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International Journal of Mass Spectrometry 252 (2006) 142–144

International Journal of Mass Spectrometry

www.elsevier.com/locate/ijms

Surface-impact ionization of alkali nanoparticles

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Received 16 October 2005; received in revised form 9 November 2005; accepted 10 November 2005
Available online 10 March 2006

Abstract

Sodium nanoparticles of ∼10 nm radius, generated in a vapor condensation source, produce copious amounts of positive ions upon colliding with a surface. The ion flux does not display an exponential surface temperature dependence, is present for both conducting and non-conducting surfaces, and carries a substantial kinetic energy. On the basis of these characteristics it is concluded that the signal arises from dissociative ionization produced by energetic impact, rather than from thermal charge transfer to the surface.

Keywords: Nanoclusters and nanoparticles; Surface ionization

1. Introduction

Surface deposition of preformed nanometer-sized clusters is a promising technique for designing new materials and surfaces [1–3]. Consequently, it is important to study the dynamics of the interaction of nanocluster beams with surfaces. One of the well-known collision-driven reactions is the generation of ionic fragments. Interestingly, positively and negatively charged ions emerge not only upon surface impact of charged cluster beams (see, e.g., the review [4]), but during scattering of neutral clusters as well. Specifically, charged cluster fragments have been observed to appear in surface bombardment by large (10^3–10^4 molecules) water [5–8], SO_2 [9,10] and some other clusters of polar molecules [9].

It has been known since the 1930s that neutral alkali atoms can be efficiently ionized by a very hot wire [11]; such Langmuir–Taylor detectors operate at ∼1500 K and are a venerable technique in spectroscopy [12]. But with beams of Na_n ($n \sim 10^4$, ∼10 nm diameter) nanoclusters, we have observed a high yield of cations already at a room-temperature surface [13], so it is interesting to inquire about the underlying mechanism in this case.

Surface collisions of alkali atoms and of nanoclusters differ in two important respects. First, the latter case offers a considerably higher kinetic energy of impact. For example, the beam produced by our vapor condensation source (see below) has an average velocity of 220 m/s. For a 20,000-atom sodium cluster, this corresponds to an impact energy of almost 120 eV, which is much higher than both the ionization potential and the binding energy of the particle. This can result in intense fragmentation and dissociative ionization upon impact.

At the same time, the ionization potential I of large metal nanoclusters is close to the bulk work function (2.8 eV for Na) and is much lower than that of the atom (5.1 eV for Na). This fact can exponentially enhance the probability of electron transfer to the surface. The Saha–Langmuir equation [14,15] states that the ionization coefficient $\beta = N_+/N$ (i.e., the ratio of the flux of re-evaporated positive ions to the incoming flux of neutral particles) is given by

$$\beta = \frac{\alpha}{1+\alpha}, \quad \alpha = \frac{g_+}{g_0}\exp\left[\frac{e(W-I)}{k_B T}\right] \tag{1}$$

Here W and T are the work function and temperature of the surface, g_+ and g_0 are the statistical weights of the ionic and neutral states. The equation assumes that the impinging particle adsorbs on the surface, thermalizes, donates an electron to the surface, and is reemitted as a positive ion. For atoms and standard surface materials, $I > W$ and the ion yield is described by a negative exponent. But for nanoparticles we can have $I < W$, so that $\alpha \gg 1$ and the ion yield β saturates at unity.

Given these two possible scenarios for cation yield from nanocluster impact (strong nonequilibrium dissociative ionization

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doi:10.1016/j.ijms.2005.11.030

and efficient thermal electron transfer), which corresponds better to the experimental observations?

2. Measurements and discussion

The experimental setup is shown schematically in Fig. 1. The nanoparticle beam is produced in a vapor condensation source. A beam of sodium atoms effusing from the nozzle of a heated reservoir is quenched in a flow of cold argon gas, resulting in cluster growth. The clusters leave the source through another nozzle, pass through a skimmer and a mechanical chopper, and fly towards the detector region. Here surface ionization takes place on a 1 mm-thick slice of highly oriented pyrolytic graphite (HOPG; Structure Probe, Inc.) mounted on a substrate heater (HeatWave Labs, Model 101491). We found it necessary to use HOPG because it became apparent that the sodium flux quickly contaminated the heater's own molybdenum surface, even at high temperatures, resulting in very poor reproducibility. We estimate that the graphite surface was approximately 100° colder than the reading of the thermocouple mounted inside the substrate heater. The pressure in the detector chamber is $\approx 10^{-7}$ mbar.

The resulting cations are focused by two ion lenses, accelerated to a conversion dynode/photomultiplier detector [16], and counted by a multichannel scaler synchronized with the mechanical chopper. Chopping the beam allows us to subtract the intense background caused by thermionic emission from the hot surface itself, and to determine the beam velocity from the ion arrival delay time.

As mentioned above, we estimate that particles contributing most to surface ionization are $\gtrsim 2 \times 10^4$ atoms in size. This is based on time-of-flight [17] and electron attachment [13] data for nanoclusters from a similar aggregation source. Because of the size, our quadrupole mass spectrometer was not used in this experiment. The quadrupole detected no small clusters in this beam with UV lamp illumination, either with argon or helium carrier gases, at variance with a somewhat similar setup described in Ref. [18] which used a time-of-flight spectrometer with pulsed laser ionization.

The graphite target was set to a chosen temperature and the resulting ion signal measured for one minute. Next, the ion lenses were biased so as to cut off the surface ionization signal, and the ion signal produced by ionizing the cluster beam with a UV arc lamp was measured for one minute. This was taken as a measure of the neutral beam intensity and used to normalize the surface ionization yield. For each surface temperature, approximately ten such cycles were repeated, after which the target was heated to 1000 °C aiming to remove any sodium deposits from the surface. Then the heater was set to a different temperature value, and the procedure was repeated.

Fig. 2(a) shows the yield of positive ions as a function of the temperature of the HOPG surface. Despite fluctuations, ascribed to instabilities in beam condensation and surface purity, it is clear that the ion yield does not display any exponential sensitivity to the surface temperature. For comparison, Fig. 2(b) shows the observations when the nanoparticle condensation source was replaced by a supersonic jet source [16]. In this case, most of the signal should be coming from Na atoms which predominate in the beam. Indeed, the temperature dependence is now clearly exponential. A fit to Eq. (1), using the literature value of $W = 4.3$–4.5 eV for HOPG [19], yields $I = 5.4$–5.6 eV, in sensible agreement with the atomic value of 5.14 eV.

This data by itself is insufficient for an unequivocal answer regarding the ionization mechanism: both dissociative ionization upon energetic impact, and the Saha–Langmuir equation with $I < W$, would suggest a lack of strong temperature dependence. Two other facts, however, strongly point towards the former mechanism.

First, we can obtain an idea of the kinetic energy of the positive ions from the stopping potentials. It was found that when the surface was bombarded by nanoparticles, Ion Lens 2 (see Fig. 1) had to be set at a retarding voltage of 120 V in order to shut off the ion signal. On the other hand, the application of less than 2 V was sufficient to completely stop the cations produced by atom impact. The latter value is consistent with thermal desorption, but the former is of the same order as the estimated kinetic energy of nanocluster impact, and can be explained only as originating from nonthermal collisional dissociation.

Secondly, it was observed that abundant secondary ion production remained when the conducting surface was replaced with glass. Electrons from adsorbed nanoclusters would not be

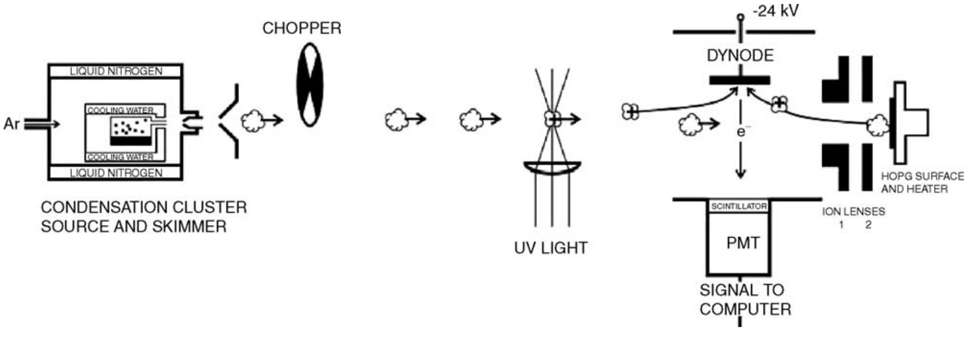

Fig. 1. Outline of the experimental arrangement (not to scale). Alkali nanoparticles are formed in vapor condensation source. The inner reservoir was kept at 440 °C, and its 2.5 mm diameter nozzle at 500 °C. The effusing atoms were quenched in cold argon fed into the source at a pressure of 4.7 mbar, and left the source through a long nozzle (length 25 mm, inner diameter 2–3.5 mm). The distance from the skimmer to the detection region is approximately 2 m. The nanoclusters are alternately ionized by surface impact or by UV lamp illumination, and the resulting positive particles are counted by an ion detector.

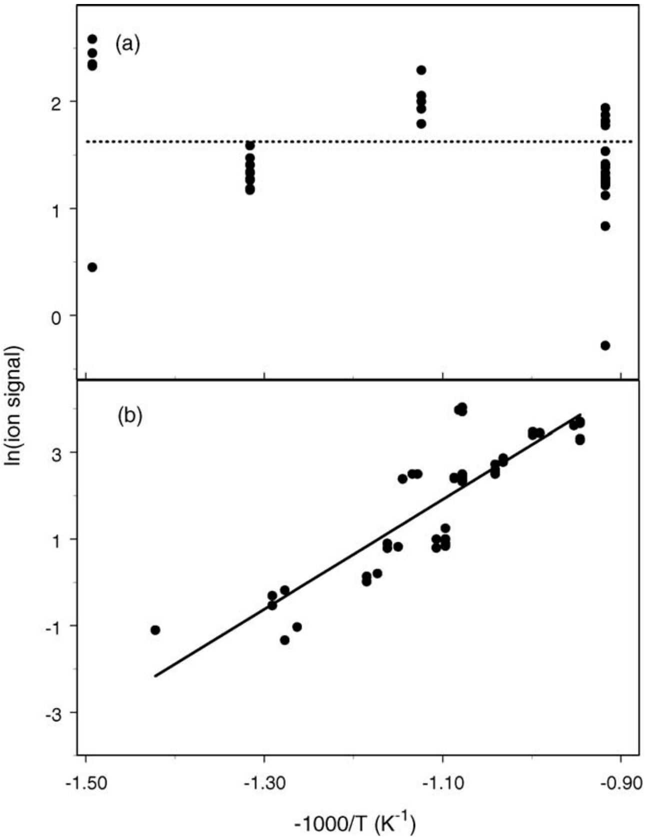

Fig. 2. (a) Ion yield (logarithmic scale) as a function of graphite surface temperature for impact by a beam of sodium nanoparticles. Dots represent individual repetitions of the measurements. Despite scatter, it is evident that the ionization coefficient is not exponentially sensitive to the surface temperature. The dotted line is a guide to the eye. (b) The same for sodium atoms carried in a supersonic beam. Here an exponential temperature dependence is clearly seen. The solid line is the linear fit to the data.

able to enter the conduction band of the insulator, therefore the charge transfer mechanism is not feasible in these circumstances.

It can be concluded that all the presented data are consistent with the following picture: nanoparticles formed by the sodium vapor condensation source are efficiently ionized upon surface impact via nonequilibrium dissociative ionization resulting from the high kinetic energy ($\gtrsim 10^2$ eV) of the collision. This is analogous to processes seen in hyperthermal atom and molecule surface scattering [20–22]. It would be interesting to investigate at what cluster sizes and velocities one may observe a transition from this mechanism to the thermal ionization channel.

Acknowledgements

We would like to acknowledge the contributions of V. Kasperovich and M. Medvetskiy in the early stages of this work. Research was supported by the U.S. National Science Foundation under grant No. PHY-0354834.

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