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Comparison of reactive nucleation of silver and alkali clusters in the presence of oxygen and water

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Abstract. The nucleation of silver-atom vapor in the presence of O_2 and H_2O molecules has been investigated by photoionization mass spectrometry and compared to the case of alkali-atom vapor. Relative intensities in mass spectra show that silver vapor does not react with H_2O molecules, in contrast with sodium vapor. When O_2 and H_2O are simultaneously present, hydroxided products are observed. Results emphasize the role of stable units, $(NaOH)_2$ or $(KOH)_2$, for alkalies, and more complex hydrated or hydroxided systems, involving trimers, for silver. Similarities are found with water dissociative adsorption on an oxygen-predosed silver surface.

PACS. 36.40.C Atomic and molecular clusters – 36.40.Jn Reactivity of clusters

1 Introduction

Early in the study of free clusters, experimental methods were developed to characterize their electronic structures. Ionization, neutralization processes, and collective excitation are all direct probes of the structure. The reactivity of clusters is another tool for studying electronic structure. It gives insight into the molecular aspects, and offers the possibility of mimicing the situations encountered with surfaces. Reactive nucleation, i.e. nucleation in the presence of a reactive gas, is an especially simple way to investigate the electronic bonding inside the neutral compounds [1, 2]. As an example, we showed [2] that it is possible to follow the valence change of a rare-earth-metal atom in its oxide as cluster size increases. A divalent to trivalent behavior is found, attributed to the promotion of f electrons in the sd conduction band [2].

In this paper, we report on preliminary results involving nucleation from silver atoms in the presence of reactive gases, oxygen, and/or water.

Silver aggregates are s^1-valence electron-per-atom systems and show alkali atom cluster like behavior for the evolution of the ionization potential with the size [3, 4], well described in the jellium approximation. In contrast, collective excitation of valence electrons portrayed through the well-known plasmon-like resonance shows characteristics that differ from those observed with alkali-atom clusters. The resonance energy of silver clusters shifts down when the cluster size increases [5]. This has been interpreted as a reduction of the $s-d$ screening at the surface of the droplets [6]. *Ab initio* calculations performed for small silver species show that it is not possible to take over the electronic and structural properties obtained for alkali clusters [7]. This raises the question of what possible effects there are on the chemical properties of that species.

We have studied reactive nucleation from silver vapor in the presence of O_2 or H_2O molecules and compared the products with those obtained from sodium and potassium vapor under similar experimental conditions.

2 Experimental

The method of the experiment is the combination of reactive nucleation and photoionization mass spectrometry. Neutral silver (sodium)-atom clusters are produced in a gas aggregation source. About 10^{-2} mbar of metallic vapor effuses in 10–20 mbar of rare gas (He, Ar, or a mixture of both). Downstream from the oven nucleation takes place in a liquid-nitrogen-cooled region. Reactive nucleation is achieved by the mixing of a small amount (a few percent) of oxygen and/or water with the carrier gas. After passing through differential pumping chambers, the neutral cluster distribution is ionized by a pulsed Nd:YAG laser beam at a photon energy $h\nu = 3.50\,\text{eV}$. The warming of the clusters during ionization leads to a rapid sequential evaporation, and the net ion cluster distribution is shifted down against the initial neutral one. The corresponding mass spectrum emphasizes the relative stability of ionized species. Charged clusters are then accelerated and focused into a tandem time-of-flight spectrometer before impinging a microsphere plate detector. A retarding potential method enables us to study the relative stability of clusters through their unimolecular dissociation, which occurs during the propagation in the first time-of-flight spectrometer [8]. For this purpose an electrostatic mass gate selects

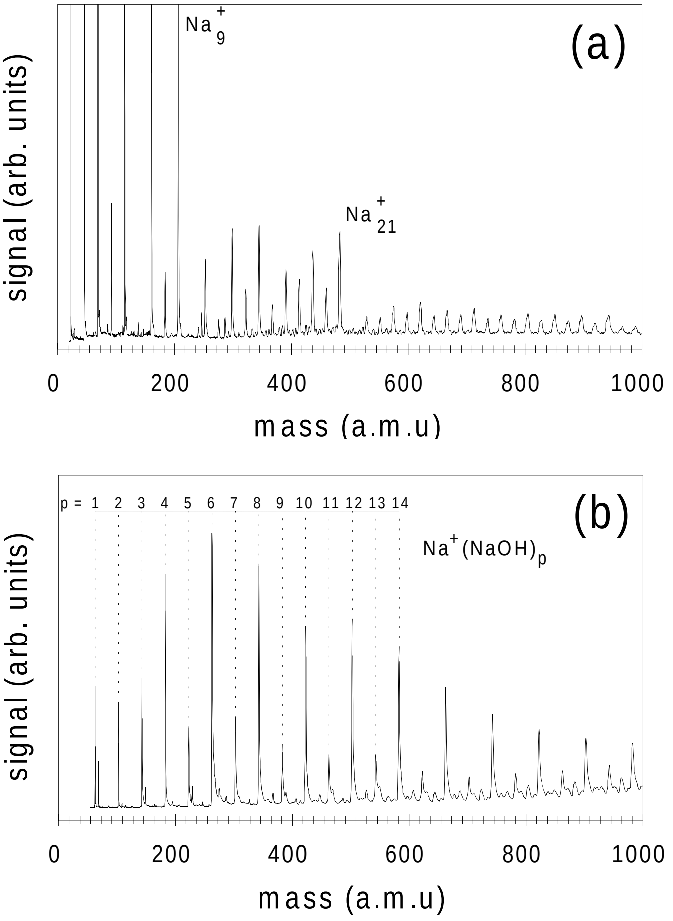

Fig. 1. Comparison of photoionization mass spectra of (a) pure sodium clusters with (b) these obtained under water-saturation conditions.

charged cluster parents in the first drift tube, according to their mass-to-charge ratio.

3 Results and discussion

3.1 Sodium vapor with O_2 molecules

The reactive nucleation of alkali-atom clusters with oxygen has been the subject of recent studies. The early work of Martin *et al.* [9] has shown that cesium vapor forms $Cs_{2p+n}O_p$ species having n delocalized 'metallic' electrons and a nonmetallic core $(Cs_2O)_p$. More recently, experiments performed with lithium atoms have shown the formation of metal-rich oxides $Li_n^+(Li_2O)_p$ at low oxygen concentration, whereas the stoichiometric series $Li^+(Li_2O)_p$ predominate under a saturation regime [10]. The metallic character of heterogeneous $Li_n^+(Li_2O)_p$ disappears when the size of the oxide core [11] is increased. It manifests itself through the vanishing of both odd–even alternation and shell effects in the relative intensities of mass spectra.

We have obtained similar results with sodium vapor. Oxygen-saturated clusters are $Na^+(Na_2O)_p$ species. The insulator building blocks Na_2O are highly stable units with a covalent bonding of 2.37 eV [12]. Neither shell effects nor odd–even alternations are present in mass spectra.

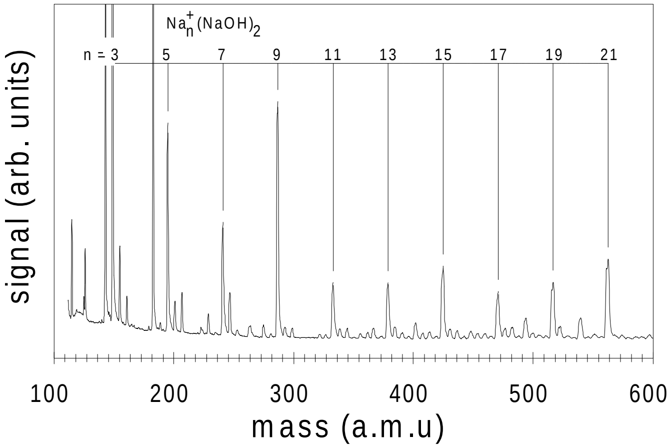

Fig. 2. Sodium-rich hydroxides $Na_n^+(NaOH)_2$ resulting from heterogeneous nucleation around $(NaOH)_2$. The survival of electronic shell effects is observed.

3.2 Sodium vapor with H_2O molecules

Alkali hydroxide clusters provide a good subject for another case study of compound stability. Strong ionic bonds may be formed between alkali ions and OH^- radicals. The $Cs-OH$ system has been investigated by Martin *et al.* [1], who found $[Cs_n(OH)_p]^+$ ($p \leq 6$) species with even-electron-numbered products as the most likely to occur. Similarly, in our experiment, metal-rich hydroxides are observed at very low water concentration. Mass spectra show odd–even alternation and shell effects; this suggests that heterogeneous clusters should be written as $Na_n^+(NaOH)_p$: shell effects occur for $n = 3$, 9, 21, etc., while odd-n species (for an even number of delocalized electrons) are predominant. Under water-saturation conditions, the stoichiometric series $Na^+(NaOH)_p$ predominates, with a markedly stronger stability for even-numbered p species. We have found similar results for potassium vapor mixed with water molecules. Figure 1 emphasizes two extreme situations: (a) the case of pure sodium clusters showing characteristic electronic shell effects and (b) the stoichiometric series obtained under water-saturation conditions.

Particular experimental conditions involving heterogeneous nucleation around $(NaOH)_2$ or $(KOH)_2$ allow us to observe only the series $Na_n^+(NaOH)_2$ (Fig. 2) or $K_n^+(KOH)_2$ in the mass spectra. Shell effects due to the metallic part are still strongly present. These results are not surprising, because of the known large dissociation energy for $(NaOH)_2$ and $(KOH)_2$ units 2.3 eV and 2.0 eV, respectively [14]. Such a nucleation was reported for $Na_n^+(Na_2O)_2$ clusters [13].

The multiphoton ionization at 3.50 eV generates warm clusters. They constitute an evaporative ensemble, and their temperature when they enter the time-of-flight mass spectrometer is determined by the time windows of the experiment [8]. We have studied the subsequent evaporative

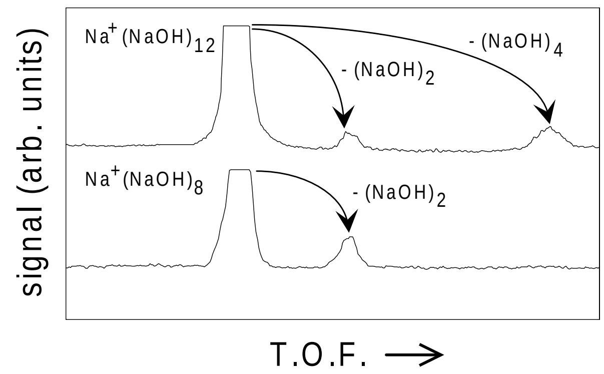

Fig. 3. Unimolecular dissociation spectra, observed for two sodium hydroxide clusters, $Na^+(NaOH)_p$, in the intermediate-size domain.

cooling, analyzing the unimolecular dissociation of some of the $Na^+(NaOH)_p$ clusters by using the retarding potential method. For $Na^+(NaOH)_4$ only one dissociation channel is present, corresponding to the evaporation of a neutral NaOH unit. Recent calculations performed in the frame of the functional density theory confirm that $Na^+(NaOH)_4$ dissociates via the evaporation of NaOH, the channel involving $(NaOH)_2$ evaporation lying 0.1 eV above the first one [15]. For $Na^+(NaOH)_8$, only the evaporation of $(NaOH)_2$ exists, whereas at larger sizes ($p = 12,15,16$), two competing channels are involved (Fig. 3).

$$\begin{tikzcd} & Na^+(NaOH)_{p-2} + (NaOH)_2 \\ Na^+(NaOH)_p \arrow[ur] \arrow[dr] & \\ & Na^+(NaOH)_{p-4} + (NaOH)_4 \end{tikzcd}$$

The fact that the bulk vapor contains essentially (NaOH) units [14] suggests that the monomer channel should prevail for the large sizes. It should be noticed that the results obtained by Buck *et al.* [16], for reactivity of *preformed sodium clusters* with water clusters leading to solvated sodium atoms $Na(H_2O)_n$, differ from those obtained here by *reactive nucleation*.

Alkali-halide clusters make for another good case study of ionic-bonded heterogeneous clusters [17–19]. The results appear different from those described here. For instance, the mass spectra of $Na^+(NaF)_p$ clusters exhibit more complex relative intensity sequences, related to structural properties of cube-like objects. Growing sequences involving Na_2F_2 and Na_3F_3 units are invoked [20].

3.3 Reactive nucleation of silver vapor

The behavior of silver vapor in the presence of oxygen and water molecules differs strongly from that of sodium vapor. With very pure oxygen at a moderate concentration, suboxides of metal-rich compounds are observed. They can be written as $Ag_n^+(Ag_2O)$ ($n \geq 1$), in agreement with shell effects observed for $n = 3$ and $n = 9$. Hydroxides are simultaneously present, indicating the strong reactivity of silver clusters with the water molecules present in the residual vacuum gas or as impurities in the oxygen gas. Indeed, any increase of the oxygen concentration promotes hydrated compounds instead of oxygen-saturated clusters.

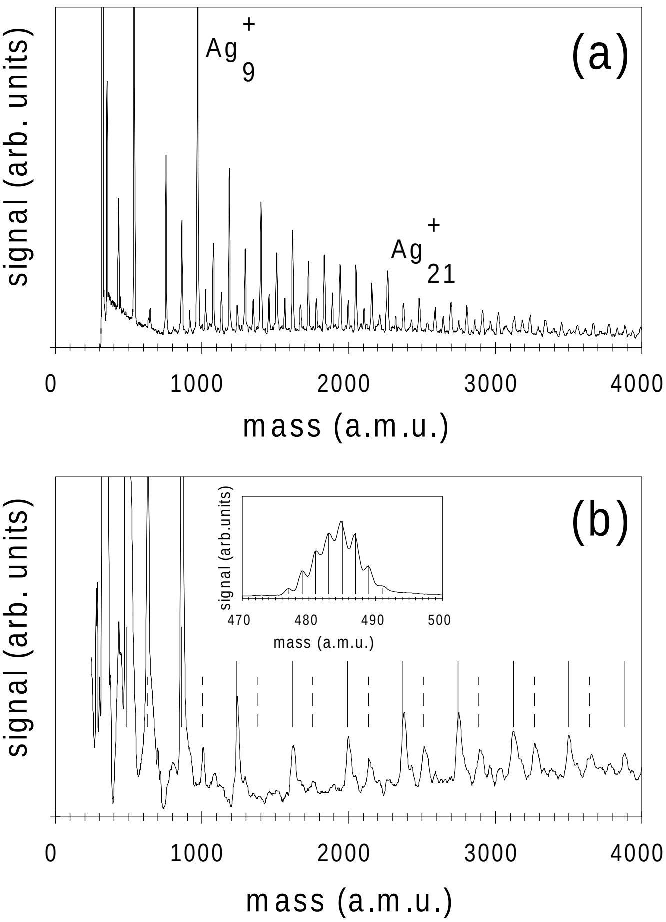

Fig. 4. Comparison of photoionization mass spectra of (a) pure silver clusters with (b) those obtained under water-saturation conditions in presence of oxygen. In the case of pure silver clusters, the intermediate ion peaks correspond to doubly charged species that are stable above the size $n = 17$. In the case of hydroxides, continuous vertical bars indicate the $(YX_n)^+$ series, and the dotted line indicates the $(ZX_n)^+$ series. The inset shows details of the Y^+ ion peak, the structure of which results from the silver isotopic composition and the presence of hydrated and hydroxided silver complexes.

Thus we performed systematic studies with H_2O. The most striking feature is that no reaction occurs when pure water vapor only is added. Reactive nucleation with H_2O requires the presence of oxygen. Then silver-oxygen-hydrogen compounds are efficiently generated, the relative abundances depending on the reactive gas concentration [21]. Under the water-saturation regime, mass spectra exhibit two main series labeled $(YX_n)^+$ and $(ZX_n)^+$, where Y^+ and Z^+ are the starting terms of the series (Fig. 4). They contain a sharp distribution of masses centered around 485 a.m.u. and 627 a.m.u. respectively. The quantity X determining the spacing of the sequences is measured as 377 ± 1 a.m.u. The limited mass resolution of our time-of-flight spectrometer does not allow us to distinguish between two successive a.m.u. at large or moderate n values. However at low values of n, our apparatus enables us to completely resolve the ion peak patterns (see Fig. 4b, inset). This lets us conclude that species contain an odd number of hydrogen atoms and that we must write

$$Y^+=(Ag_4O_3H_y)^+$$
$$Z^+=(Ag_5O_5H_z)^+$$

with $y = 1, 3, 5, 7$ and $z = 1, 3, 5, 7, 9$. In the same spirit, the X quantity must be identified as $Ag_3O_3H_y$. Note that the high-resolution spectra of small-size ion peaks allow us to rule out the presence of solvated silver clusters.

The task that remains to be addressed is a qualitative understanding of the presence of an excess of hydrogen atoms. The role and the structure of $(AgOH)_3$ units also can be considered through theoretical calculations. Preliminary results indicate a planar structure for $(AgOH)_3$ with a binding energy of 2.9 eV, much larger than the binding energies of $(AgOH)_2$ and $(AgOH)_4$ [15].

A comparison with the reactivity of solid surfaces should be fruitful. It has been shown that H_2O is physisorbed on a clean silver surface with a binding energy lower than 0.4 eV, whereas coadsorption of water on a Ag(110) surface with a fractional monolayer of oxygen strongly favors dissociative adsorption and OH formation [22]. Moreover, there are indications of a formation of $Ag_n(OH)_2(H_2O)$ $n = 2, 4$ [23]. It should be interesting to know if the same kind of complexes exist in a cluster, the structural symmetry of which differs from the translational symmetry of surface atoms.

4 Conclusion

These studies show that reactive nucleation from silver atoms and water drastically differs from that of alkali atoms and water, in which case an immediate chemical reaction leads only to hydroxide formation.

This opens up interesting questions. In the case of sodium or potassium compounds for each OH radical bound on the cluster, one valence electron is transferred from the metallic part to the hydroxyl radical. The fractional charge transfer in the case of silver compounds is different and not totally understood.

To some extent, reactive nucleation with clusters resembles that of the corresponding bulk material, despite the different structures of the two. The role of the adsorption site, and more generally, the interplay between geometrical and electronic structures, must be considered [24].

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