



ANALYSIS OF SINGLE NANOPARTICLES USING NANOPARTICLE MASS SPECTROMETRY (NPMS)

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Nanoparticles (NPs) and nanotechnology are being used in many industries such as electronics, energy, and medicine. Due to the size of nanoparticles, their physical properties are different than molecular or bulk materials. As NPs decrease in size, a larger percentage of atoms are in the surface layer, resulting in different chemical (*i.e.*, catalysis, molecular adsorption) and physical properties (*i.e.*, optical emission) when compared to their bulk counterparts. Currently, most NP measurements are averaged over a distribution of NP sizes, but even with same size particles, the shapes can vary and that can affect the optical properties and surface chemistry. With the nanoparticle ion trap mass spectrometry (NPMS) method, individual NPs can be trapped in a split-ring electrodynamic trap (SRET) and we can analyze a single nanoparticle's mass, charge, and thermal emission spectrum with precision. By heating the NP and monitoring mass vs. time, we can determine how sublimation and oxidation affects the surface chemistry for each individual NP. With the ability to trap and analyze many single nanoparticles, we can develop a better understanding of various materials' surface chemistry and assess potential health and environmental risks with the advancing nanotechnology. We can also address how size and shape influences kinetics of NPs.

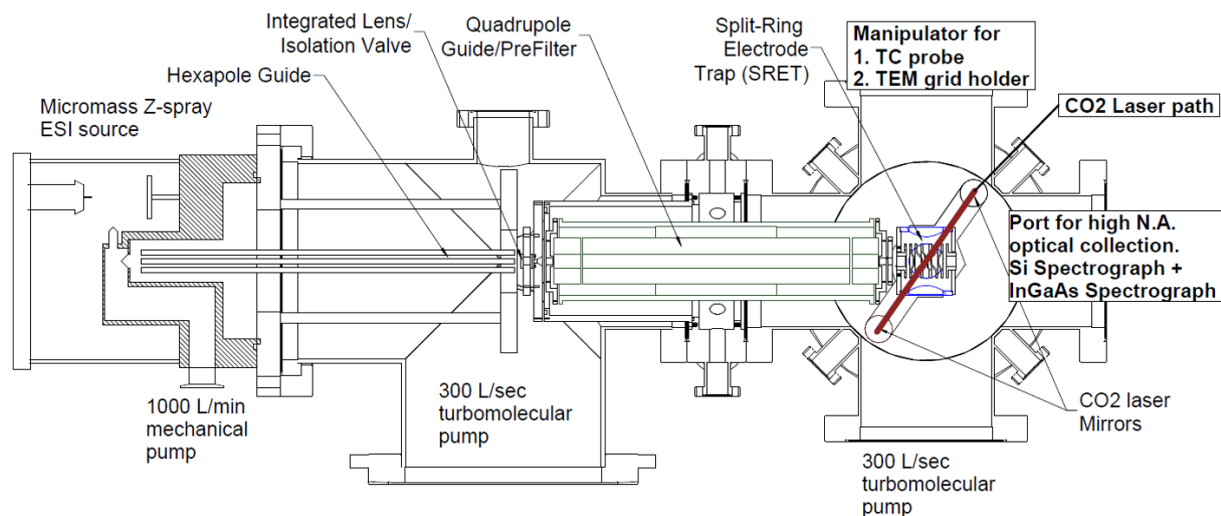


Figure 1 Cross-section of the Nanoparticle Mass Spectrometry (NPMS) Instrument. Nanoparticles are guided and trapped into the split-ring electrode trap (SRET) in argon gas

The mass of a single trapped nanoparticle is measured by applying a weak variable drive frequency potential, F_{drive} , across a lens next to the SRET and its thermal emission is monitored on an avalanche photodiode (APD). As seen in figure 2, the particle's secular axial frequency,

F_z , can be determined by a decrease in the particle's baseline optical signal when F_z is resonant with the F_{drive} . For better determination of F_z , the signal dip is fitted with a Gaussian function.

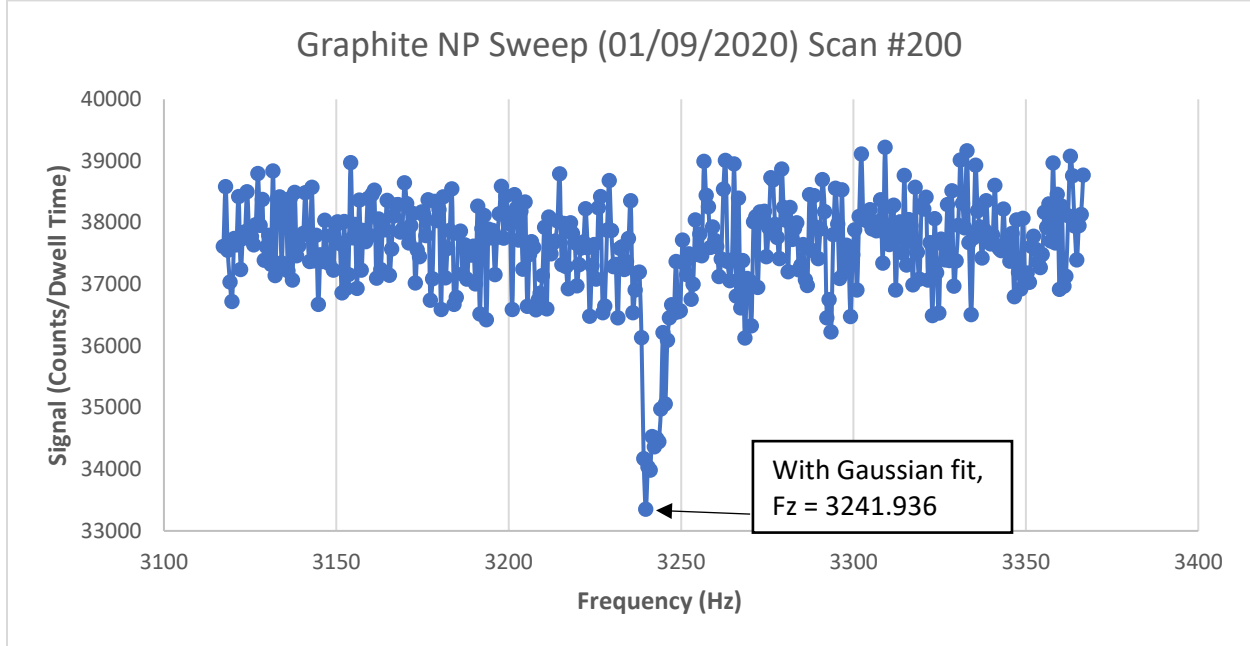


Figure 2 Frequency sweep of a graphite nanoparticle. Decrease in signal around 3240 Hz indicates that the drive frequency is resonant with the nanoparticle's secular frequency.

With the ability to measure F_z periodically, we can also determine the trapped NP's charge/mass ratio (Q/M). Single electron changes in the NP's charge state, Q , can be induced using a vacuum ultraviolet lamp (VUV) and are detected by the effects on F_z . This method of charge stepping can be used to determine the charge state before the charge step by using $Q_1 = \Delta Q * F_{z1} / (F_{z2} - F_{z1})$. An example of analyzing the charge of a graphite nanoparticle using charge stepping is shown in figure 3. Once we know the charge, we can also find the mass from the secular frequency, F_z , using equation 1:

$$M = \left(\frac{Q}{F_z}\right) \left(\frac{\sqrt{2}V_0}{4\pi^2 F_{RF} z_0^2}\right) \quad \text{Equation 1}$$

where V_0 is the amplitude of the AC frequency, F_{RF} is the frequency applied to the ion trap, and z_0 is the trap's geometric parameter.

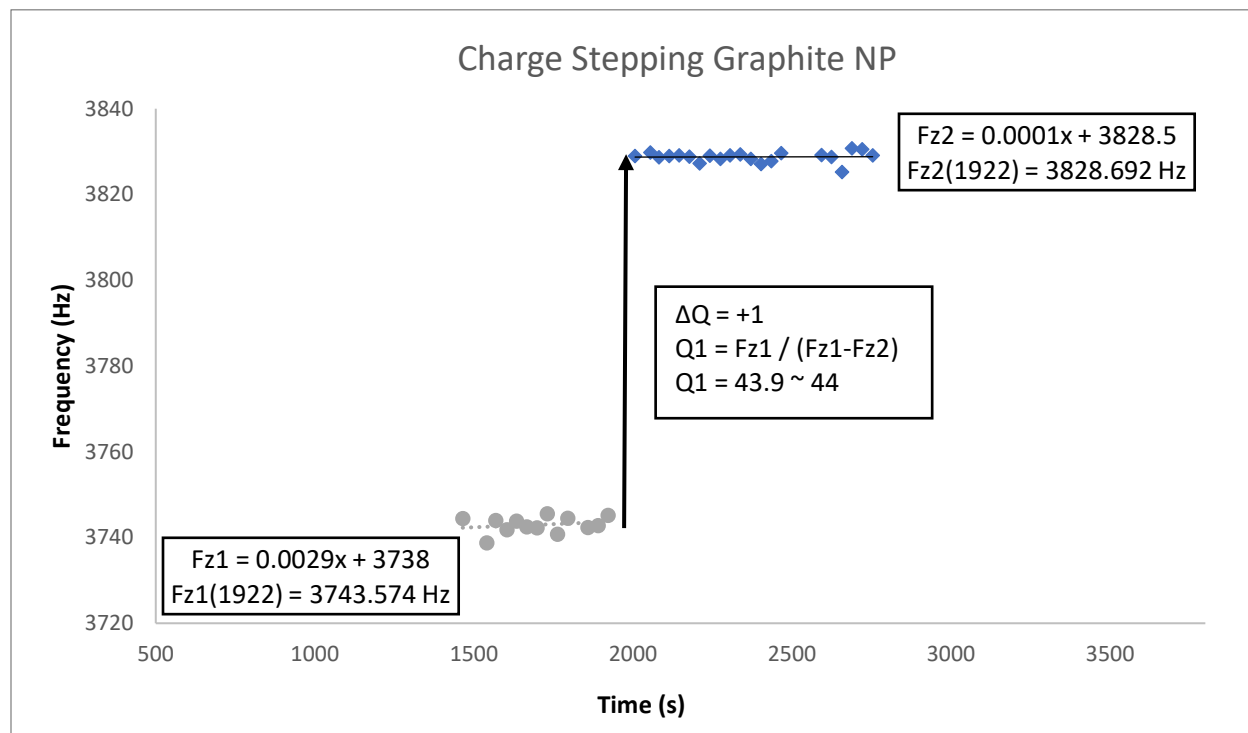


Figure 3 Determination of a particle's charge (Q1) after charge stepping. Perform a linear regression of multiple scans of the same charge. Using the regression, determine the particle's frequency at the time point before charge step occurred (t = 1922 seconds). Repeat the same steps after charge step and calculate Fz2 at time point before charge step occurred (t=1922 seconds).

The ability to measure a single nanoparticle's mass over time means that we can measure reaction kinetics by analyzing the change in mass vs. time due to reactions under different conditions. Some experiments that we have done include heating up the particle at high temperatures using a green 532nm laser in inert argon gas to study sublimation, or letting the particle react with small, controlled amounts of oxygen gas to study oxidation, or a combination of sublimation and oxidation. An example of an oxidation experiment on a graphite nanoparticle at different temperatures is shown in figure 4. In this experiment, the nanoparticle was alternately held in pure argon gas (purple background) and Ar with a small amount of oxygen gas added (cyan background) at various temperatures.

At temperatures below 1800K, the rate of change of the nanoparticle's mass in argon is small, meaning there is little sublimation occurring. However, there is a larger rate of change when oxygen is added, indicating that oxidation is faster. At temperatures over 2000 K, it is much easier to see how the mass changed with time, because at high temperatures both sublimation and oxidation are significant. The oxidation rate can be determined by subtracting the sublimation rate measured at the same temperature. It can be seen that at high temperatures, the rate of sublimation speeds up, but the rate of oxidation actually slows down. More experiments need to be conducted to understand the relationship between temperature and changes in sublimation rates and oxidation rates.

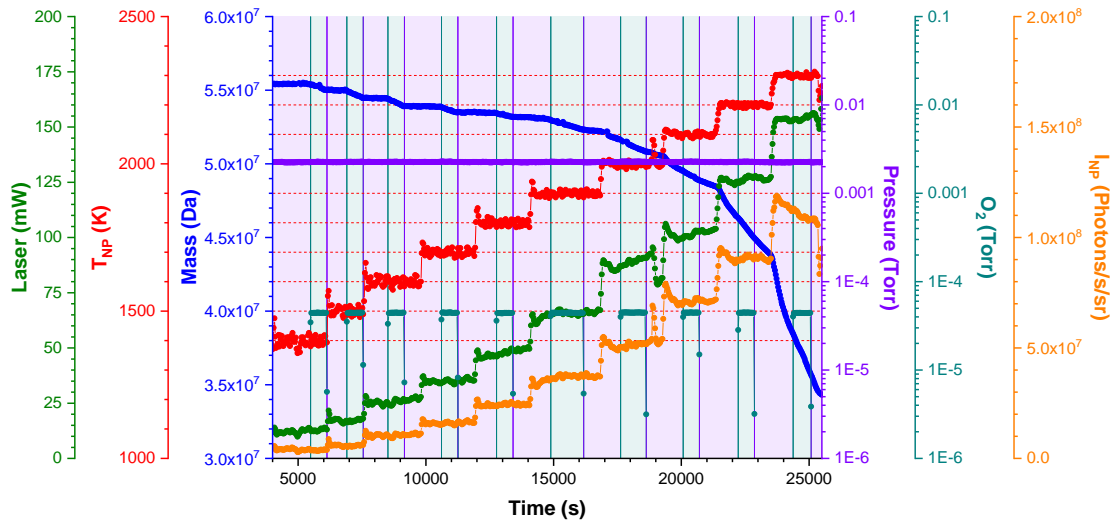


Figure 4 Experiment of graphite nanoparticle alternating between sublimation and oxidation conditions at various temperatures