

An original laser-based method for measuring the adsorption energy of aromatic compounds on carbonaceous aerosol surrogates

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Extensive global emission of fine and ultra-fine carbon-based particulates presents a well-known health risk and raises significant environmental concern. The toxicity and reactivity of carbonaceous aerosols, in particular soot, is determined by their surface composition. It is thus important to unveil the actual interaction (physisorption, chemisorption) of adsorbates with the particle surface, and get an estimation of the corresponding adsorption energy. This, however, can be a challenging task for “real-world” soot particles carrying a multitude of molecular species. Among the variety of molecules which can be encountered on a soot particle surface, Polycyclic Aromatic Hydrocarbons (PAH) are of great importance, both for fundamental mechanisms (important role in soot nucleation and growth) and for toxicology issues (proven carcinogenic effect). In this study, we propose an original method for measuring the adsorption energy of PAHs to carbonaceous substrates.

The method was validated on “surrogate soot”, i.e. a known (sub-monolayer) amount of PAHs adsorbed on various carbonaceous surfaces (e.g. carbon black nanoparticles). This method is based on the use of a two-step laser mass spectrometer (L2MS), developed in our lab to specifically probe the chemical composition of soot particles with high sensitivity and selectivity (Faccineto, 2015). Two variants of this method have been developed: the “pulse-to-pulse decay” and the “fluence curve”. In the former, successive (nanosecond) laser pulses of constant energy are applied to the same desorption spot, while in the later, various spots on the surface are probed with single pulses of increasing energy. In both cases, the desorbed neutral molecules are ionized by a UV laser and further detected by a time-of-flight mass spectrometer, thus monitoring the signal of all adsorbates present on the surface. A pseudo-exponential decay is obtained in the “pulse-to-pulse” approach, whereas a monotonic increase towards saturation is returned by the “fluence” variant. To extract the adsorption energy from the experimental

data, we developed a theoretical model employing Bayesian statistics tools in two variants. A simpler version is based on the assumption of quasi-thermal desorption of molecules (steady-state approximation) at low laser fluences (Dreisewerd, 1995), while a more refined one takes into account the fast transient surface temperature profile upon laser irradiation. A numerical approach based on a two-dimensional heat equation is implemented to calculate the space-time evolution of the surface temperature in the irradiated zone.

The proof of concept of this original method has been performed with the adsorption energies of pyrene and coronene adsorbed on black carbon, and the first results show good agreement with values reported in the literature (Bedjanian, 2010). Application of this method to other carbonaceous surfaces and “real soot” particles will be discussed.

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