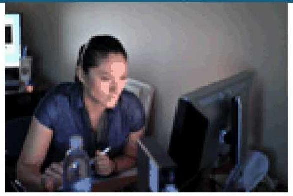
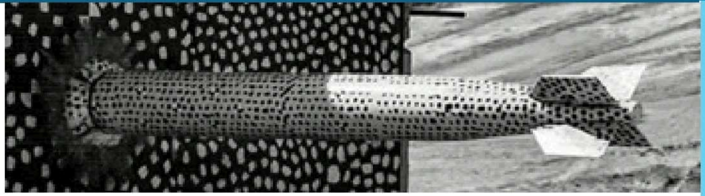
SAND2020-11003C

Ionization Mechanisms in a Laser-Produced Plasma for Single Particle Aerosol Mass Spectrometers





73rd Annual Gaseous Electronics Conference

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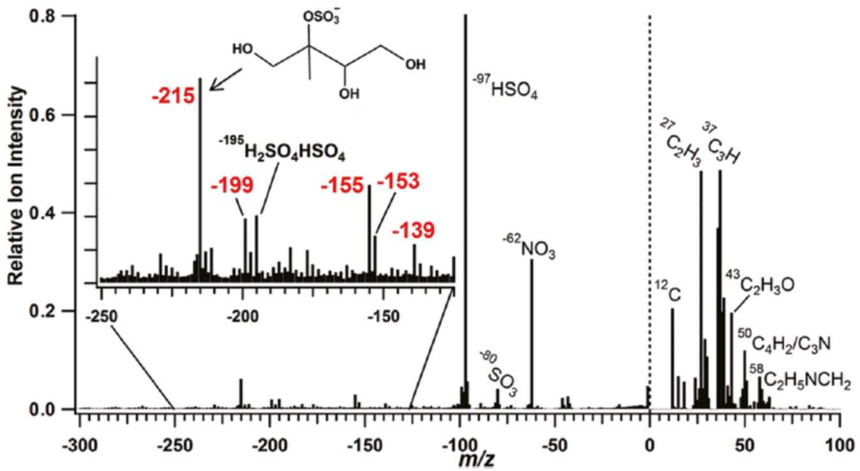
Agenda

- Single Particle Aerosol Mass Spectrometry
- Model Description
- Hydrodynamics Modeling
- Global Plasma Modeling

Aerosol Mass Spectrometry

- Aerosol mass spectrometry is critical for
  - Climate science: Cloud condensing nuclei, precipitation
  - Atmospheric monitoring: Pollution, dust storms, forest fires
- The chemical composition of particles can indicate their origin or hazardousness.
- Real-time measurements provide accurate information on reactive particles.
  - Small size and weight desirable for field/vehicle tests.
- Measuring a mass spectrum for individual particles provides more information and is especially useful for source attribution.

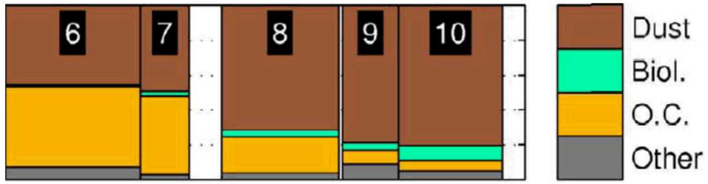
Aerosol mass spectrum collected in Atlanta, GA



L. E. Hatch et al., Environ. Sci. Technol. 45, 5105 (2011).

Aerosol mass spectrometer in a climate study in the Sierra Nevada Mountains

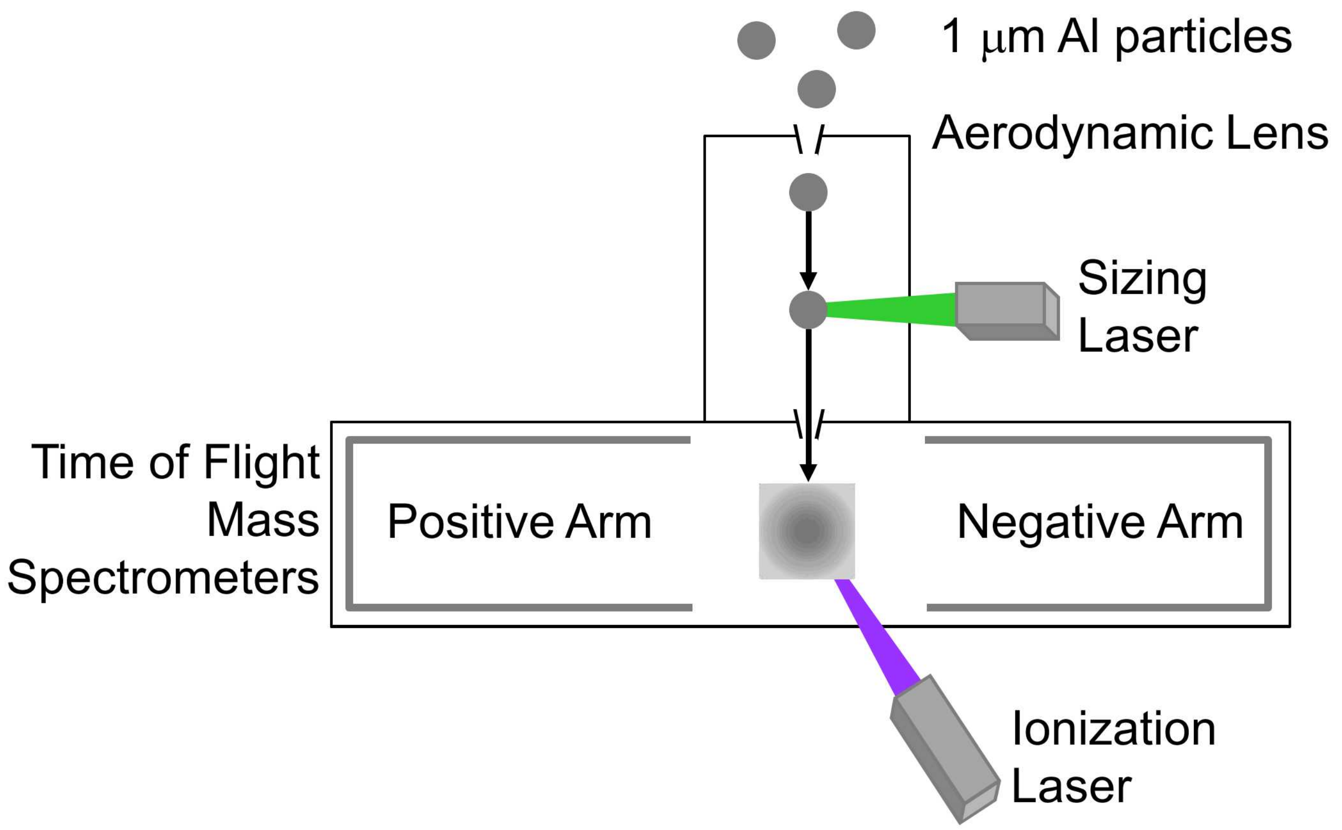
Single particle spectra facilitate categorization of particles:



A. P. Ault, et al., J. Geophys. Res. 116, D16205 (2011).

Single Particle Aerosol Mass Spectrometer (SPAMS)

- An aerodynamic lens focuses the incoming particles into a beam into a differentially pumped chamber.
- First sizing laser (405 nm, continuous) detects particle and measures its aerodynamic diameter.
- Ionization laser (248 nm, 8 ns) vaporizes and ionizes.
- Conditions similar to laser induced breakdown spectroscopy (LIBS), but SPAMS has lower laser intensity and background pressure.
  - LIBS ~ 760 Torr; SPAMS ~ 10^{-6} Torr
- In this study, we focused on 1 μm, spherical Al particles.



- Goal: Better understand ionization mechanisms in SPAMS systems using numerical modeling.
  - Results may aid in future designs and analysis of results.

Model Description

- CTH – Hydrodynamics model
  - Does not resolve phases.
  - Provides initial temperature (after vaporization) and expansion rate for global model.
- Global plasma model
  - 0-D, well-stirred reactor approximation.
  - Al, e$^-$, Al$^+$, 6 excited states.
  - 62 reactions:
    - Electrons: excitation, ionization, recombination, superelastic
    - Photon: excitation, ionization, inverse Bremsstrahlung radiation
  - Two temperatures (T_e, T_g).
  - Maxwellian energy distributions.
  - Uniform photon flux.

Global Plasma Model

Photon Reactions | Particle Reactions | Expansion

$$\frac{\partial n_e}{\partial t} = k_{MPI} n_{Al} \phi^2 + \phi \sum_i^{species} n_i \sigma_{i,iz} + \sum_j^{rxns} \left(a_{e,j}^{RHS} - a_{e,j}^{LHS}\right) R_j - \frac{n_e}{V}\frac{dV}{dt}$$

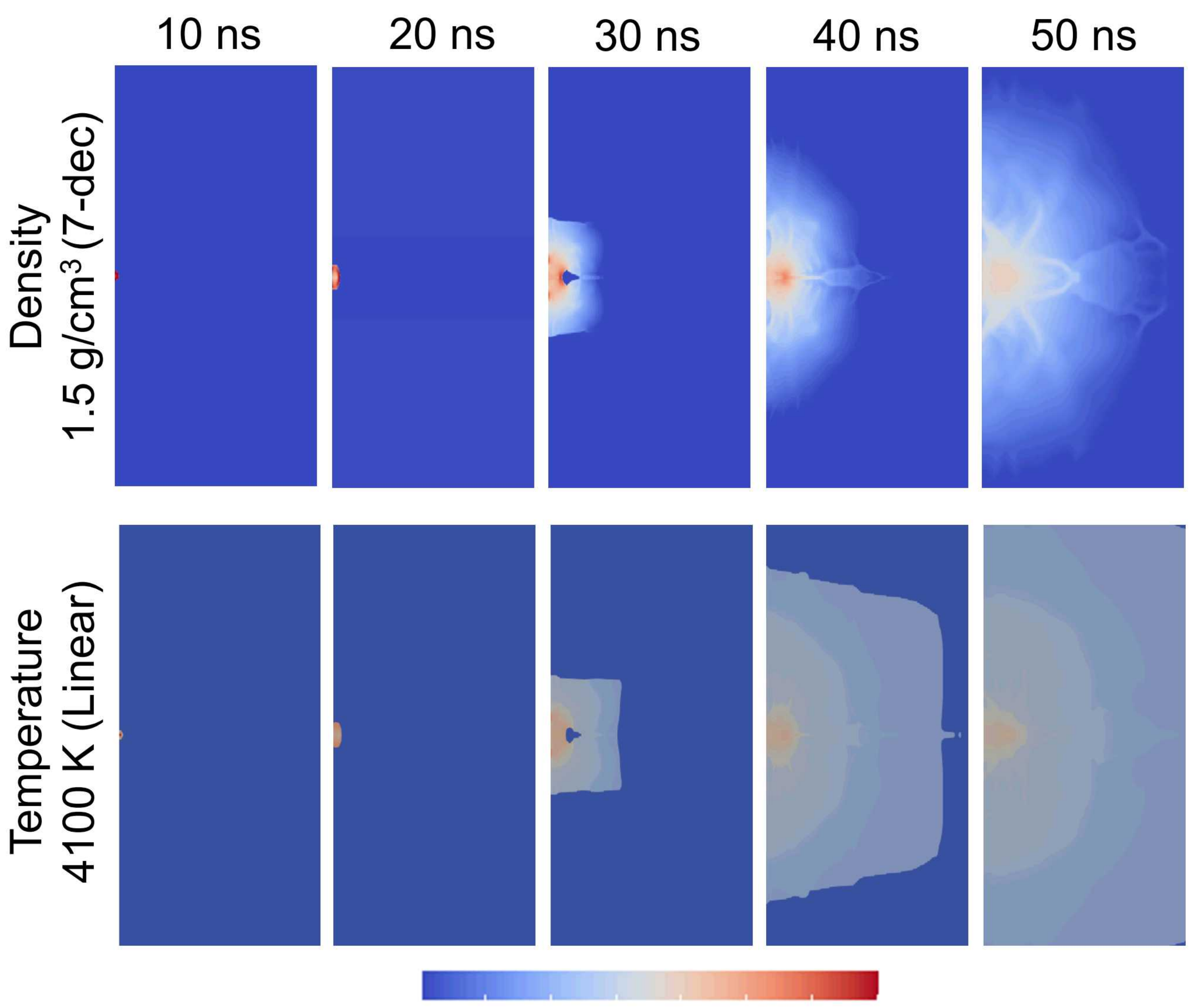
$$\frac{\partial\left(\frac{3}{2}k_B n_e T_e\right)}{\partial t} = \Delta\epsilon_{IB} k_{IB} n_e \phi + \Delta\epsilon_{MPI} k_{MPI} n_{Al} \phi^2 + \phi \sum_i^{species} \Delta\epsilon_e n_i \sigma_{i,iz} + \sum_j^{rxns} \Delta\epsilon_e R_j + P_{ohmic} - \gamma \frac{\left(\frac{3}{2}k_B n_e T_e\right)}{V}\frac{dV}{dt}$$

$$\frac{\partial\left(\frac{3}{2}k_B n_g T_g\right)}{\partial t} = \sum_j^{rxns} \Delta\epsilon_g R_j - \gamma \frac{\left(\frac{3}{2}k_B n_g T_g\right)}{V}\frac{dV}{dt}$$

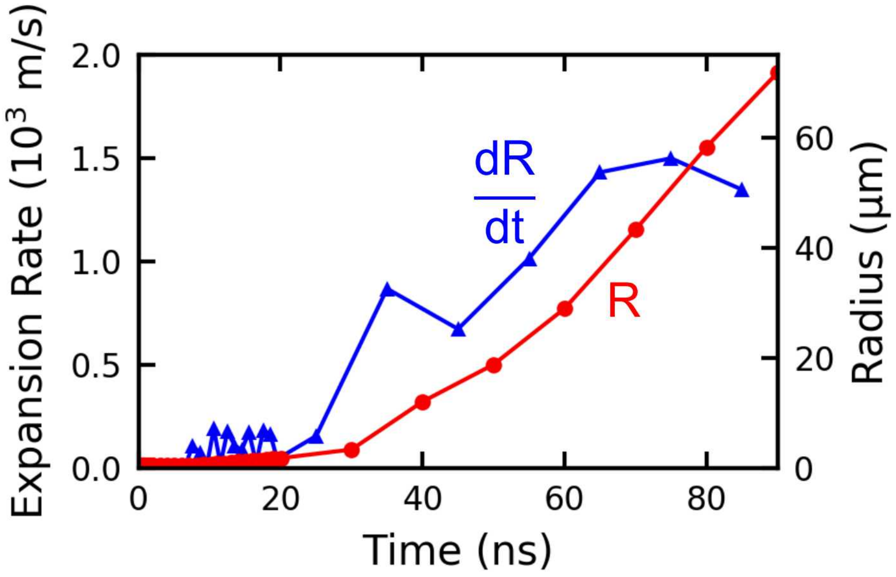
n_i = number density of species i
φ = photon flux
k_j = reaction rate of reaction j
k_{MPI} = multiphoton ionization (MPI) rate
ε = energy change
V = volume

$$R_j = k_j \prod_i^{LHS} n_i$$

Hydrodynamics and Expansion

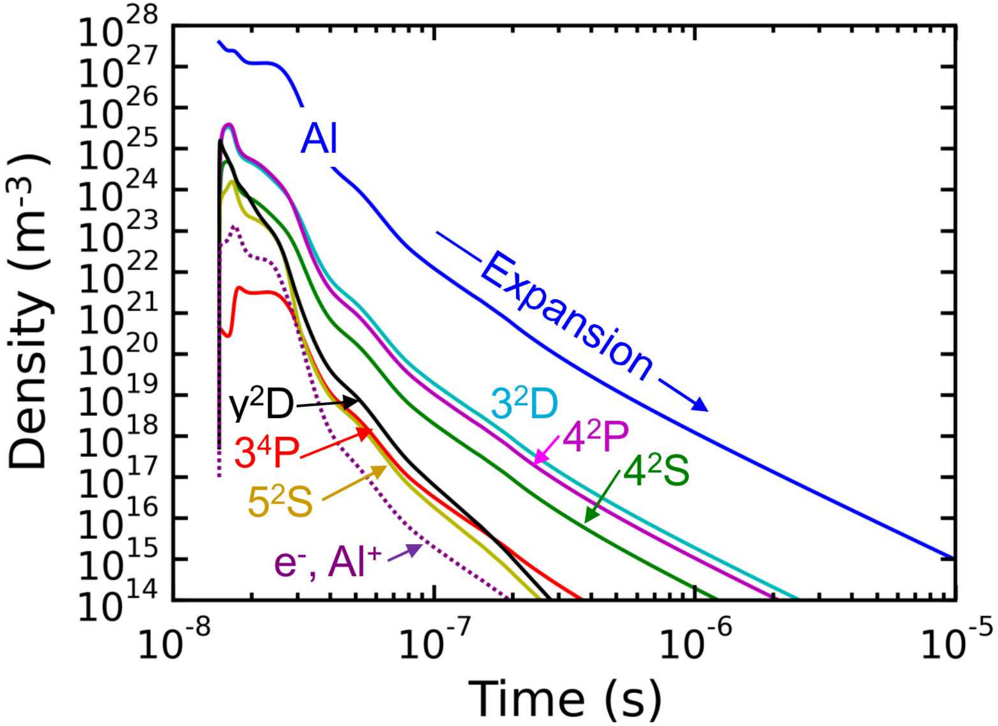


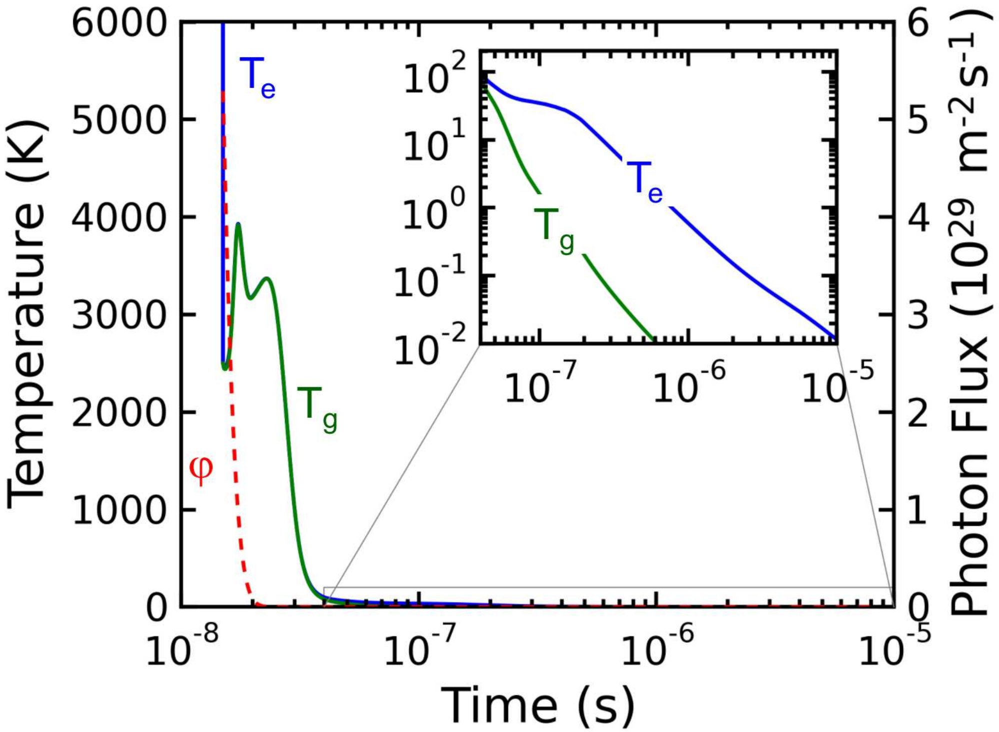
*Modeling by Jeffrey Musk



- 2-D axisymmetric, CTH.
- 1 μm Al particle
- Laser: 16 mJ, 8 ns pulse (Gaussian)
  - 4×10^{12} W/m², 3×10^{4} J/m²
- Energy deposited uniformly throughout particle. (approximation)
- 60% reflectance
- 8×10^{-6} Torr background pressure

Global Plasma Chemistry Model





- Plasma modeling begins when enough energy has been deposited to vaporize the particle (15 ns).
- Initial temperature and expansion rate from hydrodynamics model.
- Density decreases due to expansion into vacuum (9 orders of magnitude in μs!)

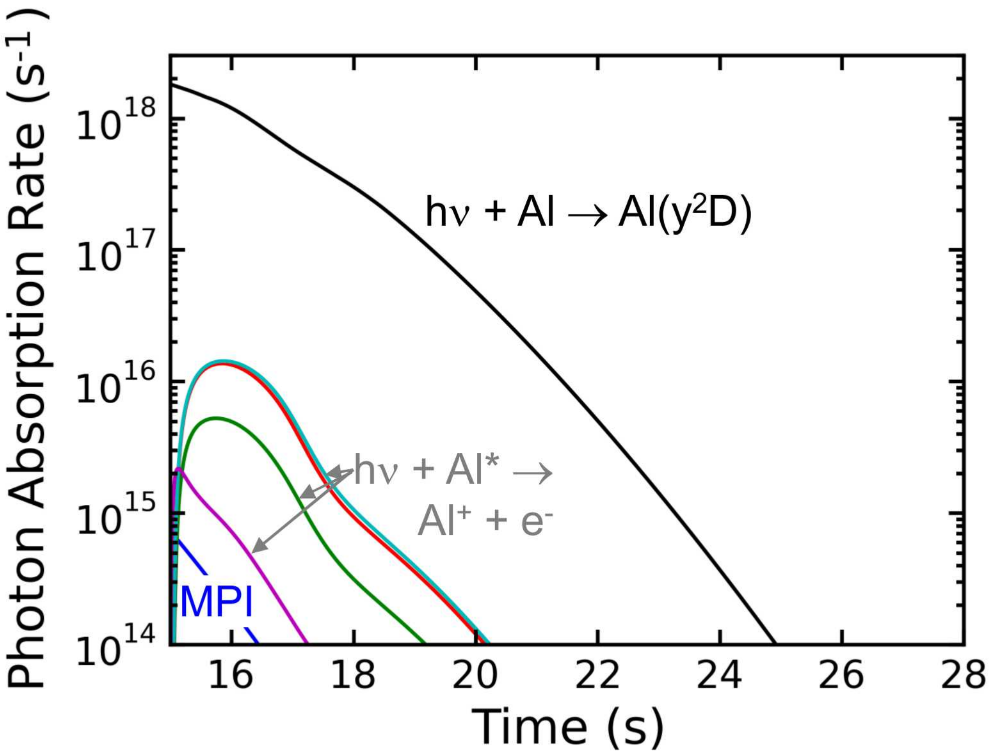
- T_e and T_g decrease due to expansion (i.e. becoming collisionless).

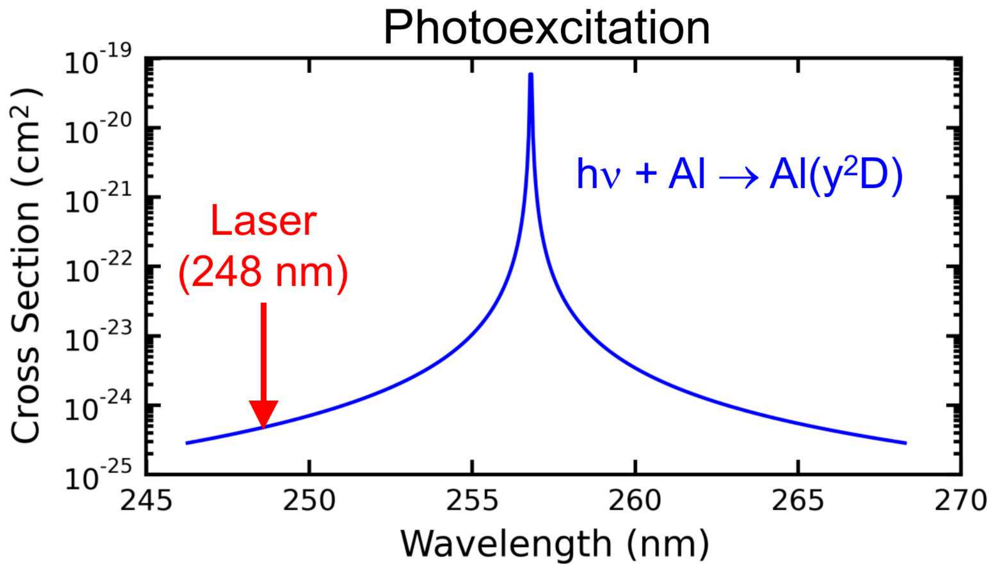
$$\left.\frac{\partial\left(\frac{3}{2}k_B n_e T_e\right)}{\partial t}\right|_{expansion} = -\gamma \frac{\left(\frac{3}{2}k_B n_e T_e\right)}{V}\frac{dV}{dt}$$

- $T_e = T_g$ until 40 ns.
- T_e lower than expected due to rapid expansion.

Photon Absorption Mechanisms

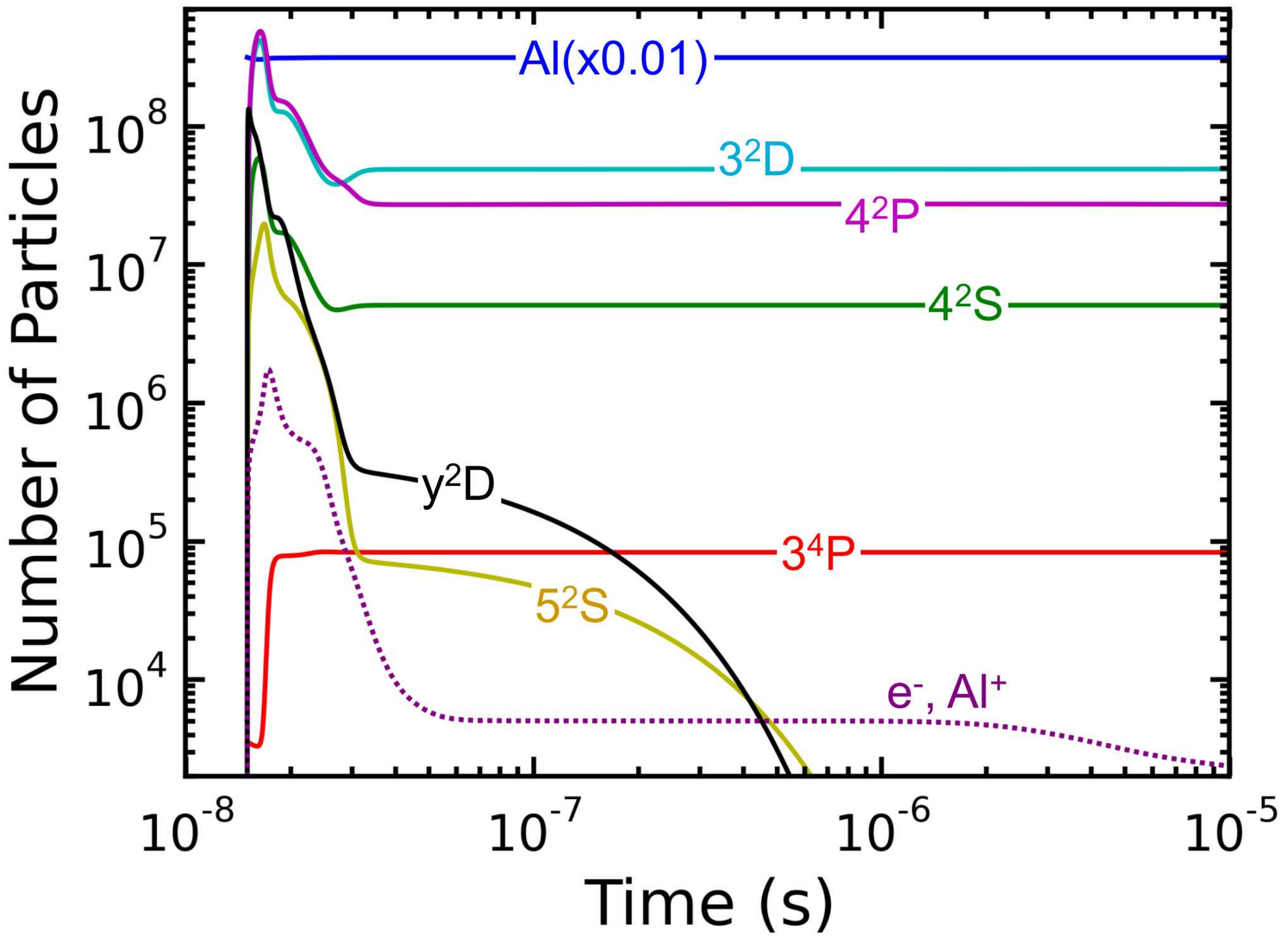
- E_{photon} (5.00 eV) < $E_{ionization}$ (5.99 eV)
  - No direct photoionization of Al
- Resonant photoexcitation is possible only with significant pressure broadening.
  - hν + Al → Al(y^2D)
  - Resonance at 4.83 eV
- Photoionization of excited states absorbs <1% of photons.
  - Al* = Al(4^2S), Al(3^2D), Al(4^2P), Al(y^2D)
- Multi-photon ionization (MPI) is not significant at this laser energy.
- Photon flux (φ) is uniform in the 0-D model:
  - Attenuation is not considered.
  - Photoabsorption rates are limited to prevent photons absorbed from exceeding incident photons.



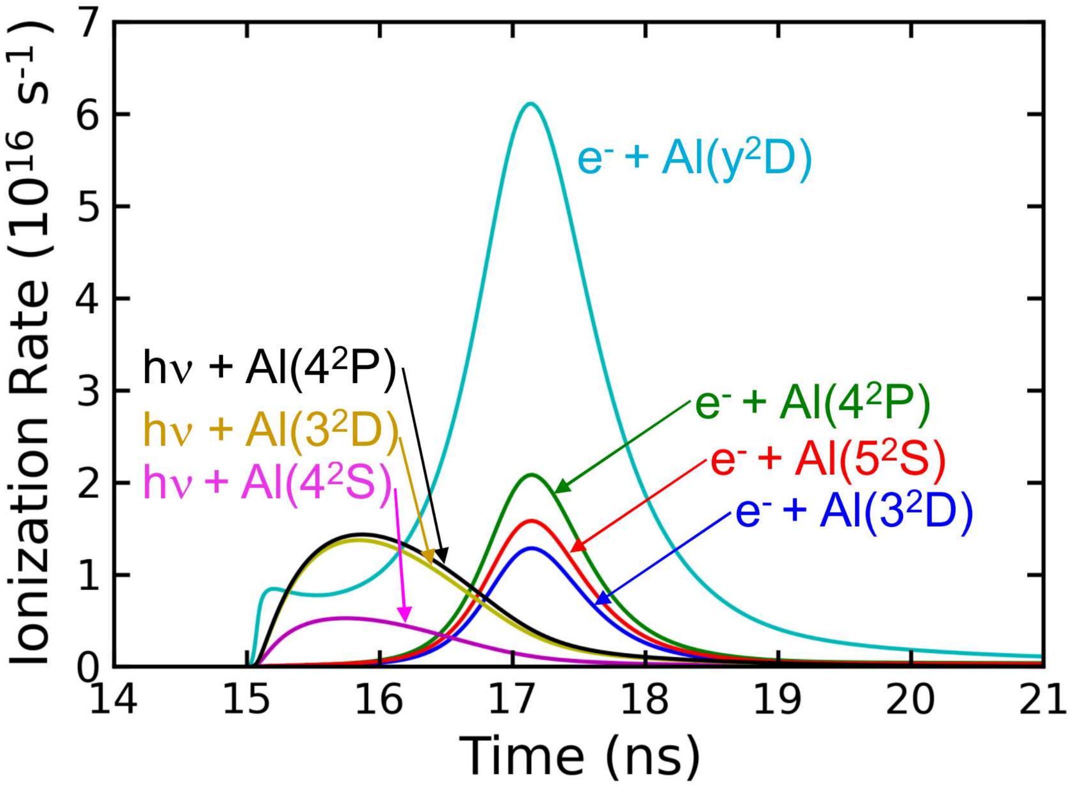


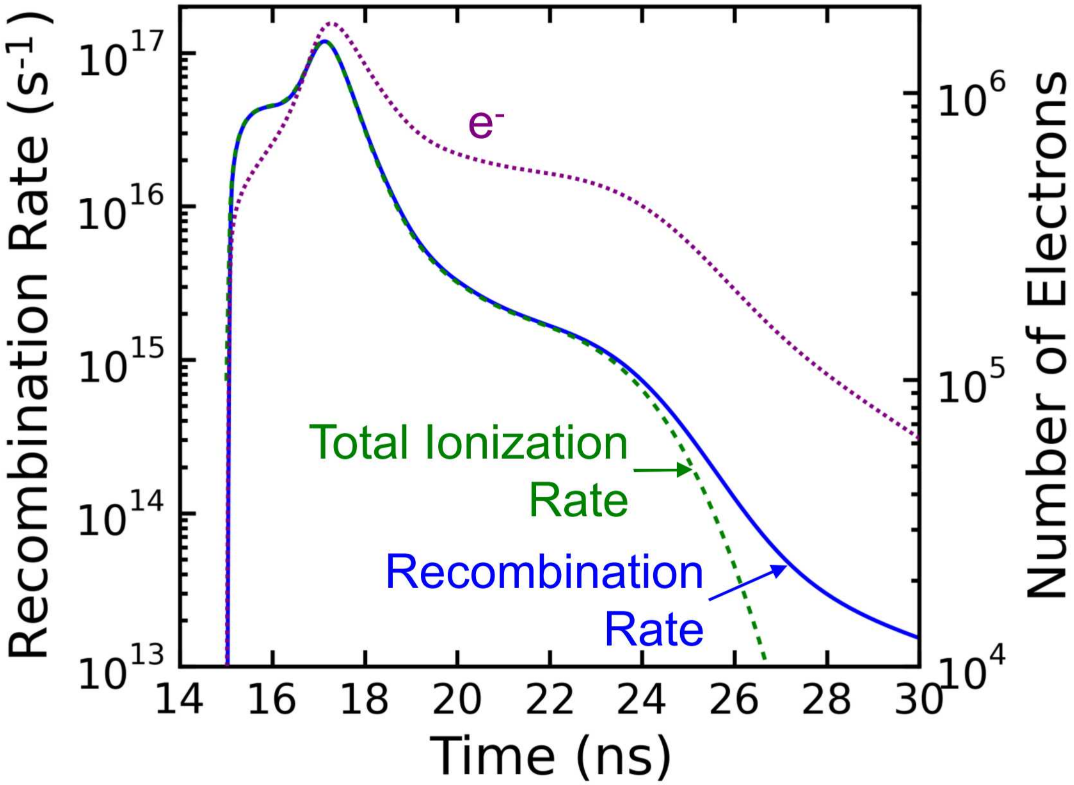
Number of Particles

- Number of particles = $n \cdot V$
- Al(y^2D) is formed by: hν + Al → Al(y^2D)
- Al(y^2D) excitation is redistributed to lower excited states by:
  - Superelastic collisions
  - Radiation
    - Al(y^2D) → Al(4^2P)
    - Al(5^2S) → Al(4^2P)
- Oscillations follow variations in T_e from expansion.
- Radiation to the ground state is assumed to be fully trapped.



Ionization Mechanisms

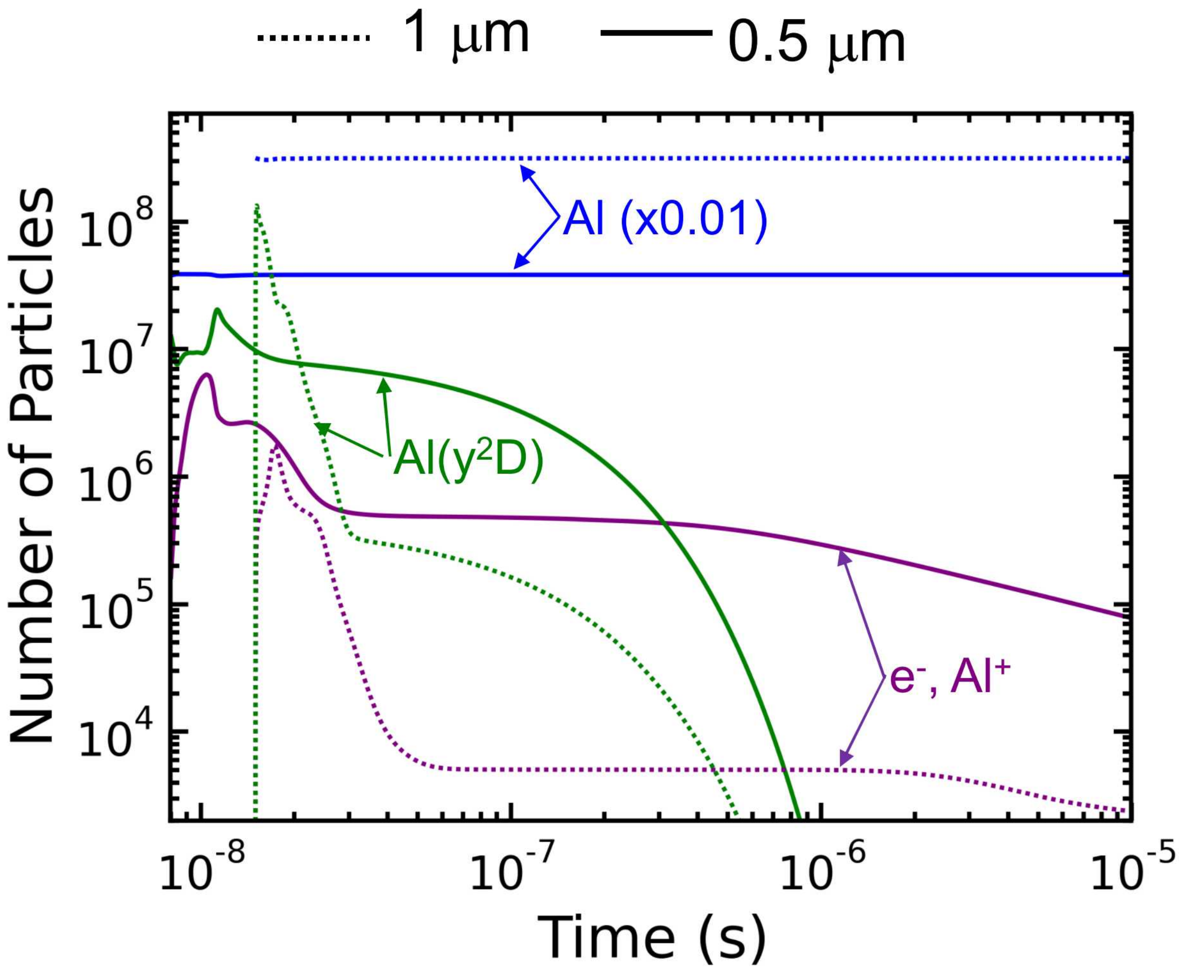




- e^- are heated by superelastic collisions with Al(y^2D)
- Hot e^- cause e-impact ionization of excited states.
- Photoionization of excited states also important.

- Three body recombination is the primary loss of e^- and Al^+.
  - Rate increases for cold electrons $\propto T_e^{-4.5}$

Particle Size



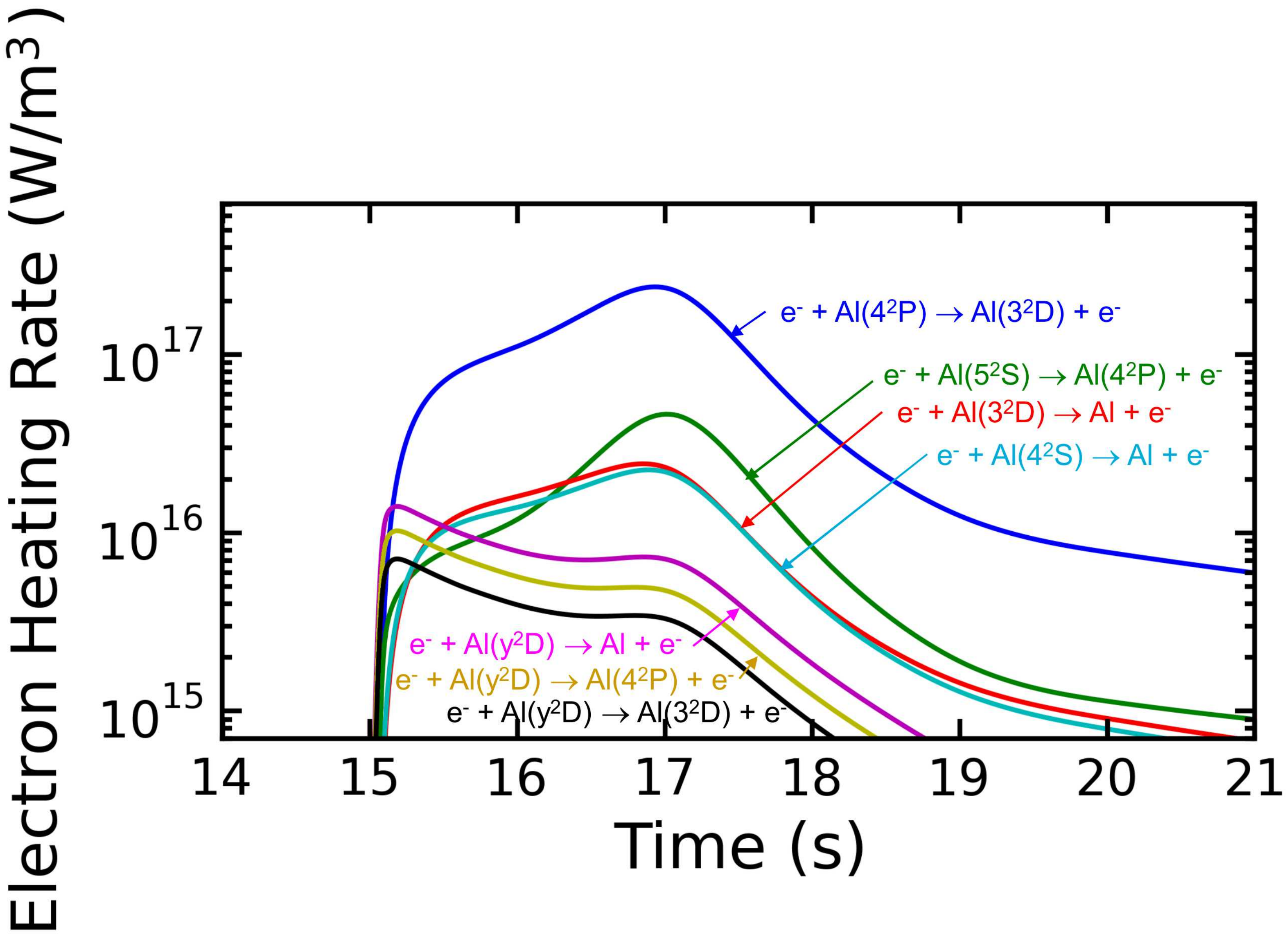
- A 0.5 μm particle is fully vaporized earlier in the laser pulse.
- The total number of ions remaining is critical for performance/sensitivity of SPAMS.
  - Final ion counts are 2 orders of magnitude higher for a 0.5 μm particle than 1 μm.
- More ions are produced initially for smaller particles:
  - Larger φ
  - Higher T_e
- More ions survive without recombining.
- Due to higher T_e, electron impact reactions are more important to ionization for a smaller particle.

Concluding Remarks

- The ionization mechanisms of an Al particle in a single particle aerosol mass spectrometer (SPAMS) have been investigated.
  - $h\nu + Al^* \rightarrow Al^+ + e^-$
  - $e^- + Al^* \rightarrow Al^+ + e^- + e^-$
- Direct photoexcitation ($Al(y^2D)$) is possible off-resonance due to pressure broadening.
- T_e decreases in ~40 ns due to rapid expansion.
- With low T_e, many ions are lost to recombination.
  - A small electric field may prevent this.
- More ions are produced with a smaller particle.
- Future Work:
  - Analyze the assumption of Maxwellian electron energy distribution.
  - Effect of externally applied electric field.

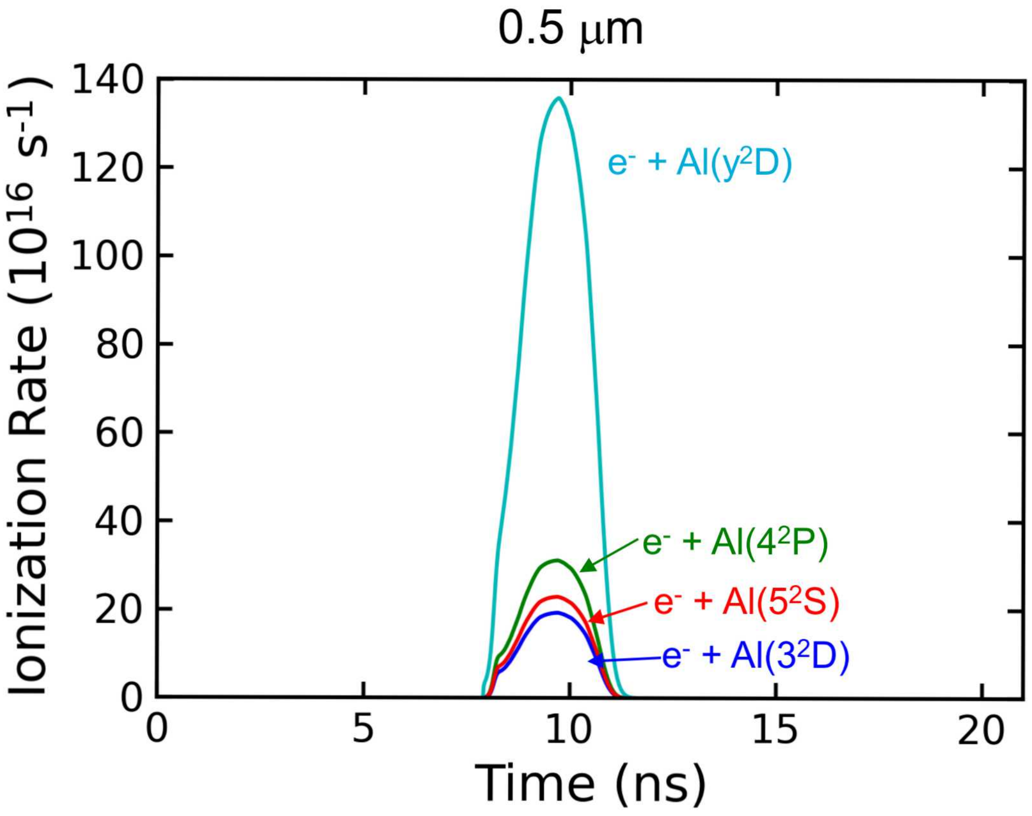
BACKUP

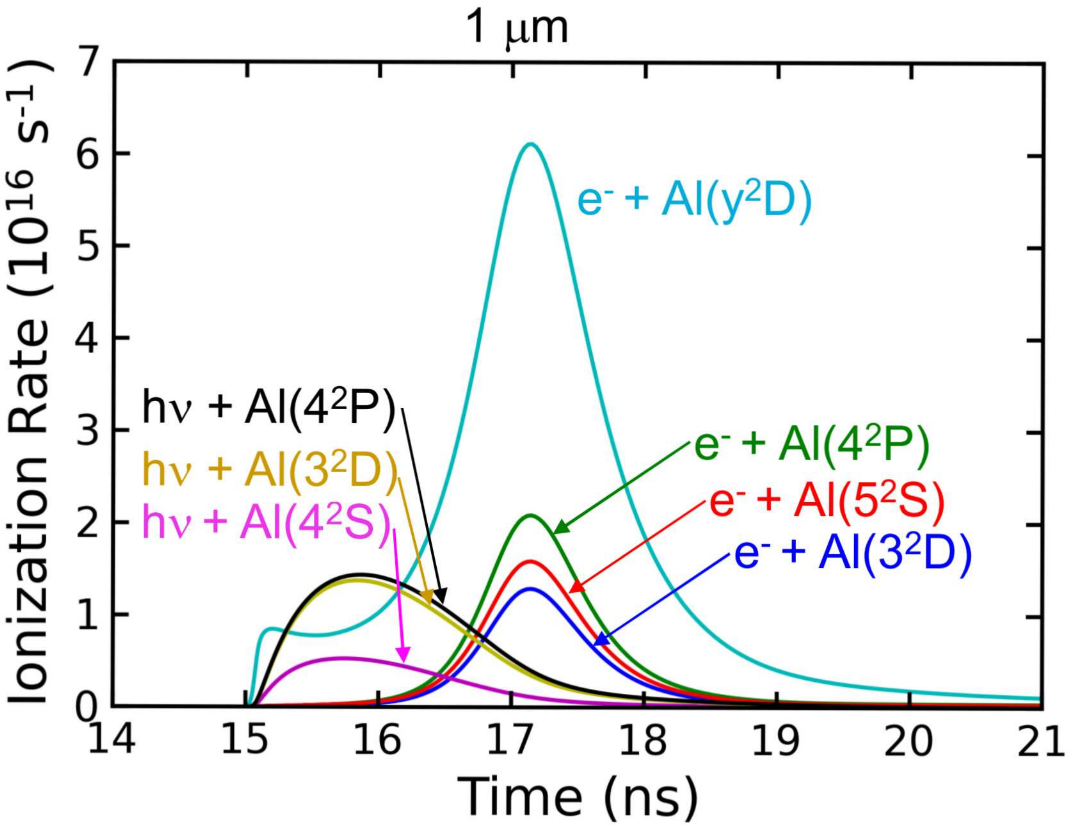
Electron Heating Mechanisms

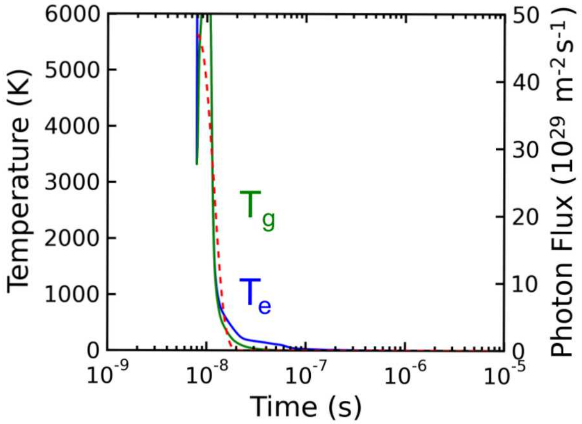


- 1 μm particle
- Superelastic collisions are the main source of electron heating

Ionization Mechanisms vs. Particle Size







- Electron impact reactions dominate in smaller particle, where ionization fraction and temperature are higher

Temperatures and Recombination