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Experimental determination of nucleation scaling law for small charged particles

Fabien Chiro, Pierre Labastie, Sébastien Zamith, and Jean-Marc L'Hermite
*Laboratoire Collisions Agrégats Réactivité, (UMR 5589 CNRS - Université Paul Sabatier Toulouse 3,
118 route de Narbonne, 31062 Toulouse Cedex 04 France*

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We investigated the nucleation process at the molecular level. Controlled sticking of individual atoms onto mass selected clusters over a wide mass range has been carried out for the first time. We measured the absolute unimolecular nucleation cross sections of cationic sodium clusters Na_n^+ in the range $n=25-200$ at several collision energies. The widely used hard sphere approximation clearly fails for small sizes: Not only vapor-to-liquid nucleation theories should be modified but also, through the microreversibility principle, cluster decay rate statistical models.

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The formation and growth of droplets, clusters and, more generally, very small particles is of considerable interest. Indeed these phenomena are essential for instance in clouds formation or crystal nucleation. The formation and growth of small particles can occur in different ways. The formation can for example start from a seed (heterogeneous nucleation), in the presence of a buffer gas or simply occur in a pure vapor (homogeneous nucleation). The growth is, for the smallest sizes, essentially governed by successive attachment of single units whereas for bigger sizes coalescence dominates. A huge amount of papers have been devoted to homogeneous nucleation, with the aim of getting a correct quantitative theory of the phenomenon. This aim has not been reached yet. A large majority of these theories originates from the so-called "Classical Nucleation Theory" (CNT), introduced by Becker and Döring [1]. It was originally developed for neutral droplets but can be applied without fundamental changes to ions (it is called in this case Classical Ion-Induced Nucleation Theory, or CIINT) [2, 3]. Ion-induced nucleation often predominates in nature because ions have a higher sticking cross section (SCS) than neutral particles. It has recently been demonstrated in the case of cirrus clouds condensation [4]. One crucial parameter in nucleation is the growth rate, which depends on the size, defined as the probability for a particle to grow by one unit per unit time. It depends on the atomic flux and the SCS [5, 6]. For large enough particles, the SCS is given to an excellent approximation by the hard sphere model. In the cluster size range however, *i.e.* for very small particles made of tenth to hundredth units, this approximation is likely to fail. Furthermore all nucleation theories based on CNT define a so-called critical size whose properties are crucial [5, 6, 7]. Unfortunately, in many systems (water [8, 9], metals [10], organic compounds [11, 12, 13]) the critical size lies in the cluster size range where the hard sphere approximation may not be relevant.

SCS's are also key parameters in the analysis of cluster decay rate. As a matter of fact, in statistical models based on the microreversibility principle (or detailed bal-

ance), the decay rate is proportional to the SCS [14, 15]. Cluster dissociation energies as deduced from their evaporation rates [16] are thus influenced by sticking cross sections.

The size dependence of the sticking cross-section has already been addressed theoretically (see *e.g.* [17, 18]). However, while many experiments have been devoted to the measurement of clusters evaporation rates [16], homogeneous SCS's of mass selected clusters have never been measured to our knowledge. We present here the first extensive measurement of clusters SCS's as a function of their size and collision energy. The experimental setup has been described in details elsewhere [19]. Sodium clusters are produced in a gas aggregation source. They are ionized by a hollow cathode discharge. They are then thermalized in a heat bath; their temperature T_i can be varied from 150 to 500 K. During cross sections measurement, $T_i \approx 150$ K in order to avoid evaporation at least until final products reach the detector. Wiley Mc-Laren type electrodes operate a first mass selection. Next, clusters enter an electrostatic device that reduces the kinetic energy spread of the mass selected clusters. It allows to decrease the kinetic energy to a few eV. Thermalized mass selected clusters then propagate slowly across a cell containing a sodium vapor ($\sim 10^{-4}$ mbar for $T=200$ °C). Finally, a second mass selection determines the new size distribution at the output of the cell.

Our raw data are the relative number of clusters which undergo a sticking I/I_0 . This quantity is measured as a function of the cluster size and kinetic energy. Assuming a Boltzmann velocity distribution for the atoms, the SCS σ_n is given by:

$$\sigma_n = -\frac{\ln I/I_0}{l\rho} \left\{ \operatorname{erf}(\sqrt{a}) + \frac{1}{2a} \operatorname{erf}(\sqrt{a}) + \frac{e^{-a}}{\sqrt{\pi a}} \right\} \quad (1)$$

with $a = E_k/(nk_B T)$ and l is the length of the cell, ρ the atomic density inside the cell, n the size of the incoming cluster, T the temperature of the vapor and erf is the error function. E_k is the kinetic energy of the cluster in the laboratory frame (in the following, kinetic energy refers to the energy in the laboratory frame and colli-

sion energy to the energy in the Center-of-mass frame). The density of atoms in the cell ρ is deduced from the cell temperature through the vapor pressure curve. We carefully measured the temperature at different positions in the cell in order to determine as accurately as possible the density of atoms from the lowest encountered temperature. The density of atoms in the cell remains nevertheless the main source of uncertainties. An error of 5 K on the cell temperature leads to a relative error of 25% on the determination of the cross section. These uncertainties can shift the curves collectively, but do not change the size dependence of the cross-section.

Note that under our experimental conditions evaporation is completely negligible. We checked for evaporation effects on a few sample masses: For Na_{110}^+ we varied T_i from 150 to 250 K and we did not see any evaporation effect. This is not surprising since the lifetime for the product Na_{111}^+ is still 450 ms at 250 K. For Na_{41}^+ we varied T_i from 150 to 200 K and found no change in the SCS: the lifetime for Na_{42}^+ is still 63 ms at 200 K. For Na_{55}^+ we varied T_i from 150 to 340 K and we did see a change in the SCS after a rather long plateau. Evaporation starts to affect the cross section at about 290 K. We find a lifetime of 300 μs for the product Na_{56}^+ at this temperature ($E_c=20$ eV) whereas the time of flight is about 130 μs . It is for sizes smaller than $n = 25$ at $E_k=20$ eV and $T_i=150$ K that the lifetime becomes comparable to the time of flight. We can thus safely exclude the effect of evaporation for the size range presented in our results.

Let us emphasize that contrary to previous experiments we work in the single collision regime with very well defined initial conditions (size, temperature and collision energy) and that we explored a wide range of sizes ($n = 25 - 200$). In the few studies where reaction cross section of mass selected particles are measured as a function of size or collision energy reactants underwent evaporation and/or the size range was quite small [20, 21, 22].

SCS's have been measured at two kinetic energies. Figure 1 presents our experimental results for $E_k=10$ eV and 20 eV. The most noticeable feature is that the two curves are different for small sizes and merge at $n = 80$. From this size on, they follow the geometrical scaling law in $n^{2/3}$ predicted by the hard sphere model (Figure 1): $\sigma_{geo} = \pi R^2 n^{2/3}$, with $R = 2.4$ Å (the Wigner-Seitz radius for sodium is 2.1 Å). For smaller sizes, the cross section departs from the hard sphere model. It drops below the geometric cross section for $E_k = 20$ eV whereas it increases for 10 eV. For sizes smaller than 80, the cross section depends on the collision kinetic energy: it decreases for increasing kinetic energy. Figure 1 also displays cross sections calculated in the frame of a Langevin model [20, 23]. The cluster-atom interaction is described by charge-induced dipole potentials. Two potentials are involved, corresponding respectively to $\text{Na}_n^+ + \text{Na}$ and $\text{Na}_n + \text{Na}^+$ (see Fig. 2). These two states are asymptotically separated by the ionization potential difference

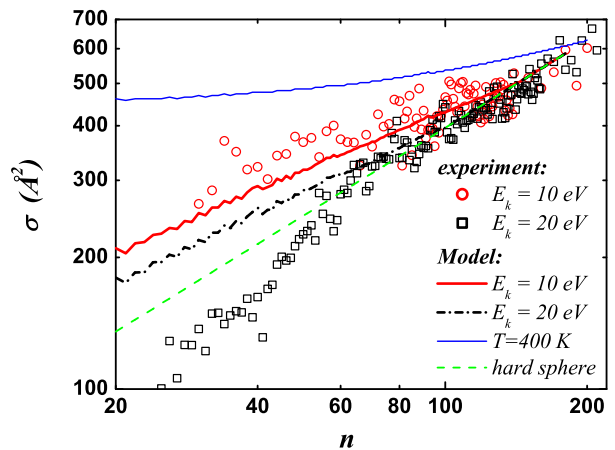


FIG. 1: Log-Log plot of the SCS as a function of cluster size at two kinetic energies. Experimental results are compared to a Langevin model and a hard sphere model. The calculated mean cross sections in a vapor at 400 K are also shown.

ΔIP between atom and cluster. In this frame, the sticking can be described as a harpooning mechanism: due to the much larger polarisability of the cluster compared to the atom, an electron transfer from the atom onto the cluster is energetically favored. The adiabatic potentials presented in Figure 2 are calculated using as a coupling the hopping integral in Na_2^+ [24]. From the Landau-Zener formula, the propagation is found to take place on the ground state potential curve. In the Langevin model, the largest reactive impact parameter b_{max} is reached when the maximum of the effective potential is equal to the collision energy. The cross-section is then given by $\sigma_n = \pi b_{max}^2$. It is taken as geometrical when the Langevin cross section becomes smaller than the geometrical one. This simple model gives satisfactory results for $E_k = 10$ eV. However, at $E_k = 20$ eV, calculated values disagree with the experiment: the model is unable to account for experimental cross sections being clearly below the geometrical ones. More elaborated models exist [25, 26, 27, 28, 29] but they would also give a cross-section larger than the geometrical one. Moreover we have a charge-induced dipole interaction whereas [25] deals with neutral particles and [26] consider molecules with permanent dipole.

One possible explanation for this behavior is the presence of non reactive excited states of the cluster. Indeed since the experiment is done at fixed kinetic energies in the laboratory frame, the collision energy E_c increases as the size n decreases: $E_c = \frac{E_k}{n+1} + \frac{3k_B T}{2} \frac{n}{n+1}$. Non reactive excited states that can be reached as the collision energy increases are likely to be responsible for the drop in the cross sections for small n . Preliminary calculations based on a two-center jellium model show the appearance of excited states corresponding to the first excitations of Na_n^+ . These excited states lay between the two curves shown in

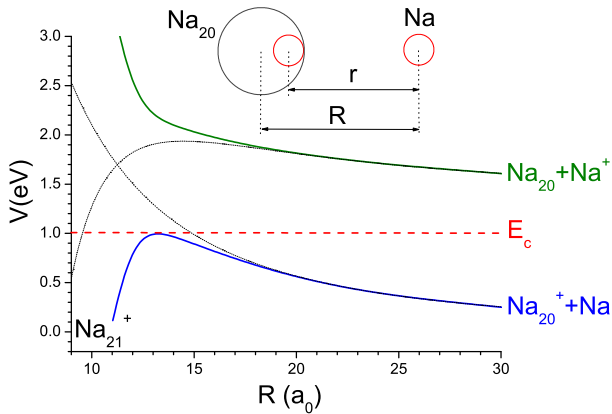


FIG. 2: Effective interaction potentials in the harpooning model in the case of the of $Na_{20}^+ + Na \rightarrow Na_{21}^+$ sticking reaction. Dotted lines: diabatic potentials. Solid lines: adiabatic potentials. The coupling is taken as the hopping integral in Na_{21}^+ at the distance r . The impact parameter is equal here to its critical value b_{max} (see text).

Figure 2 and might be responsible for quenching towards non-reactive channels [24]. Our model thus applies only at low collision energy. Practically however, nucleation and evaporation processes involve thermal range collision energies which can be considered as small in the sense defined here. Let us now examine in more details the size dependance of σ_n . First note that there are no strong structures. We introduced in our model the experimental values for the IP [30] and for the polarisabilities [31, 32]. Although these values exhibit the well known variations due to electronic shells closure [33], no magic numbers clearly appear in the cross sections. This is consistent with the unstructured mass spectra observed when clusters are produced at low temperature [34, 35].

The monotonic component does not follow a geometrical scaling law in $n^{2/3}$. Actually, this behavior is not really surprising. It has been experimentally observed in heterogeneous sticking reactions of small mass selected clusters [21]. The effect on homogeneous cluster growth of a discrepancy from the hard sphere approximation had already been theoretically suggested in the case of neutral particles interacting through a Van-Der-Waals interaction [17]. In this case, σ_n scales as $n^{1/3}$. Surprisingly, this kind of effect had never been analyzed nor *a fortiori* experimentally demonstrated in the case of charged clusters. This non geometrical sticking law has consequences for instance on clusters decay rates and kinetic energy release distributions (KERD) which are generally analyzed in the frame of statistical physics models [16]. Most of the models used today are based on the microreversibility (or detailed balance) principle, whose basic assumption is summarized by the following relation [15, 16]:

$$\frac{\gamma_n(E_n, \varepsilon)}{\beta_{n-1}(\varepsilon)} = -\frac{\Omega_{n-1}(E_n - D_n - \varepsilon) \times \Omega_{atom}(\varepsilon)}{\Omega_n(E_n)} \quad (2)$$

where γ_n is the cluster decay rate, β_{n-1} the sticking rate, E_n the internal energy, D_n the dissociation energy and ε the kinetic energy of the evaporated atom. Ω_n , Ω_{atom} and Ω_{n-1} are the densities of state respectively of the parent cluster, the evaporated atom and the product cluster. β_{n-1} is related to the sticking cross section by the relation $\beta_{n-1} = \sigma_{n-1}\rho v$, where ρ is the volumic density of atoms and v the atom velocity. The point we lay the stress on here is that in this microreversible approach the decay rate γ_n or the KERD [28, 29] are directly related to the sticking cross section σ_{n-1} .

Dissociation energies are deduced from decay times τ_n at cluster temperature T through approximations of relation 2 that can be written to a good accuracy as

$$\tau_n^{-1} = \sigma_{n-1} A_n \exp(-D_n/(k_B T)) \quad (3)$$

A_n is a prefactor independent of σ_n whose exact expression depends on the model. Dissociation energies are deduced from τ_n by inverting relation 3. For sodium clusters, the experimental temperature must be of the order of 400K in order to observe dissociation in the typical accessible time range [35, 36]. At this temperature, the cross section becomes geometrical at about $n \approx 200$ as deduced from our model (see fig. 1). One can estimate the order of magnitude of the error made by using a geometrical sticking cross section σ_{geo} . Replacing σ_{geo} by our estimated value at 400K (see fig. 1) leads to $\Delta D = \pm 4\%$. This error is at least similar to experimental uncertainty and should be corrected in future experiments on sodium. Unfortunately, a general form of the correction cannot be inferred here since it is strongly system-dependent, essentially through the energy shift and the coupling between the two (or more) electronic states involved.

Nucleation in the frame of the CNT also depends in principle on the SCS scaling law. Nucleation theories aim to estimate the nucleation rate J_i defined as the number of droplets of size i created from gas phase per unit time and volume. Although a number of different versions have been developed since the work of Becker and Döring, the basic assumptions remains the same [5, 6]. CNT is derived from the population equations:

$$\frac{\partial n_i}{\partial t} = \beta_{i-1} n_{i-1} - \gamma_i n_i - \beta_i n_i + \gamma_{i+1} n_{i+1} = J_{i-1} - J_i \quad (4)$$

where β and γ are respectively growth and decay rates. The CNT considers the steady state solution such as the flux J is constant for all i . This solution J_M is valid in a medium time range. Growth at very short delays will briefly be examined later. For very large delay, the nucleation phenomenon is qualitatively different, notably involving coalescence. Moreover, gas depletion prevents particles from growing indefinitely. All CNT-based theories arrive at an essentially common expression [5, 6, 37]:

$$J_M = K \beta_{i^*} \exp(-\Delta G(i^*)/(k_B T)) \quad (5)$$

where k_B is the Boltzmann constant, T the temperature, $\Delta G(i^*)$ the formation free energy of the critical cluster of size i^* . The critical size i^* is defined by $\frac{\partial \Delta G}{\partial i}|_{i^*} = 0$, which is equivalent to $\frac{\beta_{i^*}}{\gamma_{i^*+1}} = 1$ [6]. The prefactor K does not depend on the cross section. K includes the so-called Zeldovich factor [38] which does not depend on the sticking scaling law provided that it is a smooth function of the size [5, 6]. Relation 2, thus the microreversibility principle, makes i^* independent of the SCS scaling law. This had already been pointed out by Vasil'ev and Reiss [39]. Finally, the nucleation rate in the constant flux regime is modified only linearly through β_{i^*} . In CNT, β_{i^*} is always calculated under the assumption of hard sphere collisions. In CIINT, however, many authors consider that the stronger interaction between charged clusters and atoms leads to an enhancement of β_{i^*} . They introduce a so-called Enhancement Factor (EF)[3, 39]. If the vapor molecule has no permanent dipole, EF is generally considered as negligible, as far as clusters bear a single charge [40]. However, when evaluating EF, only the interaction between the charged cluster and the neutral particle is considered. It is demonstrated here that, at least in the case of sodium, the harpooning mechanism strongly modify the SCS's. An example of EF(n) at 400 K is readily deduced from fig.1: it is the ratio $\sigma_{400 K} / \sigma_{geo}$. EF depends on the system, the temperature, the coupling between the electronic states. So we cannot derive any general rule for estimating EF. Nevertheless, we have shown that more attention should be paid to this factor.

Let us focus now briefly on short times. There is a so-called lag time t_L that characterizes the time spent before the steady state is reached. The nucleation rate J follows approximately the law $J(t) \approx J_M(1 - \exp(-B\beta_{i^*}t))$, where the prefactor B do not depend on the SCS [41]. Here the change could be more significant; however, the effect on the steady-state nucleation rates is not significant since the lag time by itself is very short in vapor-to-liquid transformations [41]. Far from equilibrium phenomena may therefore be more influenced by a change in the sticking scaling law. Cluster nucleation in a supersonic expansion is an example of such phenomena. As mentioned above, Vigué *et al* already studied the case of neutral clusters [17]. The final average cluster size n_f can be represented by empirical scaling laws of the type $n_f \approx \Gamma^{\frac{1}{1-\alpha}}$ for a sticking law in n^α . The scaling parameter Γ introduced by Hagen only depends on the geometry, the pressure and the temperature in the source [42]. The example calculated at thermal energy on figure 1 shows that α can be close to 0. The change in n_f is obviously not negligible.

In summary, absolute SCS of mass selected sodium clusters have been measured for the first time. The non geometrical sticking law that depends on the collision energy is shown to influence not only nucleation but also

cluster evaporation measurement results.

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