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A simple method to determine the mean cluster size in a molecular beam

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Abstract. A method based upon the tandem use of the Time-Of-Flight and Surface-Induced-Dissociation techniques is proposed for estimating the average cluster size in a neutral molecular beam. It consists of sending the beam through a buffer gas and measuring the variations of the average beam velocity as a function of the buffer gas pressure. The clusters are detected at the mass of the monomer by surface induced dissociation in the ionization source. This method has been applied to an argon cluster beam and the results are in good agreement with determinations using high energy electron diffraction. This technique appears to be a simple alternative for estimating mean cluster sizes in the range of 100 to a few 1000 monomers.

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1. Introduction

There is a great deal of interest in the reactions of atoms or molecules with neutral clusters as these reactions can be a model of a transition from the gas phase to the condensed phase. In our group, we have already obtained results for the chemiluminescent reactions of barium with oxydizers by comparing the reactions with monomers to the reactions with large van der Waals clusters of N_2O, CO_2, or H_2O ($n \gg 50$) [1, 2]. In order to obtain more detailed information about these reactions, it is essential to be able to characterize the size of the neutral clusters present in the beam.

Because of the weak bonding of these van der Waals clusters, their characterization is not easy. Two methods have essentially been used: time-of-flight mass spectrometry (TOF/MS) and electron diffraction. These methods together with their drawbacks have been recently reviewed by Kappes and Leutwyler [3]. Concerning the TOF/MS technique, there are advantages like sensitivity or mass resolution. However, the distributions obtained by this method can be severely distorted with respect to the distribution of neutral clusters in the beam because of the extensive fragmentation of the clusters upon ionization. This effect does not exist in the high-energy electron beam diffraction technique and the main interest of this technique is its direct applicability to a neutral cluster beam. However, the interpretation of diffraction patterns in order to obtain information about the size of the clusters is not simple.

The purpose of the present article is to present a simple alternative method to characterize a neutral cluster beam. This method does not allow to obtain the full mass distribution of the beam but it provides an estimate of the average size of a neutral cluster beam which in itself already is important. The idea of this method is to pass the cluster beam through a chamber containing a buffer gas and to measure the variations of the average velocity of the beam remaining behind this chamber as a function of the buffer gas pressure. With a simple model of the collision of an atom with a van der Waals cluster, it is shown in the present work that this variation is linked to the average cluster size and allows an estimate of this size. In the following, we first will present results of a simulation of collisions of rare gas atoms with argon clusters to set up the basis of the collision model. Then, the experiment will be described. Finally the results obtained with Ar cluster beams will be given and discussed in terms of average cluster size.

2. Collision dynamics of an atom with a large cluster

Because a van der Waals cluster is made of many monomers bound by weak forces, the dynamics of a collision of an atom with such a cluster are very different from those of a collision with an atom having the same mass and size as the cluster. To obtain an impression of such a collision, a molecular dynamic calculation has been performed.

Molecular dynamic calculations have been extensively used to find structures of van der Waals clusters [4, 5, 6].

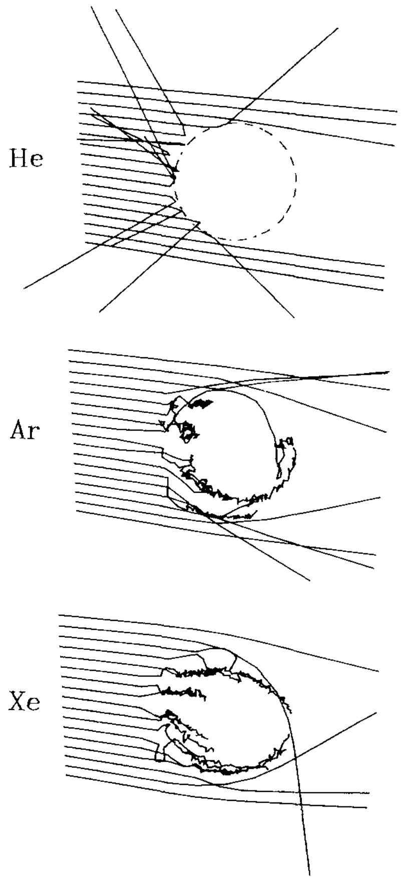

Fig. 1. Plots of trajectories of incident atoms colliding with an Ar_{125} cluster. The results are given for several impact parameters and with three different atomic projectiles He, Ar, and Xe. In the upper plot, the cluster has been drawn as a sphere. It has the same size in the other two plots but, for clarity, it is not shown. The simulation was performed for a cluster temperature of 30 K and a constant relative collision energy of 0.2 eV. For He and for an impact parameter small enough to collide with the cluster, the atom is scattered away with about 30% of collision energy transferred to the cluster, while for Ar or Xe, the atom is captured by the cluster with all the collision energy transferred into internal energy

Recently, they were applied to the interpretation of the solvation behavior of an impurity inside a cluster [7]. Our calculation considers the collision of a rare gas atom (He, Ar, or Xe) with an argon cluster ($n=125$). This calculation uses the Verlet's finite step integration algorithm to solve the classical equations of motion of the atoms [8]. The interaction between the atoms was approximated by pairwise Lennard-Jones 6–12 potentials [9]. The program was used in two steps. In the first, a 125 atoms argon cluster was generated at a chosen temperature by a classical relaxation method [4]. Once the cluster was formed, the same program was used to follow a collision of this cluster with an atom whose initial velocity and impact parameter can be varied. The details of the calculation will be given in a forthcoming paper [10].

We have chosen typical experimental conditions in the calculation, that is, 30 K internal cluster temperature [11] and a relative velocity Ar–$(Ar)_{125}$ of 1 km/s. In order to compare the various atoms (He, Ar, Xe) as projectiles, the same initial relative energy of 0.2 eV has been used. The results of the calculation for a few trajectories are displayed in Fig. 1. As can be seen in this figure, the behavior of He is completely different from that of the two heavier atoms, Ar and Xe. The He atom is scattered even at small impact parameters and the relative kinetic energy decreases by about 30%. On the other hand, except for the largest impact parameters, the heavier atoms stick to the cluster with all the relative collision energy transferred into internal cluster vibration.

The analysis of the results shows that, for helium, the combination of the small mass of He compared to Ar and of the weak Ar–He bonding does not allow good energy transfer to the cluster and the remaining kinetic energy of the atom is sufficient to overcome the He-cluster well. On the other hand, for Ar and Xe, there is good energy exchange and, because of the stronger interaction with the cluster, the incident atom remains trapped in the well. Because of the relatively low temperature of the cluster, all the collision energy is efficiently spread over the internal degrees of freedom of the cluster and no significant evaporation of the cluster is observed in the time window of the simulation (1 ps). A more complete study of the effect of the various parameters is under progress [10].

3. Principle of the experiment

The experiment consists of sending a cluster beam into a chamber containing a buffer gas. From the simulation, we have shown that the collision of an argon cluster with an argon atom results in a trapping of the atom in the cluster. The conservation of the momentum is then expressed as:

$$M\mathbf{V}+m\mathbf{v}=(M+m)\mathbf{V}' \tag{1}$$

where M, m are the masses of the cluster and atom projectile, $\mathbf{V}$, $\mathbf{v}$ their initial velocities, respectively, and $\mathbf{V}'$ is the final velocity of the cluster after having trapped the atom.

In a real experiment, the measurement is made on a very large number of clusters. This means that the apparent velocity after one collision is the average of (1) over a large number of events. Because the velocities of the atoms in the gas are not directed, $\mathbf{v}$ is averaged to $\mathbf{0}$ and, thus, the final velocity of the cluster reduces to:

$$\mathbf{V}'=\frac{M}{M+m}\mathbf{V} \tag{2}$$

On the average, at each collision the cluster is slowed down by an amount that scales as m/M.

A cluster of size n crossing the collision chamber will have on the average a number x of collisions with the buffer gas. This number is simply given by:

$$x=\frac{L}{\lambda_n}$$

where L is the length of the chamber and λ_n the mean free path of the cluster at the pressure of the chamber which is expressed as:

$$\lambda_n = \frac{V}{k_n} = \frac{1}{N_{\mathrm{Ar}}\,\sigma_n \dfrac{\langle V_{\mathrm{rel}} \rangle}{V}}$$

where k_n is the collision rate, N_{Ar} the density of argon in the collision chamber, σ_n the cross section for a collision between the cluster and an argon atom in the chamber, and $\langle V_{\mathrm{rel}} \rangle$ their average relative velocity. The ratio $\langle V_{\mathrm{rel}} \rangle / V$ is generally written as $F_{a0}(\infty, \alpha/V)$ [12] where α is the mean velocity of the argon gas at room temperature.

These x collisions will all contribute to slowing down the cluster and (2) is immediately generalized to several collisions.[1] The final velocity $\mathbf{V}_f$ at the exit of the chamber is given by:

$$\mathbf{V}_f = \frac{M}{M + xm}\,\mathbf{V} \tag{3}$$

The relative change $\Delta V/V$ in velocity of the cluster is:

$$\begin{aligned} \frac{\Delta V}{V} &\approx \frac{xm}{M} \\ &= \frac{xm}{nm_0} \\ &= L N_{\mathrm{Ar}} \frac{m}{m_0} \frac{\sigma_n}{n} F_{a0}(\infty, \alpha/V) \end{aligned} \tag{4}$$

where m_0 is the mass of one atom of the cluster (in the case of an argon cluster and an argon buffer gas, m/m_0 is 1).

As the simulation has shown that, for small enough impact parameters, every collision of an argon atom with an argon cluster leads to a capture of the atom, we have chosen a hard sphere type cross section σ_n:

$$\sigma_n = \pi\,(R_n + R_0)^2 \tag{5}$$

where R_n is the radius of the cluster and R_0 is an additional term taking into account the range of interaction between the cluster and an atom of the buffer gas. The radius of the clusters has been calculated assuming a spherical cluster and by using the lattice parameters determined by Farges et al. [11] for Ar clusters ($a = 5.34$ Å).[2]

$$R_n = \sqrt[3]{\frac{3}{16\pi}\,a^3 n \cdot} = \sqrt[3]{\Omega n}$$

where Ω is equal to $3a^3/16\pi$. The value of R_0 has been estimated by looking at the maximum impact parameter leading to the capture of an argon atom by the 125 atom argon cluster of the simulation. It leads to a value of about 3 Å and we will see later that the results are not too sensitive to this choice.

Finally, $\Delta V/V$ is given by:

$$\frac{\Delta V}{V} = \pi L N_{\mathrm{Ar}} \frac{m}{m_0} F_{a0}(\infty, \alpha/V) \times \frac{(\sqrt[3]{\Omega n} + R_0)^2}{n} \tag{6}$$

The function $\Delta V/V$ in (6) is a linear function of the buffer gas pressure whose the slope is a slowly decreasing function of the cluster size n.

4. Experiment

The experimental arrangement has already been described [13]. Briefly, we used the supersonic molecular beam of a crossed-beam machine to generate the clusters. The expansion is of the Campargue type [14], that is, an expansion through a 0.2 mm nozzle into a relatively high pressure chamber and a skimmer, which is at an optimized distance from the nozzle, extracts the central part of the beam with a minimum of perturbation of the Mach bottle. After a differentially pumped chamber, the beam passes through the main chamber (50 cm long) where it is collided with an argon buffer gas at a pressure that can be varied between 10^{-6} and 10^{-3} mbar. Behind the collision chamber, there is a time of flight system consisting of a chopper followed at 1.5 m by a quadrupole mass spectrometer. Collimators have been used so that only the central part of the cluster beam reaches the mass spectrometer, meaning that the clusters which can be detected have been deflected by less than 10^{-3} rd.

In order to efficiently detect the clusters and since we do not want to analyze their mass distribution, we have chosen to dissociate them in the ionization source of the quadrupole mass spectrometer. The cluster beam is sent into this source where a large fraction of the clusters is dissociated by collisions against the walls. Consequently, a cluster of size n will give n monomers significantly increasing the sensitivity. Moreover, all the clusters are detected at a single m/e (that of the monomer) whatever the initial size was before the surface induced dissociation (SID). The ionization source has an open geometry so that the thermalized gas does not stay in the source for more than 10 µs. This ensures that the time response of the system is sufficient to perform accurate time of flight measurements.

A typical time of flight spectrum together with its change with the pressure in the collision chamber is displayed in Fig. 2. This is the time of flight of an argon cluster beam recorded with the mass spectrometer tuned at m/e = 40 (i.e. the mass of the argon atom). The argon

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[1] If the number of collisions becomes large the temperature of the cluster increases and some monomers can be evaporated. Because this evaporation will be isotropic in the cluster frame, this will have no effect on the average cluster velocity

[2] It is known that the structure of the argon clusters is depending upon their size [11], however the density deduced from the *fcc* structure of large clusters is also a good estimate for clusters of smaller size

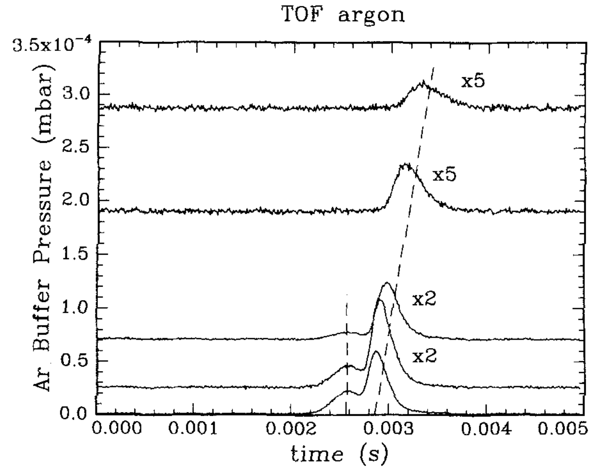

Fig. 2. Time of flight spectra of an argon beam measured at the mass of the argon atom after destruction of the clusters by collision in the ionization source of the quadrupole mass spectrometer. The various curves correspond to different argon buffer gas pressures in the collision chamber and the baseline of each TOF has been linearly displaced in function of the buffer pressure. The pressure in the stagnation chamber (4.4 bar s) corresponds to a case where the monomers and clusters give comparable signals in the mass spectrometer. Two components are observed: a fast one which is rapidly attenuated and not displaced on increasing the buffer gas pressure, and a fast one less attenuated but displaced on increasing the pressure

backing pressure for generating the cluster beam is intermediate so that the number of monomers is comparable to the number of atoms under the form of clusters. The structure of the time of flight in Fig. 2 appears bimodal with a different pressure dependence for each component. This bimodal structure has already been reported and interpreted by a velocity shift of the clusters with respect to the monomer, the fast component being due to monomers while the slow component results from fragmentation (SID) of clusters in the ion source before ionization [1, 15].

The pressure dependence of the time of flight spectra is consistent with the respective assignment of fast and slow components to monomers and clusters. First the fast component is rapidly attenuated and not shifted by increasing the buffer argon pressure. This is what we expect for an argon atomic beam: a single collision with an atom of the buffer gas is sufficient to scatter away the argon atom from the beam and a fast attenuation is expected. On the other hand, a cluster can suffer several collisions before being scattered away and the slowing down is due to the average contribution of these collisions.

In the following, we will only consider the slow component of the time of flight, that is the cluster TOF. The origin of the velocity shift between monomers and clusters even when the buffer gas pressure in the collision chamber is negligible is not totally understood. A likely explanation can found when considering collisions in the region between the nozzle and the skimmer: if the skimmer introduces a perturbation of the expansion in the Mach bottle, particles reflected back from the skimmer may collide with the clusters and slow them down.

5. Results and discussion

The experiments were carried out for argon clusters with an argon buffer gas. We chose the argon clusters because measurements of average sizes for these clusters have been done using high energy electron diffraction [16]. The results of the slowing down of clusters as a function of the argon buffer pressure are plotted in Fig. 3. In this figure, several pressures of argon in the stagnation chamber, corresponding to different clusters average sizes, have been used. What is plotted in Fig. 3 is the relative change in velocity $\Delta V/V$ of the cluster component of the time of flight after having crossed the buffer gas chamber. Two remarks can be made. First, the slowing down is a linear function of the buffer gas pressure, as expected. Second, when the backing pressure is increased, that is when the average cluster size is increased, the slowing down is decreased, again as expected.

We have calculated the mean cluster sizes that can be obtained from the experimental pressure dependences in Fig. 3 using (6). The results are displayed in Fig. 4 where the mean sizes of argon clusters are plotted as a function of the stagnation pressure. The sizes which are found, range between 100 and a few 1000.

The cluster sizes determined by high energy electron diffraction by Farges et al. [16] are also plotted in Fig. 4 for comparison. The agreement between the two sets of data is strikingly good.

For large cluster sizes, $\Delta V/V$ varies as $n^{-1/3}$ (see (6)). This means that the uncertainty in the determination of $\Delta V/V$ will be amplified in the estimation of the size. In the present experiment, it is estimated to be less than 50%. The experimental errors can be due to the measurement of the pressure of buffer gas or of the time of flight. These two causes are minimized here by the use of a viscosity presure gauge for measuring the argon pressure and by a relatively long time of flight (1.5 m) allowing accurate measurements.

Some uncertainty originates from the value of the cross section which was used. The simulation has allowed us

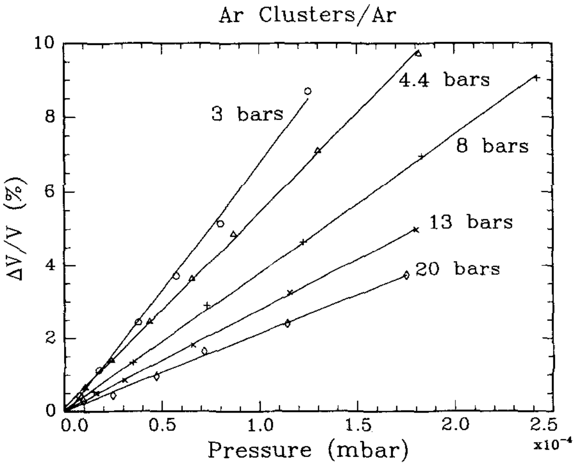

Fig. 3. Plot of the relative changes in velocity of the argon clusters in the beam as a function of the argon buffer gas pressure for several stagnation pressures generating the cluster beams. The lines are linear regressions through the experimental points

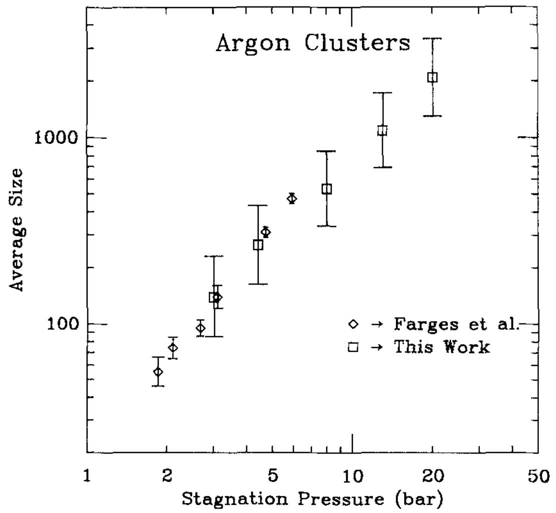

Fig. 4. Plots of the average sizes of argon clusters calculated using Eq. 6 as a function of the stagnation pressure generating the cluster beams. The squares are our results and the diamonds the values of Farges et al. [16] from high energy electron diffraction measurements

to estimate the value of the R_0 parameter in (5). This is only an estimation but we have checked that changing this value from 3 to 2.5 or 3.5 Å changes the resulting sizes by about 10 to 20% only.

Finally, the quality of the comparison of the presently determined sizes with the determinations of high energy electron diffraction indicates that in this range of cluster size the proposed method is a good alternative. This method can easily be extended to cluster beams of other atoms or molecules. This was not done here because no other determination of cluster size made under comparable expansion conditions were available for comparison.

6. Conclusion

The collisions of argon atoms with argon, clusters lead to the capture of the atom in the cluster with all the energy spread into internal energy of the cluster. This effect results in a slowing down of a cluster beam crossing a chamber containing a buffer gas. As the slowing down depends upon the cluster size, measuring the evolution of a cluster beam time of flight as a function of the buffer gas pressure allows to estimate the average size of the cluster beam. We have applied this technique to Ar cluster beams in collisions with an argon buffer gas. The clusters are detected at the mass of the monomer by surface induced dissociation in the ionization source of a quadrupole mass spectrometer. We have shown that with a simple model of the collision, the sizes obtained are in very good agreement with the sizes determined from high electron energy diffraction measurements. This method offers a simple alternative for estimating cluster sizes in a neutral beam of medium to large clusters ($n = 100$ to a few 1000).

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References

1. Visticot, J.P., Mestdagh, J.M., Alcaraz, C., Cuvellier, J., Berlande, J.: J. Chem. Phys. **88**, 3081 (1988)
2. Cuvellier, J., Mestdagh, J.M., Meynadier, P., Pujo, P. de, Sublemontier, O., Visticot, J.P., Berlande, J., Bell, A.J., Frey, J.G.: Chem. Phys. Lett. **176**, 325 (1991)
3. Kappes, M., Leutwyler, S.: In: Atomic and molecular beam methods, pp. 380, Scoles, G. (ed.), New York: Oxford: University Press 1988
4. Farges, J., Feraudy, M.F. de, Raoult, B., Torchet, G.: J. Chem. Phys. **78**, 5067 (1983);
   Feraudy, M.F. de: Thesis, Orsay 1979
5. Wales, D.J., Berry, R.S.: J. Chem. Phys. **92**, 4283 (1990)
6. Blaisten-Barojas, E.: J. Chem. Soc. Faraday Trans. **86**, 2351 (1990)
7. Perera, L., Amar, F.G.: J. Chem. Phys. **93**, 4884 (1990)
8. Verlet, L.: Phys. Rev. **A25**, 978 (1967)
9. Maitland, G.C., Rigby, M., Smith, E.B., Wakeham, W.A.: Intermolecular forces: their origin and determination, Oxford: Clarendon Press 1981;
   Hagena, O.F., Obert, W.: J. Chem. Phys. **56**, 1793 (1972)
10. Pujo, P. de: (to be published)
11. Farges, J., Feraudy, M.F. de, Raoult, B., Torchet, G.: Surf. Sci. **106**, 95 (1981)
12. Berkling, K., Helbing, R., Kramer, K., Pauly, H., Schlier, Ch., Toschek, P.: Z. Phys. **166**, 406 (1962);
    Busch, Fr. von, Strunck, H.J., Schlier, Ch.: Z. Phys. **199**, 518 (1967);
    Lang, N.C., Lilenfeld, H.V., Kinsey, J.L.: J. Chem. Phys. **55**, 3114 (1971)
13. Cuvellier, J., Mestdagh, J.M., Berlande, J., Pujo, P. de, Binet, A.: Revue Phys. Appl. **16**, 679 (1981);
    Mestdagh, J.M., Berlande, J., Cuvellier, J., Pujo, P. de, Binet, A.: J. Phys. **B15**, 439 (1982)
14. Campargue, R.: J.Phys. Chem. **88**, 4466 (1984)
15. Cuvellier, J., Binet, A.: Revue Phys. Appl. **23**, 91 (1988)
16. Farges, J., Feraudy, M.F. de, Raoult, B., Torchet, G.: J. Chem. Phys. **84**, 3491 (1986)