

Sodium-sizer for neutral nanosized molecular aggregates: Quantitative correction of size-dependence



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ABSTRACT

The sodium-sizer is a device for the measurement of size-distributions of neutral molecular aggregates with sizes in the nanometer range (<20 nm). This work provides a quantitative correction for the size-dependent overall detection efficiency for this instrument. Four processes contribute to the overall detection efficiency: the Na-capture, the Na-sticking, the photoionization, and the detection efficiency at the micro-channel plate detector. We demonstrate that the Na-sticking and the photoionization efficiencies are not size-dependent and thus do not require corrections. Size-dependent corrections, however, are needed for the capture and the micro-channel plate detection efficiencies. Expressions for corresponding corrections are provided. Our results show the importance to operate the sodium-sizer under single Na-doping conditions and at high ion acceleration voltages to ensure that the raw data are of sufficient quality so that the corrections can be applied.

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1. Introduction

The characterization of neutral nanosized molecular aggregates (also referred to as clusters or aerosol particles) is crucial for the understanding of confinement effects and the evolution of bulk properties. Volatile and semi-volatile (also referred to as weakly-bound) ultrafine molecular aggregates of a wide range of chemical compositions participate in aerosol and cloud formation and influence various industrial processes. One of the biggest challenges of fundamental size-dependent studies of such aggregates is the determination of the size distribution itself. The investigation of any size-dependent property requires independent and accurate size information. The size determination is particularly difficult for neutral weakly-bound aggregates in the nanometer size range because most sizing methods either do not work for neutral systems, are not soft enough for weakly-bound aggregates, or are not applicable in the nanometer-regime (see Ref. [1] for a short discussion of different methods).

We have recently shown that the “sodium-sizer” (“Na-sizer”) allows the determination of accurate size distributions for neutral weakly-bound molecular aggregates that are investigated in molecular beam apparatuses [1–5]. The Na-doping method was originally proposed by Buck and co-workers [6–8], who used it to demonstrate that electron ionization of weakly-bound molecular

aggregates leads to substantial fragmentation of the original particle size distribution and therefore cannot be considered a soft ionization method. The Na-sizer combines an ultrasoft ionization method with mass spectrometric detection of the aggregates’ sizes. The working principle is sketched in Fig. 1 and explained in more detail in Section 2 and Refs. [1,3,6–9]. In brief, the molecular aggregates (usually a distribution of particles of different sizes) in the beam traverse a sodium oven where a fraction of the particles pick up a single Na atom. The Na in the Na-particle complexes are then ionized with a low energy photon (typically 266 nm) and the masses of the Na-particle complexes are determined by mass spectrometry. Subtraction of 23 mass units (for the mass of Na) from each mass peak results in the mass distribution of the particles, which can be converted to a particle size distribution (requires information on the density and the shape of the aggregates).

Previous studies from the Buck group and from our group demonstrate two important features of the sodium-sizer: (i) aggregate sizes can be detected over a broad range from dimers up to particles with radii of about 20 nm (the number of molecules per aggregate changes over six orders of magnitude!). (ii) Weakly-bound aggregates can be sized because the sodium-sizer is an ultrasoft method that leaves the aggregates largely intact (see Refs. [2,6,7], and the short discussion in Section 3.3). However, our previous study in Ref. [1] revealed that the size distributions recorded with the Na-sizer do not represent the original size distribution in a quantitative way because the overall detection efficiency of the device depends on the size of the aggregates and on

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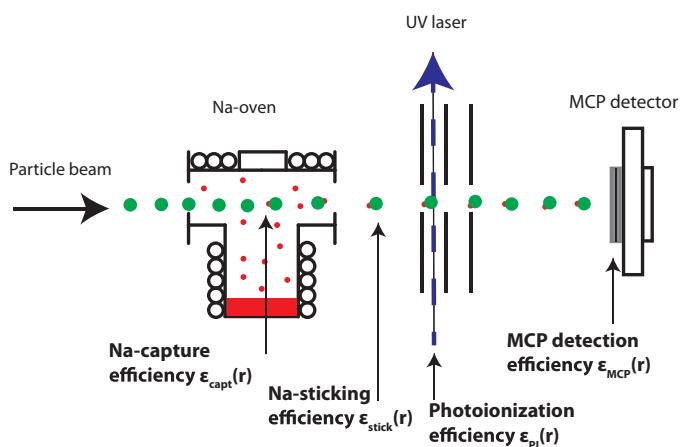


Fig. 1. Sketch of the Na-sizer. The overall detection efficiency is a product of contributions from (i) the Na-capture, (ii) the Na-sticking (iii) the photoionization (iv) the detection at the MCP detector.

their chemical composition. To obtain quantitative size distributions corresponding corrections for the overall detection efficiency need to be applied to the measured size distributions. The present contribution provides such quantitative corrections for the size-dependence of the overall detection efficiency. More accurately, we determine corrections for the relative (and not the absolute) abundance of aggregates of different size to make the Na-sizer a quantitative sizing method. An assessment of the dependence of the overall detection efficiency on the chemical composition will be the subject of forthcoming publications and is not discussed in the present contribution.

2. Na-sizer and experimental

2.1. Detection efficiency of the Na-sizer

The sketch of the Na-sizer in Fig. 1 depicts the four processes that contribute to the overall detection efficiency, namely the Na-capture, the Na-sticking, the photoionization, and the detection of the ions at the micro-channel plate (MCP) detector. Because the efficiencies of these different processes can be size-dependent (r denotes the particle radius) one needs to correct the measured size distribution $M(r)$ to retrieve the original size distribution $c(r)$.

$$c(r) \propto \frac{M(r)}{\varepsilon_{\text{tot}}(r)} = \frac{M(r)}{\varepsilon_{\text{capt}}(r)\varepsilon_{\text{stick}}(r)\varepsilon_{\text{PI}}(r)\varepsilon_{\text{MCP}}(r)} \quad (1)$$

where $\varepsilon_{\text{total}}(r)$, $\varepsilon_{\text{capt}}(r)$, $\varepsilon_{\text{stick}}(r)$, $\varepsilon_{\text{PI}}(r)$, and $\varepsilon_{\text{MCP}}(r)$ are the overall detection efficiency, the Na-capture efficiency, the Na-sticking efficiency, the photoionization efficiency, and the detection efficiency at the MCP, respectively. (Note that Eq. (1) does not include the loss of aggregates from the beam due to particle scattering. We found it to be negligible under typical conditions (see remarks in Section 3.2)). Sections 3.1–3.4 describe how explicit expression for the different efficiencies can be obtained, which allow for the reconstruction of the original size distribution $c(r)$ using Eq. (1). Because the expressions “capture” and “sticking” are often not consistently defined in the scientific literature we are providing here a brief clarification of the meaning of these terms as used in the present paper (see also [1]): with Na-capture we denote the formation of the metastable or stable Na-particle collision complex in the Na-oven (“reactive collision”). The Na-sticking probability describes the lifetime of the Na-particle collision complex after its formation, i.e., the lifetime with respect to the loss of the Na atom. This lifetime must be on the order of several ten microsecond for the complex to reach the ionization region

without losing the Na (see Fig. 1). The efficiency for ionizing the Na atom in the Na-particle complex by a single photon is referred to as “photoionization efficiency”. For the current study, we used an MCP detector for the detection of the positively charged Na-particle ions, the corresponding efficiency is called “MCP detection efficiency”.

2.2. Experimental

A sketch of the experimental setup is shown in Fig. 2. Neutral aggregates of ammonia (NH_3 , Air Liquide, >99.999%) or benzene (C_6H_6 , Sigma-Aldrich, >99.7%) were generated in the source chamber by free supersonic expansions of a gaseous sample through a pulsed nozzle (Parker Hannifin, General Valve series 9). The pulsed nozzle had an orifice diameter of 500 μm and was operated at a frequency of 20 Hz and pulse durations on the order of 500 μs . For the generation of $(\text{NH}_3)_n$ aggregates (n is the number of molecules per aggregate), neat NH_3 gas was expanded at backing pressures between 2.0 and 3.5 bar. For the generation of $(\text{C}_6\text{H}_6)_n$ aggregates, helium gas (Helium 5.0, Pangas) at pressures between 2.5 and 3.5 bar was bubbled through liquid C_6H_6 (temperature ~ 294 K) and then expanded through the nozzle. Typical aggregate sizes varied from small oligomers that contain a few molecules and have radii far below a nanometer up to large aggregates with radii of about 20 nm that consist of many ten thousands of molecules. This covers a mass range from a few amu/e to several hundred thousand amu/e (numbers are given for ammonia aggregates).

The pulsed particle beam was skimmed by a 1 mm diameter nickel skimmer (Beam Dynamics, Inc.) before it entered the actual Na-sizer (see also Fig. 1), which consists of the Na-oven chamber and the time-of-flight (TOF) chamber. The Na-oven in the oven chamber is a cylindrical cell with an entrance and exit aperture to allow passage of the particle beam and a reservoir for the Na (Na, Sigma-Aldrich, 99.0%). The Na-oven is temperature controlled using a home built driver and PID control loops with two independent K-type thermocouples as a feedback. The Na vapor pressure in the oven is controlled by the oven temperature T_{oven} , which can be varied between 294 K and 573 K (Na vapor pressure between 10^{-10} and 2×10^{-2} mbar [10]). After passing the oven chamber, the particle beam entered the TOF chamber through a round aperture of 20 mm diameter. We used photons of 4.66 eV energy (266 nm wavelength) from the output of a portable Nd:YAG laser (Quantel Ultra 50) for the ionization of the aggregates (between the first and second plate of the ion optics). The generated ions are accelerated by a Wiley–McLaren type extractor and separated in a 86 cm long TOF mass analyzer. The impact energy of the ions on the MCP detector, which is the key

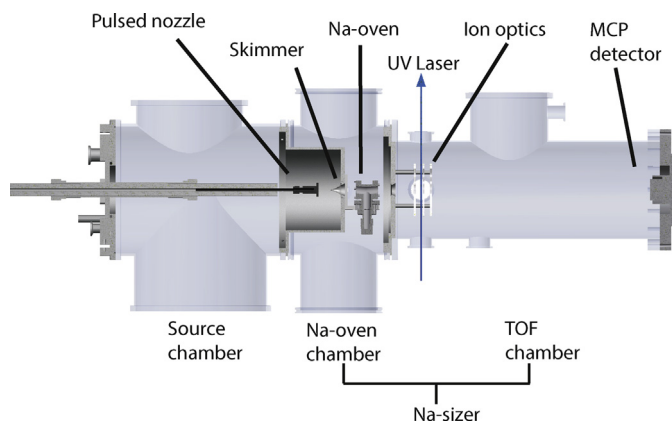


Fig. 2. Sketch of experimental setup. The setup consists of the source chamber and the Na-sizer (Na-oven chamber and TOF chamber).

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