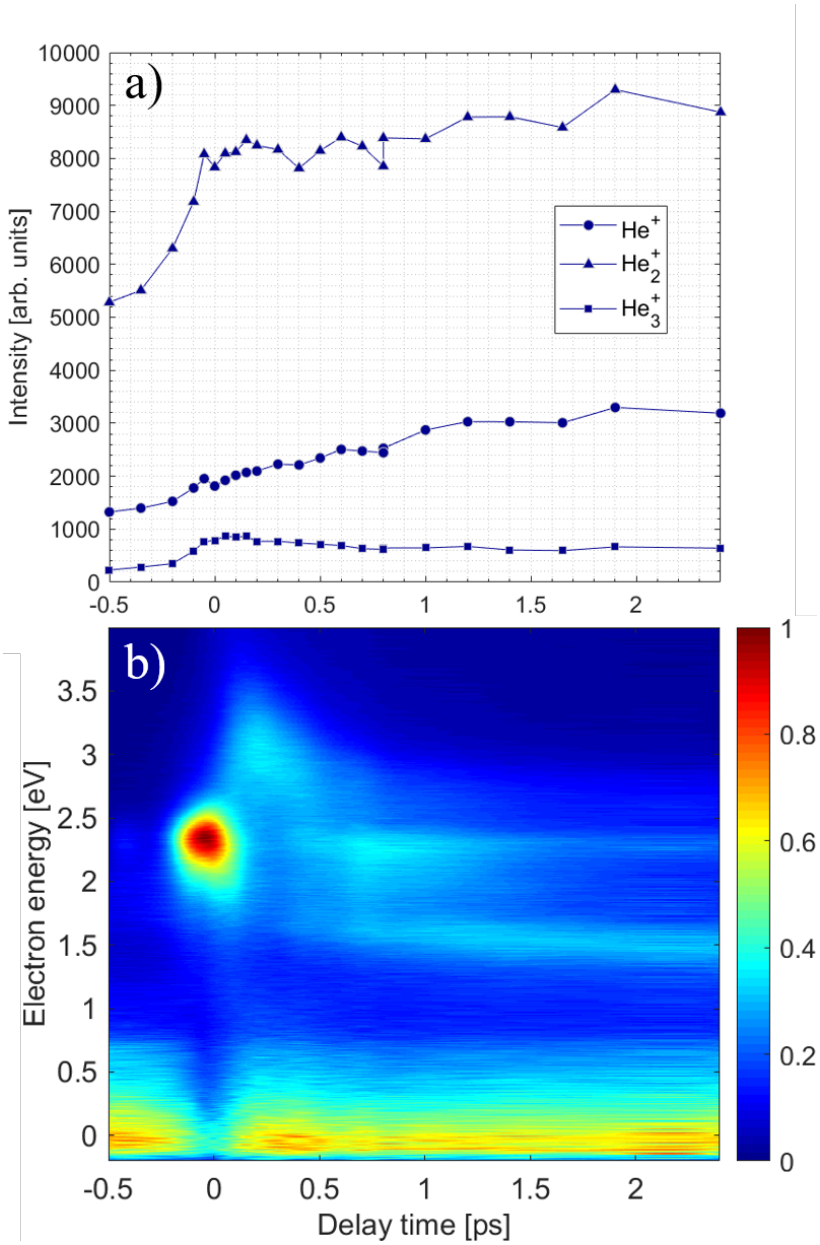
Supplementary Fig. 2: Ion yields (a) and electron spectra (b) of He nanodroplets ($\langle N \rangle = 4.1 \times 10^4$) photoionized by XUV pump pulses (1.7×10^{10} Wcm^{-2}) and UV probe pulses (2.6×10^{11} Wcm^{-2}).

broadening is attributed to elastic scattering of the electrons at the He atoms in the droplet.

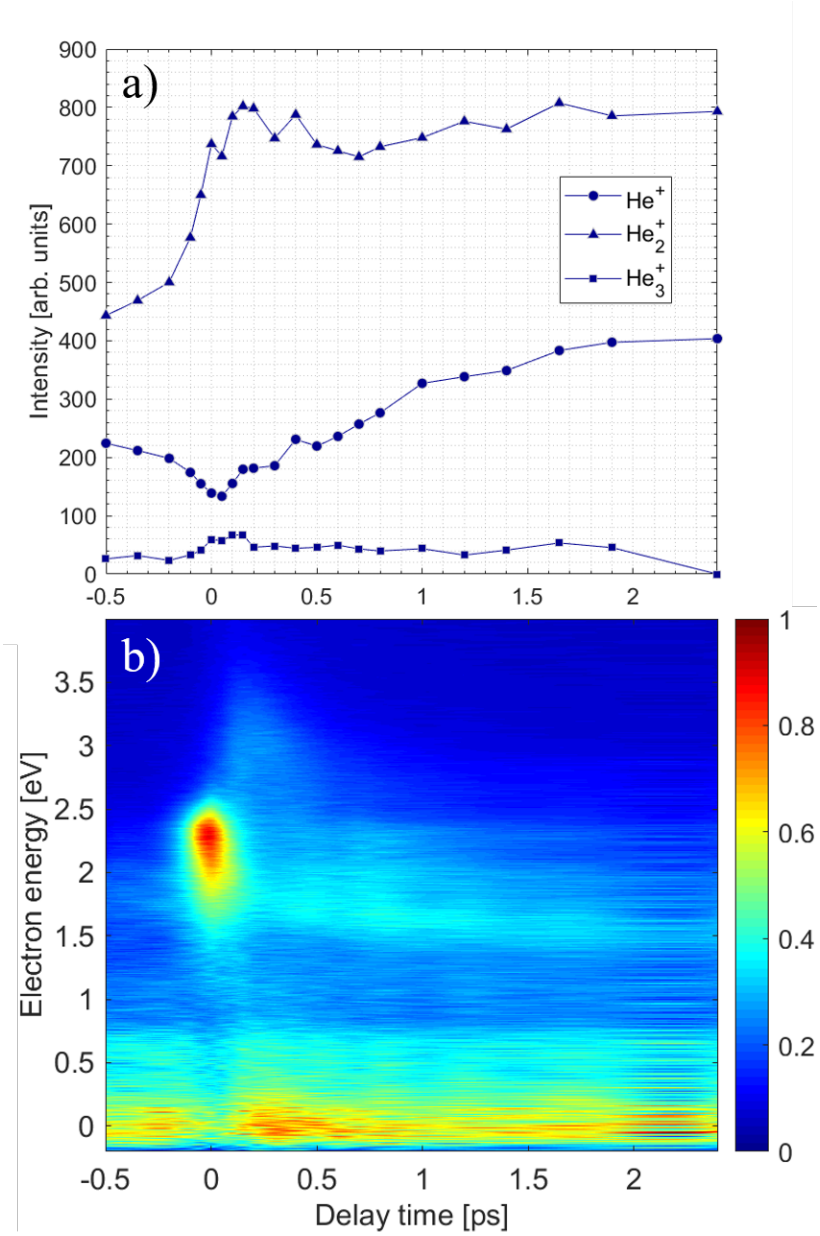
At even larger droplet size ($\langle N \rangle = 7 \times 10^5$), see Supplementary Fig. 5, the line broadening is even more pronounced to such an extent, that the individual spectral components are hardly distinguishable. Note that the HHG experiments by the Berkeley group [3], which suffered from lower spectral resolution, were performed at a similar droplet size. Indeed, their electron spectra resemble more those of Supplementary Figs. 4 and 5.



Supplementary Fig. 3: Ion yields (a) and electron spectra (b) of He nanodroplets ($\langle N \rangle = 4.1 \times 10^4$) photoionized by XUV pump pulses (3.1×10^{10} Wcm^{-2}) and UV probe pulses (2.4×10^{12} Wcm^{-2}).



Supplementary Fig. 4: Ion yields (a) and electron spectra (b) of He nanodroplets ($\langle N \rangle = 1.7 \times 10^5$) photoionized by XUV pump pulses (1.8×10^{10} Wcm^{-2}) and UV probe pulses (2.6×10^{11} Wcm^{-2}).



Supplementary Fig. 5: Ion yields (a) and electron spectra (b) of He nanodroplets ($\langle N \rangle = 7 \times 10^5$) photoionized by XUV pump pulses (1.3×10^9 Wcm^{-2}) and UV probe pulses (2.6×10^{11} Wcm^{-2}).

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