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Homogeneous and heterogeneous clustering in the accretion regime

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Abstract. Condensation of nano-droplets in a supersaturating vapor decomposes in two steps: the formation of a nucleation center, also called critical nuclei or nucleation seed, and the growth sequence, by accretion of further atoms on the nucleation center. These two steps have been investigated separately through the clustering of homogeneous particles Na_n and heterogeneous particles Na_nX in a helium buffer gas ($X = (Na_2O)_2$ or $(NaOH)_2$). The growth sequence is analyzed with preformed molecules X injected in a supersaturating sodium vapor and driving production of Na_nX clusters. Cluster distribution mean sizes are controlled by sodium concentration and by the condensation cell effective length. The signal intensities observed for homogeneous and heterogeneous clusters are proportional to the homogeneous and heterogeneous nucleation center numbers respectively. We can measure the efficiency for the homogeneous nucleation center production versus sodium concentration. This process is the onset of the condensation phase transition.

PACS. 36.40.-c Atomic and molecular clusters – 36.40.Jn Reactivity of clusters – 36.40.Sx Diffusion and dynamics of clusters

1 Introduction

Nucleation is the process initiating the formation of new phases and is thus a general phenomenon in nature and industrial processes. Among numerous of examples, one may mention the influence of sirocco on the clouds, where a sand grain coated with sulfate is responsible for initiating the condensation of water molecules and then leading to rain [1]. The fundamental concepts of nucleation are taught in such diverse fields as thermodynamics, physical chemistry, solid state physics, surface science, atmospheric physics, and geophysics. Condensation phase transitions have been studied for many years, mostly theoretically [2–9]. A renewed interest has grown recently in the nanoscale domain, where the onset of nucleation leads to the building of clusters, a new phase of materials properties of which are quite specific and differ from those of the vapor phase and from those of the corresponding bulk phase [10,11]. The basic processes in condensation phase transition could be cluster-cluster aggregation (coalescence), coarsening or also nucleation and cluster growth by atomic accretion [12,13]. The last process, nucleation and growth, can be studied experimentally via free atomic clusters in a condensation cell [14]. Most research on nucleation relate to homogeneous process, for sake of simplicity. However, studying heterogeneous nucleation, which takes place in numerous phase transitions, can improve our knowledge on that process, by driving independently seeds production (nucleation) and accretion of atoms (growth).

In this paper, we will focus on the early steps of seeds formation for homogeneous and heterogeneous processes. This experiment is based on the use of a gas aggregation source, followed by a time-of-flight mass spectrometer. Seeding a vapor of sodium with oxygen (or water) molecules leads to the formation of heterogeneous clusters and one can observe homogeneous and heterogeneous aggregate size distributions on the same mass spectrum. This demonstrates the coexistence of two distinct nucleation centers for cluster growth. To go further, we show influence of experimental parameters on the distribution patterns, by varying either impurities injection or sodium vapor pressure in the source.

2 Experimental

The technique used in this investigation is time-of-flight (T.O.F.) photoionization mass spectrometry. The experimental apparatus has been fully described elsewhere [15]. Basically, sodium is evaporated from a stainless steel crucible that is resistively heated and the sodium vapor effuses into helium buffer gas at 15 mbar pressure. The oven is placed in the condensation cell (see Fig. 1) in front of a copper pipe cooled by a liquid nitrogen flow. Clusters are

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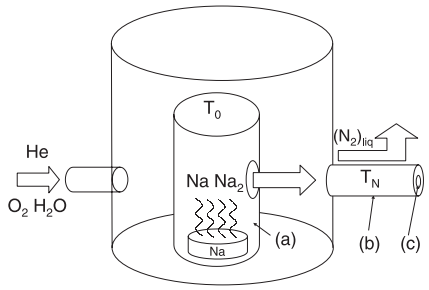

Fig. 1. Experimental source for cluster formation; (a) oven; (b) copper pipe, cooling area; (c) nozzle.

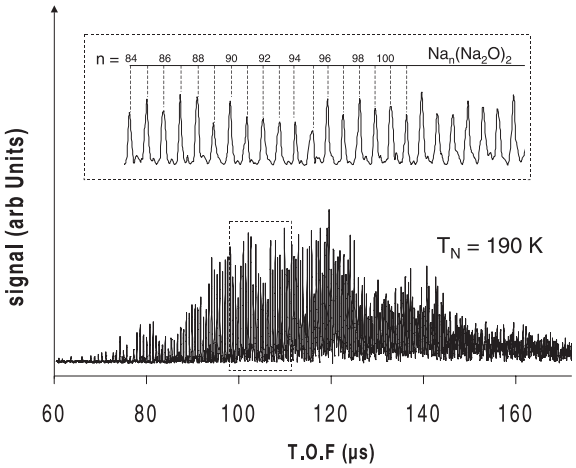

Fig. 2. Low laser fluence mass spectrum when 0.5% of O_2 is added in the cooling helium gas entering the condensation cell, driving formation of $Na_n(Na_2O)_2$ species. With $T_N = 190$ K, no Na_n signal is observed without O_2 injection.

carried by the helium gas stream through the nozzle and cross differential pumping chambers. The residence time of clusters in the source is typically in the millisecond range. They are then photoionized in a high vacuum chamber with unfocused 10 ns, 350 nm, XeF excimer laser pulses. The 3.50 eV photon energy allows single photon ionization for Na_n clusters of more than 20 atoms [11], and a two photons ionization for smaller ones. The photo-ionization laser fluence is kept low in order to avoid fragmentation and so as to observe a cluster size distribution mean value independent on the laser power. In that case, the interaction with the laser produces a single photon ionization and very little fragmentation: the ion mass distribution observed by mass spectrometry corresponds approximately to that of the neutral clusters produced in the source [16]. The ionized clusters are then accelerated into a linear T.O.F. mass spectrometer thanks to a Willey-Mc Laren accelerating system with a kinetic energy of 8.5 keV. At the end of a 2.4 m drift tube, the particles are post-accelerated at 11 keV and detected on microchannel plates.

Let us focus on the specific source region where nucleation and growth of clusters take place. Experiments were conducted with a constant helium flow, where an adjustable quantity of oxygen (or water) could be added. Oven temperature was set between $T_O = 650$ K and $T_O = 680$ K. In this range of temperature, the ratio between dimer and monomer vapor pressures is typically 0.05 [17]. The copper pipe temperature can be set at either $T_N = 190$ K or $T_N = 130$ K, according to the liquid nitrogen flow. Homogeneous clusters are produced by quenching the supersaturated sodium vapor in the cooled helium gas. The experimental conditions allowing homogeneous clustering in our setup (15 mbar He, $T_O = 650$–680 K and $T_N = 130$ K) will be called "standard conditions". Heterogeneous clusters are observed when O_2 (or H_2O) molecules are added to the buffer gas and injected in the condensation cell [18].

3 Results and discussion

3.1 Homogeneous and heterogeneous centers of nucleation

Under "standard conditions", homogeneous Na_n particles are observed. By increasing nozzle temperature from $T_N = 130$ to 190 K, no clusters are detected: homogeneous Na_n formation is no longer allowed. When adding in those conditions traces of oxygen in the sodium vapor (0.5% typically), $Na_n(Na_2O)_2$ clusters are observed in the mass spectra (Fig. 2). It is worth noting that, as homogeneous Na_n clusters are not formed, heterogeneous $Na_n(Na_2O)_2$ clustering cannot come from a reaction between oxygen molecules and preformed Na_n clusters. Measurements are interpreted as follows: a chemical reaction between O_2 and Na or Na_2 produces stable $(Na_2O)_2$ molecules (dissociation energy 0.83 eV [19]) which diffuse in the sodium vapor. They constitute centers of nucleation (also called seeds or germs) for $Na_n(Na_2O)_2$ clustering with an accretion mechanism. In the case of water injection (almost 0.5%), the process is similar: only $Na_n(NaOH)_2$ clusters are observed in the mass spectra in conditions where Na_n clusters cannot be formed. This result is interpreted as accretion of sodium atoms on $(NaOH)_2$ centers of nucleation. *To conclude, our experiment is equivalent to inject preformed $(Na_2O)_2$ or $(NaOH)_2$ seeds in a supersaturating sodium vapor.*

From heterogeneous clustering experiments, we observe that the presence of a seed is essential for initiating growth. Homogeneous clustering should follow the same scheme. We showed in [18] that nucleation of small particles Na_{n^*} ($n^* = 4$) constitutes a bottleneck in the growth sequence leading to larger Na_n clusters. In the following, Na_{n^*} will be called the homogeneous nucleation center. Once homogeneous nucleation centers have been formed by passing over the bottleneck, further growth is thermodynamically favorable and larger Na_n particles can be produced. Keeping a constant sodium concentration, it was observed to be the case for $T_N = 130$ K but not for $T_N = 190$ K. This emphasizes the crucial role of the buffer gas temperature in the nucleation process. We also deduce that homogeneous seeds in our source are formed in the cold part of the condensation cell (copper pipe, see Fig. 1).

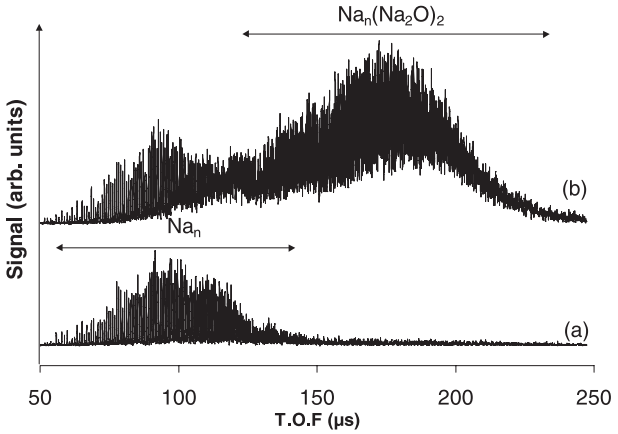

Fig. 3. Low laser fluence mass spectra, without oxygen (a), with 0.5% of oxygen in the helium cooling gas (b). The vertical scale is the same for traces (a) and (b).

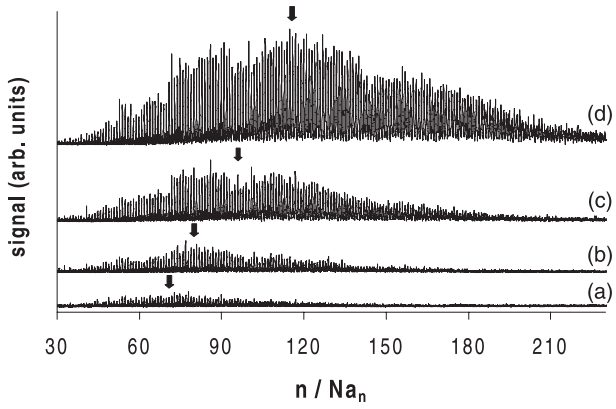

Fig. 4. Homogeneous cluster mass distribution, for increasing sodium concentration in the condensation cell (low laser fluence, copper pipe temperature $T_N = 130$ K). Traces correspond to T_O set between 660 K (trace (a)) and 680 K (trace (d)). The vertical scale is the same for traces (a)-(d).

3.2 Nucleation and growth processes

Once the role of heterogeneous and homogeneous seeds identified, we can focus on the behavior of the resulting cluster mass distributions under various experimental conditions with T_N maintained at 130 K. Under 'standard conditions', mass spectrum exhibits a distribution of homogeneous clusters Na_n as shown in trace (a) Figure 3. We note $S_o = \sum I_n$ the integrated signal of homogeneous clusters where I_n is the signal measured for Na_n particles, proportional to the number of clusters. The mean size is given by $\langle n_o \rangle = \sum nI_n/S_o$. In Figure 3a, the mean number of atoms of the mass distribution is $\langle n_o \rangle = 100 \pm 10$ atoms. When typically 0.5% of oxygen is injected in the helium buffer gas, a new distribution of clusters appears (Fig. 3b) and is explicitly identified as $Na_n(Na_2O)_2$ species. The integrated signal for heterogeneous clusters is noted S_e. When a similar quantity of water is injected in the source, we observe $Na_n(NaOH)_2$ species. The mean number of atoms for those heterogeneous distributions is approximately $\langle n_e \rangle = 230 \pm 20$ in both cases (with the same $\langle n_o \rangle$). It can be seen in Figure 3 that the emerging heterogeneous cluster distribution does not affect the homogeneous one: S_o remains constant. This highlights two points. First, it confirms that heterogeneous particles do not result from a reaction of O_2 or H_2O molecules on preformed Na_n clusters. Heterogeneous species are then necessarily obtained by atoms accretion on additional centers of nucleation, $(Na_2O)_2$ or $(NaOH)_2$ in those experiments. Second, it indicates that the number of homogeneous and heterogeneous germs is negligible compared to that of Na and Na_2 particles in the gas phase.

3.3 Heterogeneous clustering

The T.O.F. mass analysis demonstrates that the heterogeneous particles formed in the source contain only one $(Na_2O)_2$ or $(NaOH)_2$ seed. Then, the integrated signal S_e, proportional to the particle number, is also proportional to the number of seeds. With a constant sodium concentration in the source, the quantity of impurities injected (oxygen or water) is varied over one order of magnitude, keeping a "weak injection regime" where only one seed per cluster is observed. First, the mean size of heterogeneous clusters distribution remains unchanged while increasing impurities injection in the source: the number of atoms stuck on the heterogeneous germ remains the same. Second, the signal ion peak of heterogeneous distribution increases as impurities injection. *Therefore the impurity concentration drives the number of heterogeneous seeds but does not affect the growth mechanism (accretion of atoms).* It is worth noting that, while increasing impurity concentration in the buffer gas above 5%, Na_mX_n clusters are observed (X = $(NaOH)_2$ or $(Na_2O)_2$ for water or oxygen injection respectively) in the mass spectrum, with m and $n > 1$. In such a case, heterogeneous X seeds are no longer diluted in the source and sticking between germs or clusters becomes possible.

3.4 Homogeneous clustering

The analysis of homogeneous clustering is more complex: the germ cannot be discriminated from species sticking on it, nucleation and growth are no longer controlled independently in the source. Homogeneous distribution is observed with increasing sodium concentration (Fig. 4). This parameter is controlled by setting the oven temperature between $T_O = 650$ and 680 K. We deduce from the corresponding vapor pressure a sodium density [Na] variation from 2.8×10^{21} to 6.1×10^{21} atoms/m^3 in the oven. The arrows in Figure 4 traces (a)-(d) point the corresponding mean sizes $\langle n_o \rangle$. As a result, it is observed that $\langle n_o \rangle$ doubles when [Na] varies by a factor of two. A similar result was observed for $\langle n_o \rangle$ and $\langle n_e \rangle$ on mass spectra with Na_n and $Na_n(NaOH)_2$ species [18] or on mass spectra with Na_n and $Na_n(Na_2O)_2$ aggregates. *In those experimental conditions, the condensation cell produces homogeneous and heterogeneous cluster mass distributions the mean sizes of*

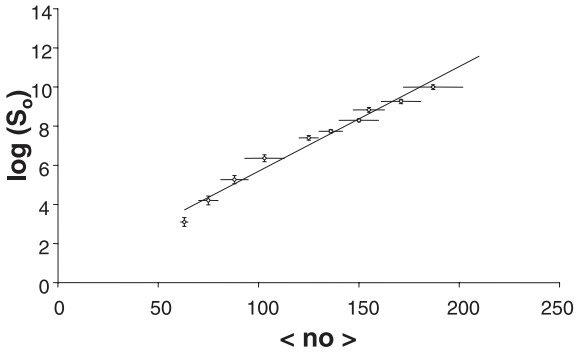

Fig. 5. Logarithmic plot of the homogeneous cluster integrated signal versus mass distribution mean size. S_o and $\langle n_o \rangle$ are measured from Na_n mass spectra observed with oven temperatures set between $T_O = 650$ and 680 K.

which vary proportionally to the sodium vapor concentration.

We showed that heterogeneous clusters are formed by accretion of sodium atoms on $(Na_2O)_2$ seeds. As growth process appears to evolve similarly with [Na] for homogeneous and heterogeneous clustering, we deduce that in those experimental conditions each Na_n cluster grows by accretion of atoms on a single initial homogeneous seed.

We come back now to the results presented in Figure 3. $\langle n_e \rangle$ is observed to be larger than $\langle n_o \rangle$, which seems contradictory to an identical accretion process for heterogeneous and homogeneous clustering. Heterogeneous seeds are formed as soon as impurities react with sodium, near the oven. Homogeneous nucleation centers are formed in the cold part of the condensation cell (Fig. 1, position b). The difference between their effective diffusion lengths in the sodium vapor gives the main contribution to the interpretation of $\langle n_o \rangle$ and $\langle n_e \rangle$ relative values [18].

Finally, we discuss the evolution of homogeneous integrated signal S_o with sodium concentration. We have plotted on a diagram log S_o versus $\langle n_o \rangle$ and found a linear variation (Fig. 5). As justified above, experimental conditions correspond to an accretion regime where S_o is proportional to the number of homogeneous seeds Na_{n^*} formed in the condensation cell and consequently to the seed formation rate. We checked experimentally that in this oven temperature range $\langle n_o \rangle$ varies proportionally to the sodium concentration. It is deduced from Figure 5 that homogeneous seed formation rate varies exponentially with the vapor concentration.

The results obtained either on nucleation or on growth have to be compared to the predictions of the Classical Nucleation Theory (C.N.T.) developed assuming thermal equilibrium [4,5]. Large Na_n and Na_nX particles are expected to have very similar thermodynamical properties. Consequently, a thermal equilibrium between the condensed droplets and the vapor should lead in both cases to the same mass distribution. With $\langle n_e \rangle$ significantly larger than $\langle n_o \rangle$, the clustering in the condensation cell is obviously not limited by thermal equilibrium. Therefore a direct comparison with C.N.T. is not possible.

4 Conclusion

We characterized in this paper a gas phase clustering mechanism based on accretion of sodium atoms on a single initial germ. The growth sequence is not limited by thermal equilibrium and the number of atoms stuck on the germ increases proportionally to sodium concentration [Na]. The heterogeneous nucleation is controlled by injection of impurities (O_2 or H_2O) in the source whereas the homogeneous seed formation rate varies exponentially with the sodium vapor concentration.

References

1. Z. Levin, E. Ganor, V. Gladstein, J. Appl. Meteorology **35**, 1511 (1996)
2. M.V. Schmoluchowski, Z. Phys. **17**, 585 (1916)
3. J. Frenkel, Z. Phys **26**, 117 (1924)
4. R. Becker, W. Döring, Ann. Phys. **24**, 719 (1935)
5. T.A. Ring, Adv. Coll. Interf. Sci. **91**, 473 (2001)
6. D.W. Oxtoby, Acc. Chem. Res. **31**, 91 (1998)
7. J.S. Bhatt, I.J. Ford, J. Chem. Phys. **118**, 3166 (2003)
8. J.A.D. Wattis, C.D. Bolton, P.V. Coveney, J. Phys. A **37**, 2895 (2004)
9. D.B. Duncan, A.R. Soheili, Appl. Num. Math. **37**, 1 (2001)
10. M. Brack, Rev. Mod. Phys. **65**, 677 (1993)
11. W.A. de Herr, Rev. Mod. Phys. **65**, 611 (1993)
12. J.M. Soler, N. García, O. Echt, K. Sattler, E. Recknagel, Phys. Rev. Lett. **49**, 1857 (1982)
13. J. Yang, B.J. Mc Coy, G. Madras, J. Chem. Phys. **124**, 024713 (2006)
14. C. Bobbert, C.P. Schulz, Eur. Phys. J. D **16**, 95 (2001)
15. C. Bréchignac, Ph. Cahuzac, J.Ph. Roux, D. Pavolini, F. Spiegelmann, J. Chem. Phys. **87**, 5694 (1987)
16. C. Bréchignac, Ph. Cahuzac, J.Ph. Roux, J. Chem. Phys. **87**, 229 (1987)
17. *Thermochemical properties of inorganic substances*, edited by O. Knacke, O. Kubaschewski, K. Hesselmann, 2nd edn. (Springer Verlag, 1991)
18. P. Feiden, J. Leygnier, Ph. Cahuzac, C. Bréchignac, Chem. Phys. Lett. **432**, 230 (2006)
19. A. Goerke, G. Leipelt, H. Palm, C.P. Schulz, I.V. Hertel, Z. Phys. D **32**, 311 (1995)