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Trapping single nanoparticles in the gas phase to perform action spectroscopy

Nanometer sized materials between the size range of clusters, where each single atom can be important, and macroscopic dimensions with bulk properties have become increasingly accessible for synthesis, characterization and application. Among them are metal nanoparticles (NPs), that can exhibit a collective motion of conduction electrons (a localized surface plasmon resonance) upon absorption in the optical spectrum, which is unique to nanometric particle sizes. The strong, highly size-tunable absorption offers a wide range of applications for sensing, cell imaging and enhancing Raman spectroscopy or catalysis. Another prominent class of NPs are semiconductor crystals (quantum dots) that typically have a broad absorption cross section, ranging down to the optical or infrared range. Photon absorption creates an electron-hole pair that efficiently relaxes to the band gap energy, which gives rise to a narrow fluorescence emission spectrum with high quantum efficiency. Applications of the tunable and bright emission include single photon emitters, thermometry and fluorescence labelling in super-resolution microscopy.

The intermediate size of NPs both provides opportunities for exciting material properties and applications and poses challenges for their characterization. Owing to their small size, absorption spectroscopy is routinely performed only for ensembles or particles in solution and the obtained averaged spectra suffer inhomogeneous broadening. This is especially pronounced as they contain thousands to hundreds of millions of atoms which makes precise control of their size, shape and structure impossible and gives rise to significant physical and chemical heterogeneity. Precise characterization therefore requires single particle techniques. These mostly rely on surface deposition to probe NPs optically or by atomic force microscopy while this article focuses on the use of nanoparticle mass spectrometry (NPMS) in the gas phase with the goal to probe intrinsic NP characteristics unperturbed by neighbours or a support. Our specific aim is the non-destructive characterization of single NPs and their surfaces under cryogenic conditions by absorption spectroscopy and temperature programmed desorption (TPD) like approaches that are both mediated by mass spectrometry.

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Nanoparticle mass spectrometry

Mass spectrometry (MS) of single nanoparticles can roughly be divided into two approaches. Electrostatic traps with charge detection MS are for example applied to study virus particles, ion emission from salt clusters or for velocity-controlled surface scattering in the groups of Jarrold, Willams and Continetti. We follow the ion trap approach that has been used to study charging and fluorescence in the groups by Gerlich and Bieske and is actively applied to reaction kinetics in the Anderson group. Ion traps are ideal for complex single particle experiments because they allow indefinite trapping times. Measurement of the NP's secular frequency by the detection of emitted light in combination with charge stepping allows absolute mass determination [1] and is the basis to study charge states, particle sizes, mass loss by sublimation and gas phase reactions, or adsorption and desorption on a NP.

Single nanoparticle action spectroscopy

The Asmis group has implemented a cryogenic NP ion trap to study the adsorption on cold NP surfaces as a basis for single nanoparticle action spectroscopy (SNAS). The basic approach is depicted in Fig. 1. By cooling the trap housing with a helium cryostat, temperatures down to below 10 K can be reached. Mediated by collisions of the buffer gas with the trap walls and subsequently with a trapped NP, the latter is cooled in turn.
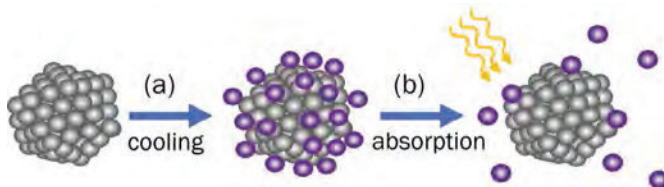
Fig. 1: Cartoon demonstrating the principle of single nanoparticle action spectroscopy. (a) Cooling of the particle allows to adsorb a weakly interacting messenger species from the ambient gas in the ion trap. (b) Light absorption leads to heating of the particle surface that leads to desorption and mass loss.

Seeding a messenger species into the buffer gas, that is weakly interacting but stickier than the buffer gas itself, allows controlled adsorption to the NP surface, which is continuously monitored by mass spectrometry. The coverage in the order of a couple of monolayers depends on the partial pressure of the messenger gas and the particle's surface temperature. For spectroscopy, the NP is illuminated by a CW light source

with tuneable wavelength that is turned on and off in alternating intervals of a few minutes, long enough for some secular frequency measurements. In case the NP absorbs at a particular wavelength, the absorbed energy eventually leads to heating of the NP surface followed by enhanced messenger desorption that is observed as a mass loss. In comparison to solution spectra, we could demonstrate that the absorption cross section is proportional to the mass difference between the on and off intervals [2]. As opposed to direct absorption spectroscopy, the mass loss is only sensitive to light absorption but not to inelastic light scattering, which is especially suitable for larger particle sizes, where extinction spectra are dominated by the scattering contribution.

While measuring plasmon resonance spectra of individual gold NPs that could be quenched by laser heating [3] was a success, it turned out that reproducibility and in particular the surface preparation needed for high quality spectra, for example to investigate chemical interface damping of the resonance by different messenger species, is yet a challenge. To tackle this task, to moreover convert mass loss spectra into heat and absolute cross sections, and to perform surface characterizations by TPD-MS protocols (based on weighing the amount of adsorbed material), it is crucial to gain control on particle temperatures and to assess surface binding energies.

Thermometry of a cold trapped nanoparticle

Due to an open ion trap design that has been chosen for good optical access for spectroscopy and efficient light detection, the trapped NP is subject to collisions with buffer gas and black body radiation of both room and trap temperature in addition to laser heating. The need for reliable temperature information for quantitative absorption spectroscopy and to interpret temperature dependent desorption data therefore requires techniques to measure particle temperatures.

For hot NPs, temperatures can be routinely measured and controlled by thermal emission spectroscopy, which is actively used to investigate sublimation and reaction kinetics [4]. In contrast, for our goals of non-destructive characterization and SNAS, low temperatures are required where thermal emission shifts into the IR range and becomes too weak for detection. In a collaborative project we instead followed the approach of fluorescence thermometry with CdSe core/CdS shell quantum dots (QDs) whose shell material with a higher band gap protects the core from defects and surface charges to preserve the high quantum efficiency of the emission [5]. After calibration by measurements on a cryogenically cooled wafer, the QD temperature inside the ion trap can be directly measured by recording fluorescence emission spectra that have a temperature dependent center wavelength.

Combining this thermometry scheme with mass spectrometry serves as a starting point to develop temperature-controlled schemes such as TPD-MS methods to characterize sorption dynamics and binding sites. So far, we used QD
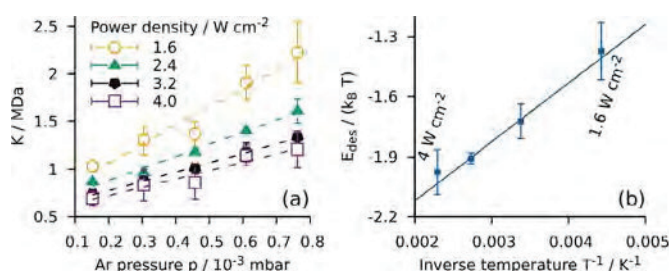
temperatures as a function of trap temperature to validate a model of the dominant heating and cooling processes that will be refined for different experimental conditions to predict temperatures of NPs to which the scheme is not applicable. This paves the way to inducing controlled temperature changes by adjusting laser intensity or buffer gas pressure. Our first application of the published model is to estimate the average binding energy of argon on a silica NP.

Adsorption on a nanoparticle and binding energy

As a first approach to characterize cryogenic adsorption on a 100 nm diameter silica NP without direct temperature control, we have recorded mass growth curves of argon seeded in helium at a trap temperature of 55 K. Short heating periods allow to regularly reset the particle to its initial mass and start new growth curves. This is repeated for different argon partial pressures (keeping constant total pressure to achieve roughly constant cooling power) and laser intensities. Fitting each growth curve gives an estimate of the equilibrium constant of the final amount of adsorbed argon, which is the ratio of adsorption rate k_{ads} proportional to pressure p and desorption rate k_{des} proportional to an Arrhenius factor with the binding (desorption) energy E_{des}:

$$K = \frac{k_{ads}}{k_{des}} \propto p \, exp\left(\frac{E_{des}}{k_B T}\right) \ \Rightarrow \ ln\left(\frac{K}{p}\right) \approx const + \frac{E_{des}}{k_B T}$$

Different laser intensities lead to different NP temperatures T, that are estimated from the new temperature model coarsely calibrated to the onset of SiO_2 sublimation. According to the equations, the set of linear fits in Fig. 2 (a) and the fit of the logarithms of the resulting slopes in Fig. 2 (b) gives a result of 2.4 kJ mol^{-1} for the average binding energy E_{des} of argon on the silica NP surface. The value is 2 to 3 times smaller than published values for argon on zeolites, which shows that our preliminary result is in the expected range.

Fig. 2: Linear fits to determine the binding energy E_{des} of argon on a silica NP. (a) Equilibrium constant versus pressure. (b) Fitting the slopes of the linear regressions in (a) as a function of inverse NP temperature yields E_{des}.

This result is a step toward the characterization of single NP surfaces in the gas phase with TPD-MS approaches. It has become possible with fluorescence thermometry paving the way to temperature controlled cryogenic single NP experiments. Both developments will support and complement our single nanoparticle action spectroscopy approach in the gas phase.

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Björn Bastian studied physics at the University of Freiburg. His PhD work on ion-molecule reaction dynamics at the University of Innsbruck led him into the field of physical chemistry. He continued his research as a postdoc at Aarhus University to investigate electronic decay processes in helium nanodroplets for two years. Since 2022, he is an academic assistant in the Asmis group at the Wilhelm Ostwald Institute for Physical and Theoretical Chemistry in Leipzig. His research focuses on the characterization of single nanoparticles in the gas phase, based on the development of single nanoparticle action spectroscopy and related techniques.

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