Single Particle Laser Ablation Time-of-Flight Mass Spectroscopy: An Instrument Under Construction

D. Imre and A. Zelenyuk

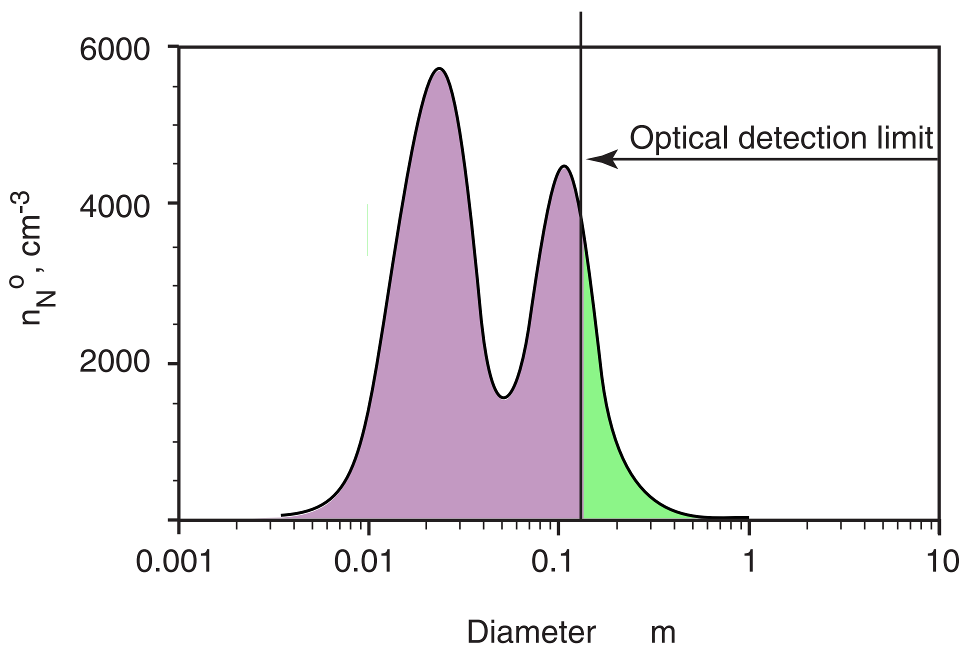
Brookahven National labor

Introduction

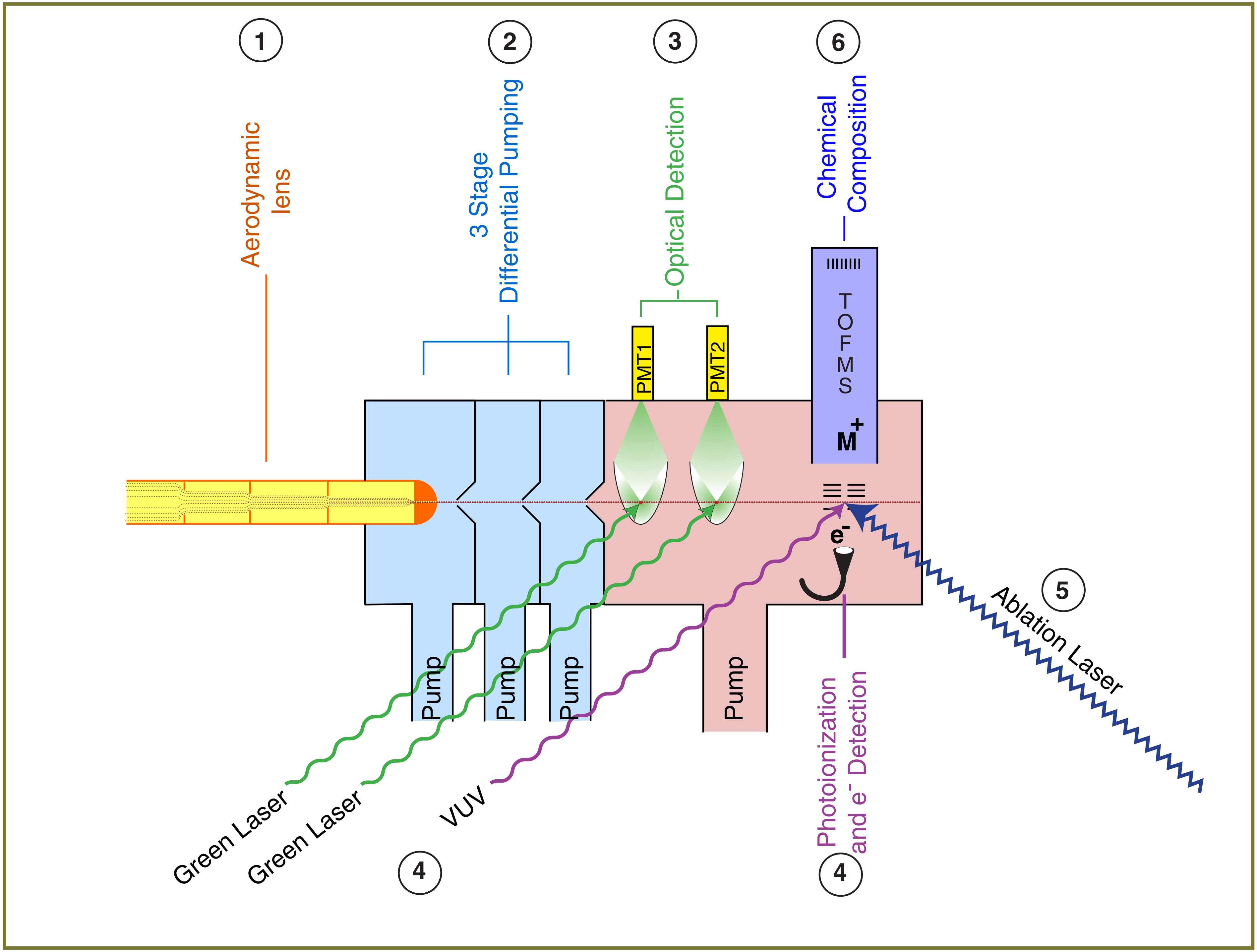
A Single Particle Laser Ablation Time of Flight Mass Spectrometer (SPLAT-MS) for, *in-situ*, size and chemical composition characterization of *individual* atmospheric aerosol particles over a wide size range has been designed and is currently under construction.

The ideal ambient atmospheric aerosol research tool should be able to provide information on the size and chemical composition of individual aerosols. Various applications of mass spectroscopies with great successes have recently been applied to this end. What makes this problem particularly difficult is the fact that atmospheric aerosols can be as small as a few nm or as large as tens of microns. While aerosols larger than 100nm can be detected optically the smaller ones cannot. Consequently, laser ablation single particle mass spectrometers operate in one of two modes: Large particles are detected and sized optically and a synchronous ablating pulse is used to generate a mass spectrum. Particles smaller than ~150nm can be observed by randomly firing the ablation laser in search of a coincidence.

The present instrument is intended to be a universal tool for measuring aerosol from tens of nanometers up to tens of micrometers. Here two detection modes will operate at all times making it possible to synchronize the firing of ablation laser with the particle's arrival for all sizes. This will be achieved by using VUV photoionization technique for small particle detection and conventional light scattering for the large ones. Both methods operating simultaneiously.



Typical aerosol size distribution
adapted from Seinfeld and Pandis


1
Aerodynamic lens
2
3 Stage Differential Pumping
3
Optical Detection
6
Chemical Composition
PMT1
PMT2
TOFMS
M+
e-
Pump
Pump
Pump
Pump
5
Ablation Laser
Green Laser
Green Laser
VUV
4
Photoionization and e- Detection
4

Schematic Representation Of The SPLAT-MS Instrument

(1) Ambient aerosols are focused by the aerodynamic lens system, and accelerated during supersonic expansion through a nozzle to velocities between 100 and 400 m/sec, depending on particle size

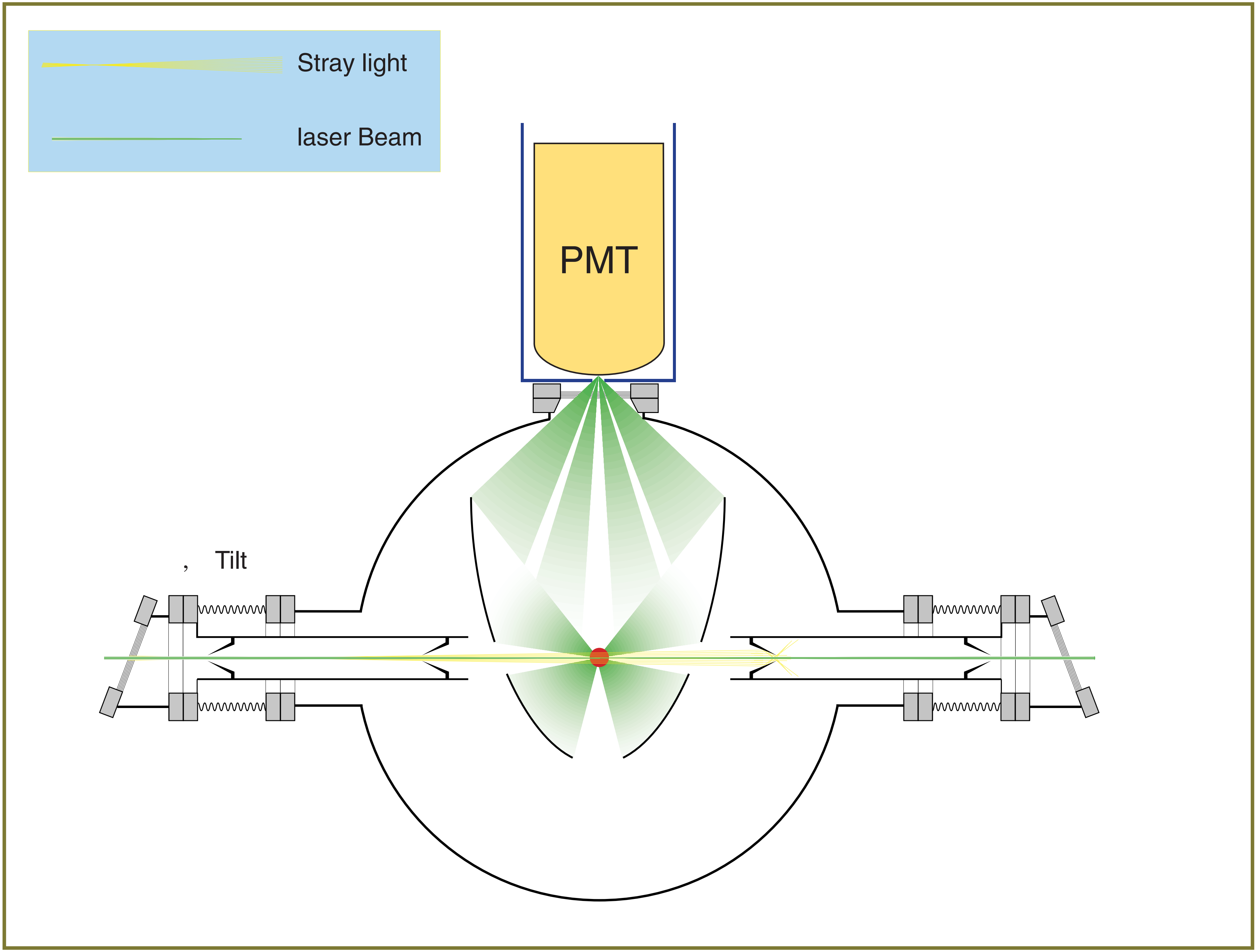
(2) Three stages of differential pumping

(3) Two stages of optical detection used to indicate the presence of particles larger than 80nm and for velocity/size determination. Particle velocities can be obtained from a measurement of the time difference between the detected light scattered by a particle as it passes through two CW diode-pumped green laser beams spaced by 16 cm. Besides being an important characteristic of aerosol size, determination of particle velocity allows for an accurate synchronization in the firing of the ablation laser with the particle's arrival into laser focal spot;

(4) A continuous VUV light source for nanoparticle detection and characterization by photoionization and electron detection. It will be also used for larger particle detection along with optical detection;

(5) An excimer laser used to ablate particles and generate ions.

(6) Time of flight mass spectrometer for single particle composition analysis.

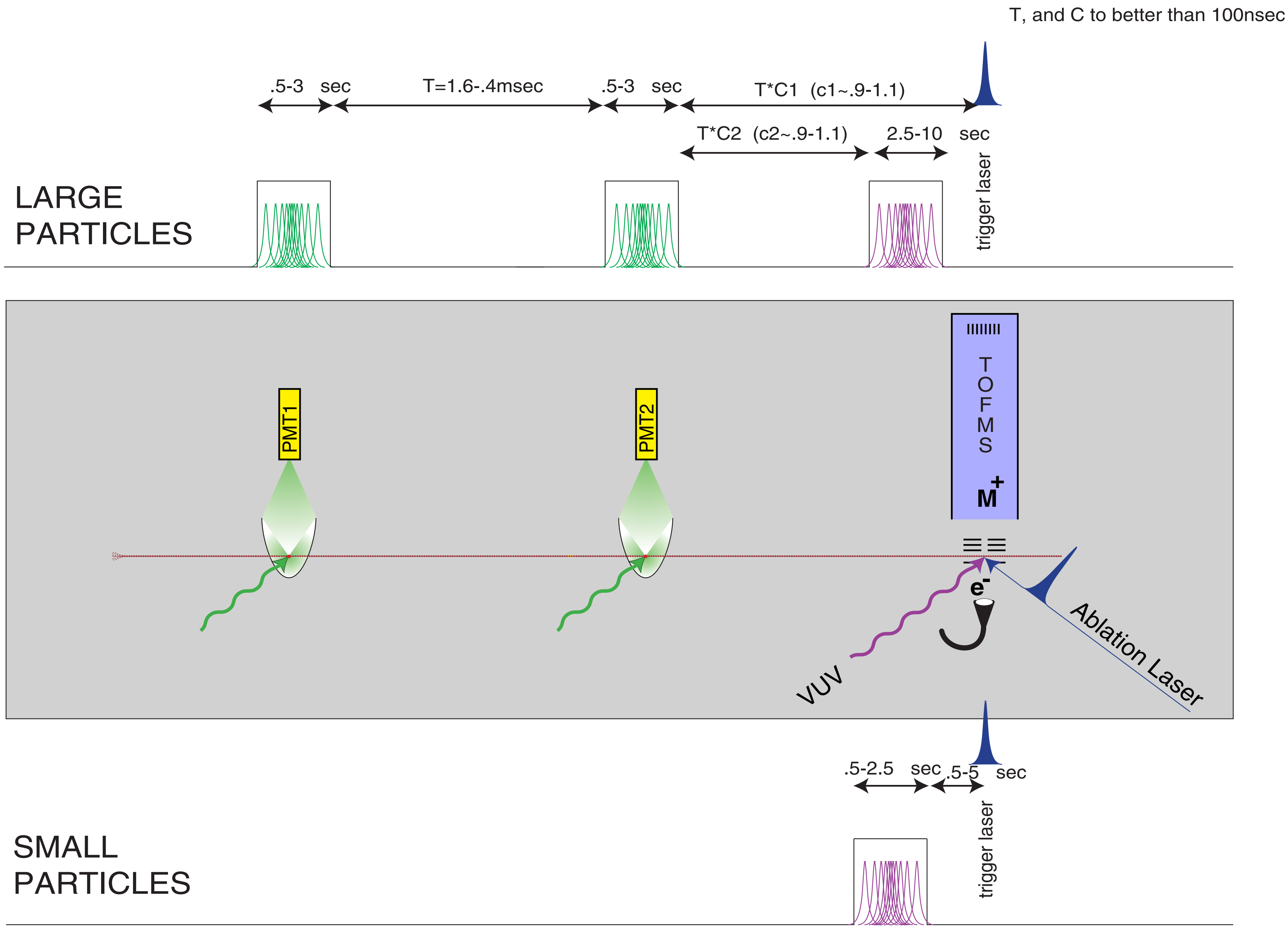

Stray light
laser Beam
PMT
Tilt

Particles Larger Than ~80nm – Optical Detection

The optical detection scheme was improved by minimizing stray light using baffles at the entrance as well as at the exit, and by optimizing the scattered light collection efficiency using large ellipsoidal reflectors.

To maximize the contrast between particle and gas, the signal is integrated for ~1 microsecond – the duration a particle remains in the laser beam – and discriminated against background. In addition a requirement for a coincidence signal between the two laser beams provides a second layer of signal discrimination.

TIMING SCHEME



Particles Smaller Than ~80nm – Photoionization Detection

For particles smaller than ~80nm it is no longer possible to synchronize the firing of the ablation laser with particle's arrival, based on particle detection by conventional elastic scattering. The solution to this problem has thus far been to randomly fire the ablation laser such that on the rare occasion of coincidence between laser and particle a spectrum is produced. This approach results in a very low duty factor.

This size limitation can be overcome by taking advantage of the difference in the ionization threshold between gas and particle. In particular, most carrier and atmospheric gases have ionization thresholds that are significantly higher than those of the condensed phase aerosol. This difference can be exploited to generate a signal that signifies the presence of a particle. The choice of ionization radiation is crucial in order to maintain a high contrast between particle and the gas the wavelength must be selected, so that particles alone would be ionized.

Here a high flux rare gas VUV light source will be used. This light source is capable of delivering ~10^{16}photonssec^{-1}sr^{-1}. When operating with He, this light source will definitely ionize both aerosol and surrounding gas (HeI - 21.2eV). But using the Ar (ArI – 11.8eV), Kr (KrI – 10 eV) or Xe (XeI – 9.6eV) will allow us selectively ionize aerosols. The detection of a free electron indicates the presence of a particle and can be used to generate a trigger signal to fire the ablation laser and obtain a TOF-MS. Alternatively, whole particle mass can be to determine using the TOF-MS directly.

At present this scheme will enable determination of particle size distributions, in whole particle mass analysis, or particle composition. Once the system will be in operation we will explore various schemes to obtain simultaneously size and composition information about nanoparticles. We will test the feasibility of deriving particle size from the total photoelectron signal or from the total ion signal or both. We will also explore the possibility of VUV elastic scattering for size and detection. Here the use of HeII with a ~30nm wavelength which is rather close to the particle's size may prove to be a useful tool in distinguishing nanoparticles from gas phase molecules.