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Shell-localization of light energy in Au@Pt NPs: A photoelectron and ultrafast transient absorption spectroscopy study

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Harnessing sunlight and storing the energy in chemical bonds is an important element in the transition towards green and sustainable technologies. Solar fuel production requires photocatalysts that (1) absorb large parts of the solar spectrum, (2) generate charges with significant lifetimes and appropriate energies, (3) catalyze relevant chemical transformations from abundant, low-energy starting materials, and (4) are stable under operating conditions. A new avenue within solar fuels involve plasmonic nanocatalysts. These materials have tunable optical properties, exciting catalytic behavior, and can be more stable under operating conditions. One promising plasmonic nanocatalyst architecture consists of dispersed Pt atoms on plasmonic gold nanoparticles. Here, we study the surface structure and ultrafast dynamics in such Au@Pt core-shell NPs using photoelectron spectroscopy, and femtosecond transient absorption spectroscopy, in view of their potential as plasmonic photocatalysts.

SURFACE STRUCTURE FROM PHOTOELECTRON SPECTROSCOPY (PES)

- Au and Pt 4f spectra contains a resolvable surface component.
- Pt is concentrated at the surface (XPS vs EDX).
- Pt_{surf} vs Pt_{bulk} does not change significantly with loading indicating subsurface Pt and surface alloying in all Au@Pt NP samples.
- Low Pt loading leads to significant surface roughening.

- Both Au and Pt surface increase when adding 10 wt% Pt.
- Surface smoothens above 10 wt% Pt.
- Surface goes from Au rich to Pt rich between 20 and 30 wt% Pt.
- SCLS increases for gold and drops for Pt as surface alloy becomes more Pt rich at higher Pt loadings.
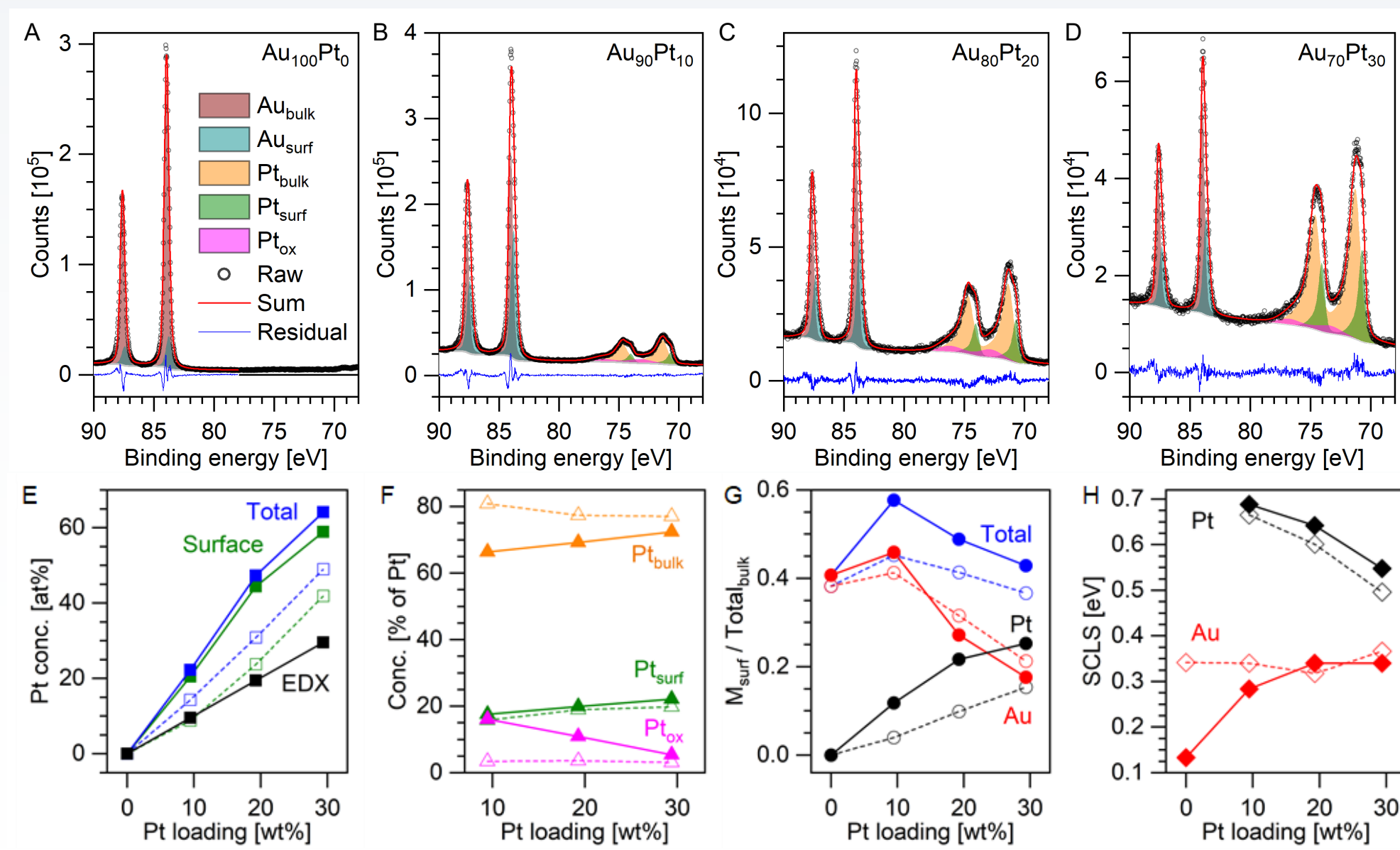

Figure 2. High-resolution Au and Pt 4f core-level photoelectron spectra recorded at the Antares beamline at Soleil Synchrotron. The spectra are deconvoluted with five spin-orbit doublets representing surface and bulk components for both metals, as well as an oxidized component for Pt. Raw data in circles, fit sum in red, and fit residual in blue. (E-H) Trends in core-level deconvolution as function of Pt loading obtained at 220 eV (filled symbols) and 700 eV (empty symbols). (E) Surface (green) and total (blue) concentrations of Pt compared to bulk concentration from EDX (black). (F) Relative Pt component composition. (G) Surface-to-total-bulk ratios for Au (red), Pt (black) and Au+Pt (blue). (H) Surface-to-core-level shifts for Au (red) and Pt (black)
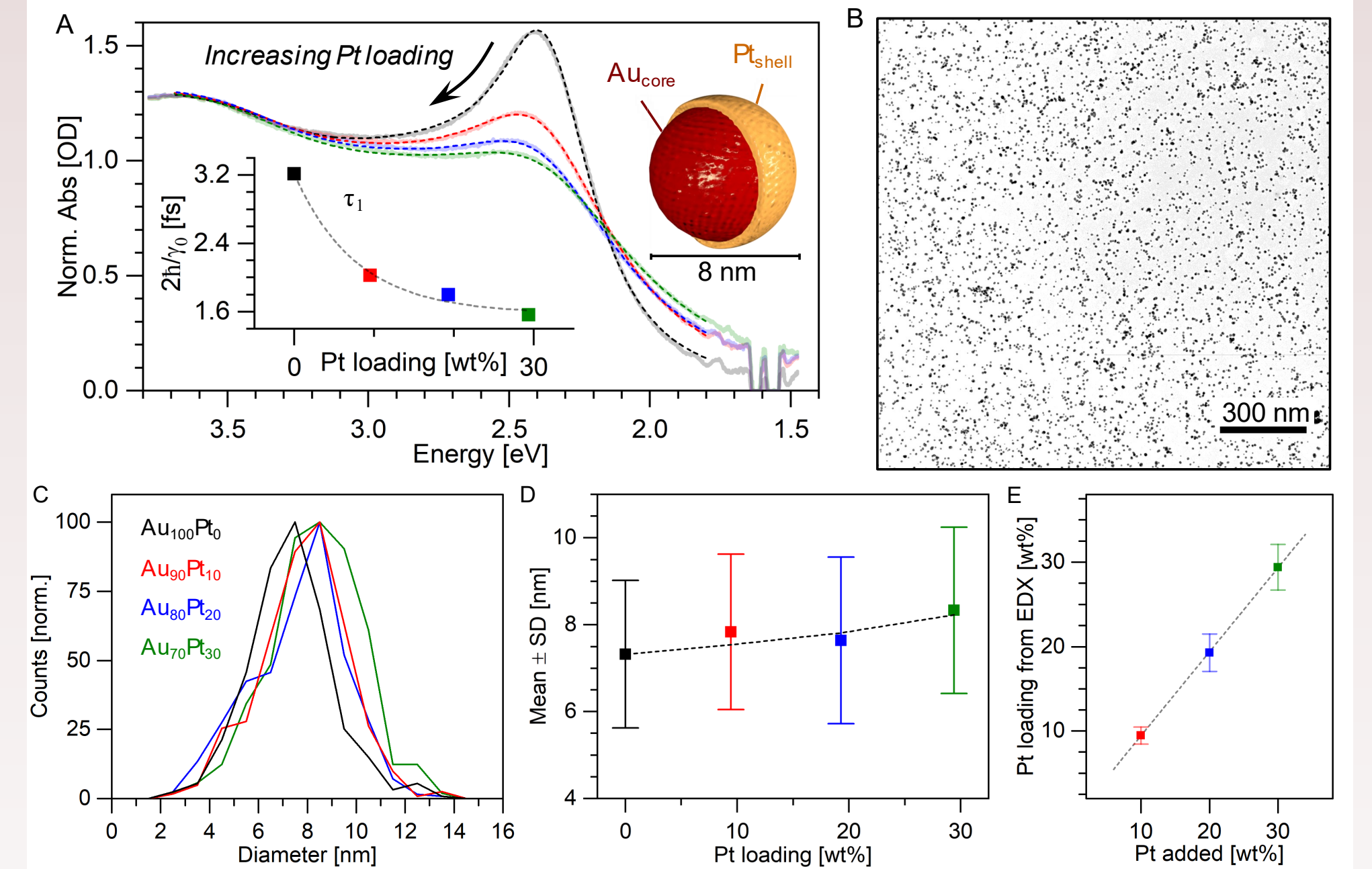
STEADY-STATE ABSORPTION and TEM

Figure 1. (A) Steady-state absorption spectra. Dashed lines show fits. Insets show estimated plasmon dephasing time vs. Pt loading. (B) Representative TEM image of $Au_{70}Pt_{30}$. (C) Overlay of size distributions from TEM. (D) Au@Pt mean size vs. Pt loading and estimated size based on Au:Pt ratio from EDX. (E) Pt loading from EDX vs. wt% Pt added during synthesis.

- 8 nm spherical NPs with controllable Pt loading (up to 30 wt% Pt).
- Close to complete recovery of metal added during synthesis.
- Steady state (SS) absorption spectra fitted by simplified model:

$$A(E) = \frac{c_0}{\pi} \frac{\gamma_0/2}{\left(E - E_0\right)^2 - \left(\gamma_0/2\right)^2} + \frac{c_1}{1 + e^{\left(\frac{E - E_1}{\tau_1}\right)}} + \frac{c_2}{1 + e^{\left(\frac{E - E_2}{\tau_2}\right)}} \quad eq.\ 1$$

- Three contributions to absorption:
  1. Visible interband transition (vis IT) fitted as broadened step.
  2. Ultraviolet interband transition (UV IT) fitted as broadened step.
  3. LSPR fitted by a Lorentzian line shape.
- SS fitting parameters serve as input for the TA fitting.
- LSPR width (γ_0) directly reflects the coherent plasmon lifetime, which drops exponentially with Pt loading to 1.6 fs at 30 wt% (time constant τ_1).

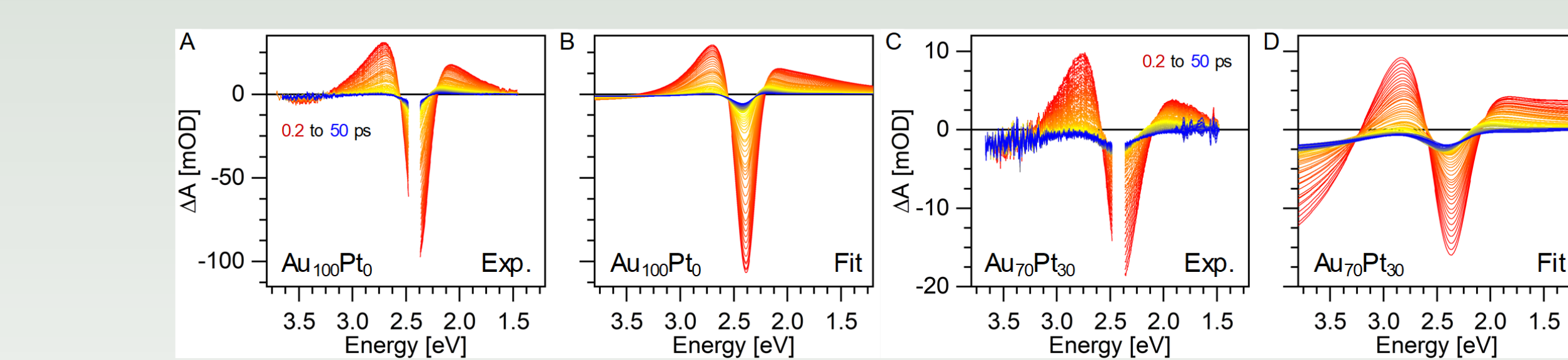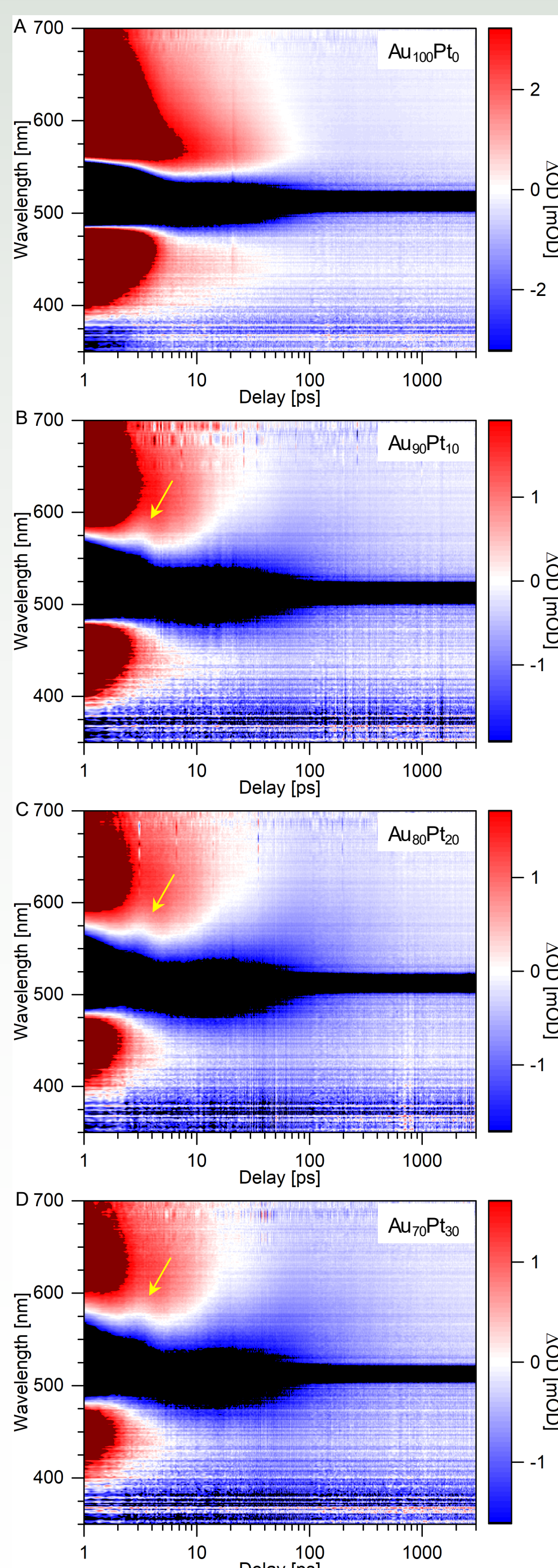## ULTRAFAST TRANSIENT ABSORPTION SPECTROSCOPY (TAS) and CARRIER DYNAMICS

Figure 4. Fitting of transient absorption spectra from 0.2 (red) to 50 ps (blue) with the model in Eq. 1 as the difference between transient data and steady state, $A(E)_t - A(E)_{SS}$, where time-dependence is given to the five colored parameters in Eq. 1 (LSPR and vis IT). Examples are shown for (A–B) $Au_{100}Pt_0$, and (C–D) $Au_{70}Pt_{30}$. (A) and (C): Experimental. (B) and (D): Fits.
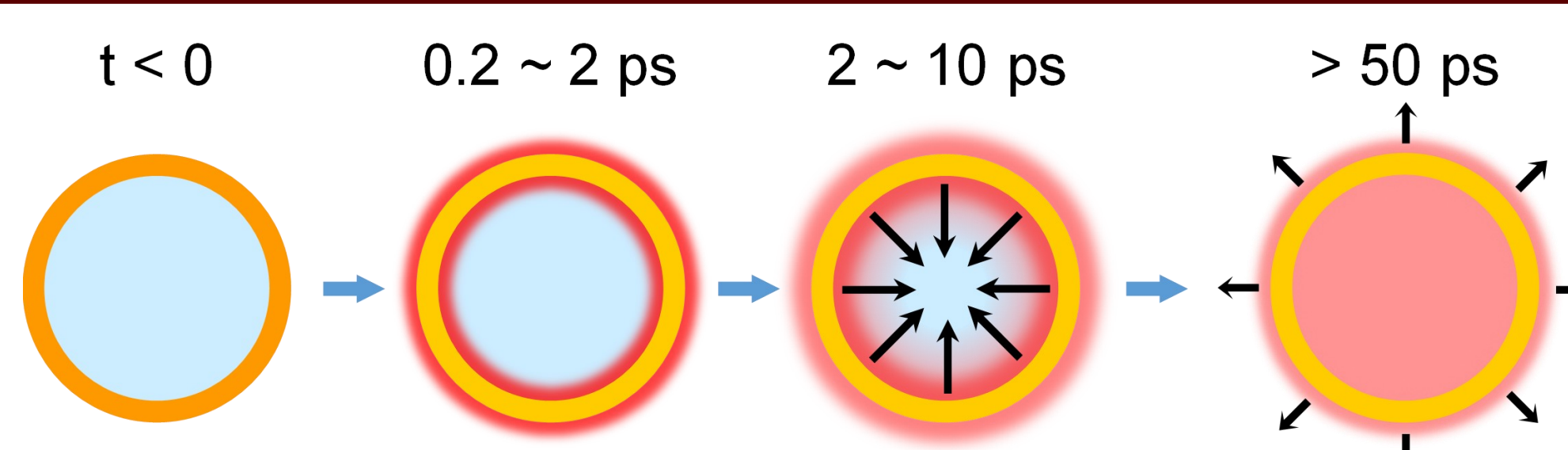
- Au@Pt samples show a feature at 2–3 ps. not seen in AuNPs.
- Slow kinetics (> 20 ps) are fitted with biexponential dynamics up to 3 ns (time constants τ_4 and τ_5, data not shown).
- Model in Eq. 1 with 5 time-dependent parameters reproduce well the transient spectra.
- Parameters for widths and amplitudes of LSPR and vis IT display biexponential dynamics in the early kinetics (< 50 ps, time constants τ_2 and τ_4)
- Time-dependence of LSPR shift (E_0) show an additional decay component between τ_2 and τ_4 (τ_3) only in Au@Pt NPs – not in AuNPs.

Figure 5. Time-dependence of all five fitting parameters of the LSPR and vis IT (Eq. 1) for all for samples (0–30 wt% Pt) from 0–50 ps (inset shows 0 –5 ps).

Figure 6. (A) Overlay of LSPR shift dynamics (E_0) for $Au_{100}Pt_0$ (black), $Au_{90}Pt_{10}$ (red), $Au_{80}Pt_{20}$ (blue), and $Au_{70}Pt_{30}$ (green). Solid lines show three-step relaxation fits. (B) Overlay of LSPR width dynamics (γ_0). Solid lines show biexponential decay fits. Insets in (A) and (B) show a magnified view of the greyed out areas.

Samples	τ_1 [fs]	τ_2 [ps]	τ_3 [ps]	τ_4 [ps]	τ_5 [ps]
$Au_{100}Pt_0$	3.2	2.0		46	
$Au_{90}Pt_{10}$	2.0	1.1	≈ 2	52	> 500
$Au_{80}Pt_{20}$	1.8	0.8		61	
$Au_{70}Pt_{30}$	1.6	0.7		66	

← Figure 3. Transient absorption raw data showing excited state absorption in red and bleach in blue. Constant "bleach" around the excitation wavelength is an artefact from the pump laser. A feature around 2-3 ps is seen in all Au@Pt samples (arrow), and not in (A) the pure AuNPs. Note the logarithmic time scale.

MECHANISM and CONCLUSIONS

t < 0   0.2 ~ 2 ps   2 ~ 10 ps   > 50 ps

- The LSPR decay dynamics in 8 nm NPs change dramatically upon addition of small amounts of Pt due to surface roughening and Pt d-electrons.
- The plasmon dephasing time decreases exponentially with Pt loading due to scattering at the surface and on Pt d-electrons.
- The initially generated hot and expanded e-gas cools efficiently by scattering at the Pt-rich surface.
- Equilibration with the lattice (phonons) now occurs from the shell towards the NP center at the speed of sound.
- Finally, the lattice cools by heat dissipation to the environment. This process is impeded by the lower thermal conductivity of Pt.

The PES and TAS studies demonstrate how the deposition of small amounts of Pt on AuNPs creates a rough and alloyed surface, and how this structural change dominates the ultrafast kinetics. Hot carriers are efficiently generates and localized on the Pt shell, which is expected to greatly enhance plasmon-driven, Pt-catalysed chemical reactions.
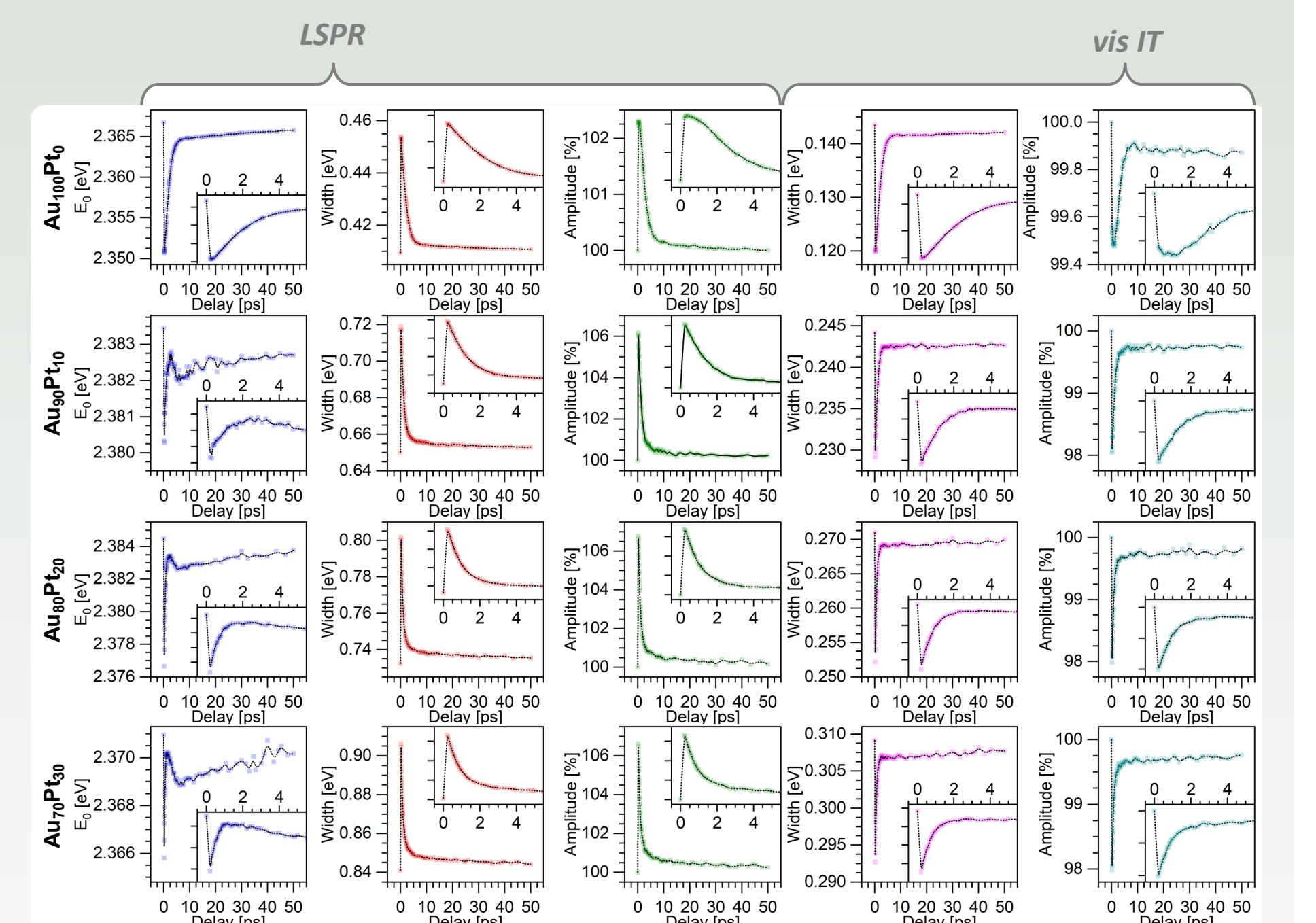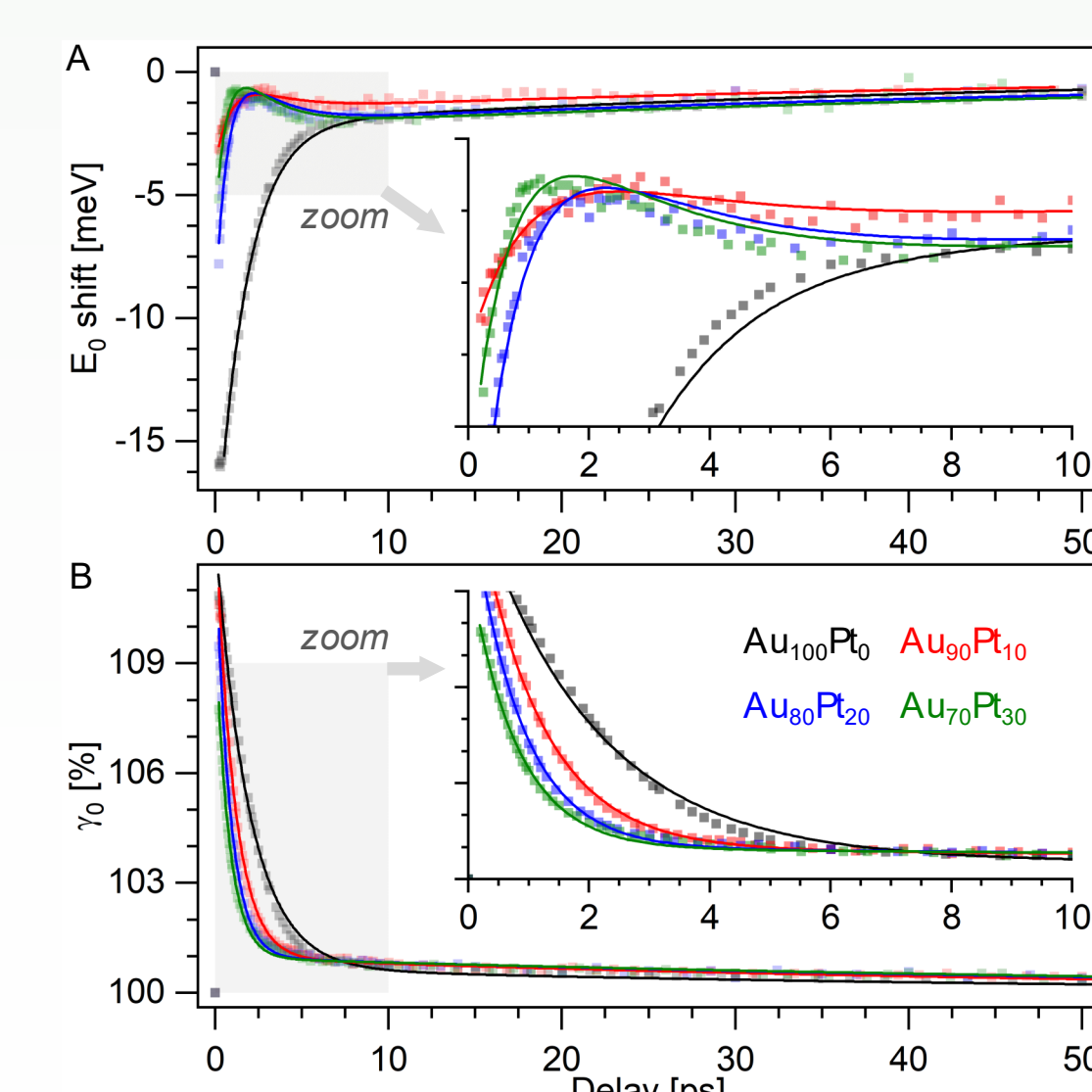
ACKNOWLEDGEMENTS