Doubly charged clusters - neutral atom charge transfer: the role of the Coulombic repulsion

C. Bréchignac, Ph. Cahuzac[a], B. Concina, and J. Leygnier

Laboratoire Aimé Cotton[b], bâtiment 505, Université Paris-Sud, 91405 Orsay Cedex, France

Abstract. We have studied experimentally the collisional charge transfer between a neutral atom and a multicharged metal-atom cluster. The charge transfer cross section measured for Na_{31}^{++} + Cs is in the range of 400 $Å^2$. The time-of-flight mass analysis of the singly charged collision products demonstrates that an energy of about 0.5 eV is deposited in the cluster fragment during the charge transfer collision. This effect can be interpreted as a charge transfer to an excited state of the metal cluster. The measured cross section for Na_{31}^{++} + Cs is larger than the one for Na_{31}^{+} + Cs collisions. This difference between these two systems is due to the existence, for the first one, of a Coulombic repulsion term in the collision output channel.

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1 Introduction

Among various atomic or molecular collisional processes those involving charge transfer are specially interesting as the electron transfer can be viewed as the most elementary chemical process. Charge transfer implying a surface is also of primary importance in surface science *e.g.* in the domain of catalysis. Numerous of works have been devoted to that subject since a long time. To a less extend, collisional charge exchange (CCE) between atoms and clusters have been explored, more recently [1–5]. Following the idea that such a process can be considered as the inverse process of the ionization, it has been shown that it constitutes a useful tool to probe the electronic structure of the clusters [6]. In the relevant experiment, singly (positively) charged clusters are colliding with a neutral atomic target. The physical property which is determined is the cross section associated with the neutralization of the cluster, as function of the collision energy. We present here results involving doubly-charged alkali-atom clusters Na_n^{++}, Li_n^{++} in interaction with neutral cesium atoms. Cross sections are measured for a single electron capture by the cluster, leading to singly charged products which then can be easily mass analyzed. Results show a very efficient CCE process as compared to the case of singly charged alkali-atom clusters, and an energy transfer during the collisional exchange.
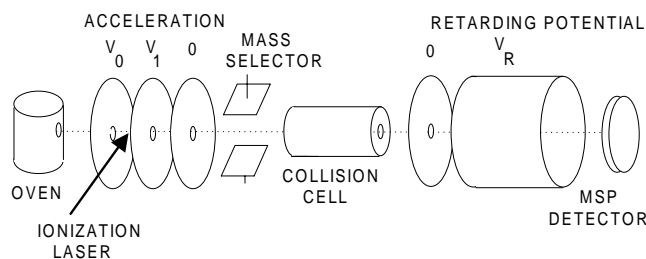

Fig. 1. Basic elements of the experimental set-up. The detector is a 5 cm^2 Microsphere Plate system (El Mul company [10]). Total length of the tandem time of flight 240 cm.

2 Experimental

A distribution of neutral clusters generated by a gas aggregation source is ionized by a pulsed U.V. laser. The charged species are accelerated by the multigrid acceleration device of a tandem Wiley-Mc Laren time-of-flight mass spectrometer [7,8] (Fig. 1). In the first drift tube clusters of a given mass/charge ratio are selected by an electrostatic gate and then propagate along a heat-pipe kind cell [9] providing a metallic vapor at low pressure. Downstream the cell, but upstream the second drift tube an electrostatic potential V_R used as a retarding field, allows to separate in time the charged products according to their mass/charge ratio and the neutral packets. All these species are detected by a MSP detector [10].

The ionization photon energy $h\nu = 5$ eV is delivered by a KrF excimer laser. It produces a large amount of singly and doubly charged alkali-atom clusters

[a] e-mail: philippe.cahuzac@lac.u-psud.fr
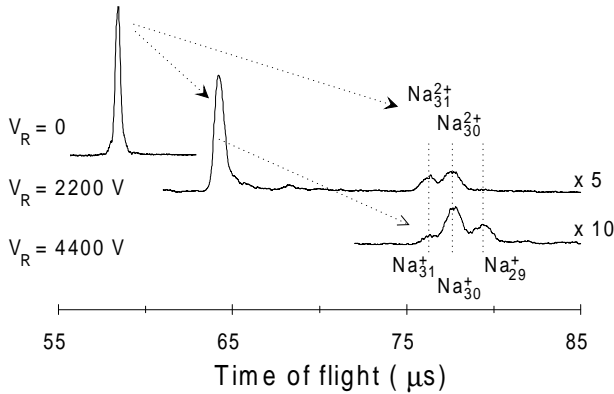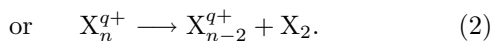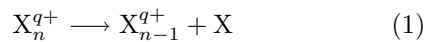[b] CNRS UPR 3321

Fig. 2. Time-of-flight mass spectra for three values of the retarding potential V_R.

Fig. 3. Velocity profiles of the charge transfer cross section σ for the reactions involving (1) doubly charged Na_{31}^{++} parent clusters, (2) singly charged Na_{31}^{+} parent clusters.

X_n^{q+} (X = Li, Na). The ion kinetic energy determined by the acceleration voltage is varied in the 1–9 keV range. Within this energy the cross section σ associated with the CCE is measured. The low value of the metallic pressure n_{at} inside the cell (active length l) ensures single collision conditions. σ is deduced from a simple Beer law, *i.e.* $r_n(n_{at}) = [1 - \exp -\sigma n_{at}l]$ where $r_n(n_{at})$ is the measured charge exchange ratio given by $r_n(n_{at}) = \frac{S^{q-1}}{S^q + S^{q-1}}$. In the equation S^x is the intensity of the X-charged species ion signal, and $S^q + S^{q-1}$ is the peak intensity of the mass selected parent when the retarding potential is maintained to zero. Actually, in the open heat-pipe cell, $n_{at}l$ is not well determined [9] and our measurements are calibrated by comparing the values of σ obtained for the monomer $n = 1$ to the absolute ones determined by Perel and Daley for the same collisional system in the same collision energy range [11].

3 Results

In addition to the CCE, several processes may affect the features displayed by the product mass spectra.

The parent clusters produced by an evaporative ensemble contain an amount of internal energy. They partially dissociate when they propagate in the first drift tube. For alkali-atom clusters this *Unimolecular Dissociation* (UD) proceeds *via* the evaporation of a neutral monomer or dimer [14]

$$X_n^{q+} \longrightarrow X_{n-1}^{q+} + X \qquad (1)$$
$$\text{or} \quad X_n^{q+} \longrightarrow X_{n-2}^{q+} + X_2. \qquad (2)$$

The fractional dissociation ratio X_{n-p}/X_n ($p = 1, 2$) is determined by the time window of the experiment according to the "Evaporative Ensemble" that constituted the ionized cluster distribution [12,13].

The products from Unimolecular Decay propagate in the field free tube with the velocity of the the parent. They are spatially resolved into individual mass packets in the
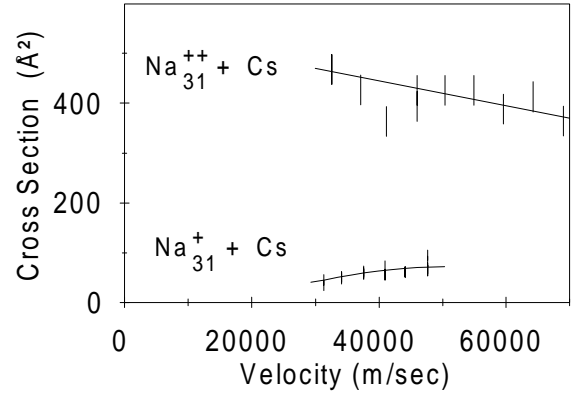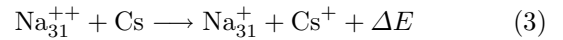
second drift tube, thanks to the retarding potential, and are observed when the pressure of cesium in the collision cell is zero (inactive cell).

For a given cesium pressure, the structure displayed by the retarding field images the combined effects of the UD and CCE processes.

We present and discuss below in details the case of the reaction

$$Na_{31}^{++} + Cs \longrightarrow Na_{31}^{+} + Cs^{+} + \Delta E \qquad (3)$$

which is typical of our observations in a single collision regime. ΔE is the energy balance of the process.

Fig. 2 shows mass spectra corresponding to three values of the retarding potential $V_R = 0$, $V_R = 2200$ V, $V_R = 4400$ V. When the retarding potential is switched off the selected ion peak signal contains all the collision products and is nothing else than $S^q + S^{q-1}$. For $V_R = 2200$ V one observes from shorter toward larger time-of-fight a huge peak identified as the direct singly charged products of CCE, and a twined structure which is the residual Na_{31}^{++} ion parent and the heavy charged fragment Na_{30}^{++} from its Unimolecular Dissociation. The relative intensity of these twined peaks is the same as the one observed for an inactive cell, showing that they correspond only to Unimolecular Decay and not to Collisional Induced Dissociation. Increasing V_R to 4400 V, increases the mass discrimination and the singly charged mass peak appears now as the superposition of three components identified as Na_{31}^{+}, Na_{30}^{+} and Na_{29}^{+}. The Na_{31}^{++} and Na_{30}^{++} signals are now out of the scale. By comparing the fragmentation patterns for the clusters with no collisions (doubly charged clusters) to those of the clusters which have undergone one charge transfer collision, we observe an additional fragmentation following the charge transfer. This characterizes the deposition of internal energy in the cluster during the charge transfer collision.

From the measurement of the relative intensities, one deduces σ. The results are plotted *versus* the collisional velocity in Fig. 3 for collision energies between 1 and 9 keV

in the laboratory frame together with the cross sections obtained for the reaction $\mathrm{Na}_{31}^+ + \mathrm{Cs} \longrightarrow \mathrm{Na}_{31} + \mathrm{Cs}^+$, implying the corresponding singly charged cluster. It appears that the CCE is much more efficient for doubly charged clusters than for singly charged species having the same size. This result occurs for all studied cluster sizes of sodium and lithium-atom clusters with cesium or potassium atoms as target.

The high value of σ in a non-resonant case suggests that the charge exchange takes place at large interparticle distances.

4 Discussion

They are two possible origins for the Na_{31}^+ CCE products fragmentation. (i) The charge exchange may lead to a component $X_n^{(q-1)+}$ less stable than the initial parent X_n^{q+}. The internal energy contained initially in X_n^{q+} is large enough to promote a dissociation step of $X_n^{(q-1)+}$ during the experimental time window before the mass analysis. This effect, already observed in a previous experiment [15] cannot play a role here because with an even number of delocalized electrons, Na_{31}^+ is more stable than the odd-delocalized electron number Na_{31}^{++}. (ii) The charge exchange involves an excited state of the cluster in the output channel. Then the electronic excitation is rapidly converted into vibrationnal energy and gives rise to the cluster dissociation. This is expected when the energy balance ΔE is positive *i.e.* when the ionization potential of $X_n^{(q-1)+}$ is larger than the ionization potential of the target atom. This is the case here: $\mathrm{IP}(\mathrm{Na}_{31}^+) = 5.5$ eV (deduced from the metallic drop model [16]) and $\mathrm{IP}(\mathrm{Cs}) = 3.89$ eV and we conclude that this effect should be responsible for the measured fragmentation.

The additional fragmentation of the singly charged clusters obtained from the mass selected Na_{31}^{++} particles permits an estimate of the internal energy δE deposited in the cluster by the charge exchange collision process. From Fig. 2, we deduce an average size value for the doubly and singly charged species by the relation

$$\overline{n}^{(q+)} = \frac{\sum n_i I_i^{q+}}{\sum n_i} \tag{4}$$

where I_i^{q+} is the intensity of the n_i-atom peak holding q charges. If D is the mean dissociation energy for clusters in this size range [13], we deduce δE by

$$\delta E = (\overline{n}^{(++)} - \overline{n}^{(+)})D. \tag{5}$$

For $D = 0.87$ *eV* [13], we obtain $\delta E = 0.55 \pm 0.05$ eV. It has to be noted that we do not find any dependence on the collision kinetic energy in the range 3–9 keV. A quantitative analysis including the dynamics of evaporation is given in [6].

To go further we calculate the CCE cross section in the frame of a two levels system following classical models developed for atom-ion charge exchange [17–19]. At large
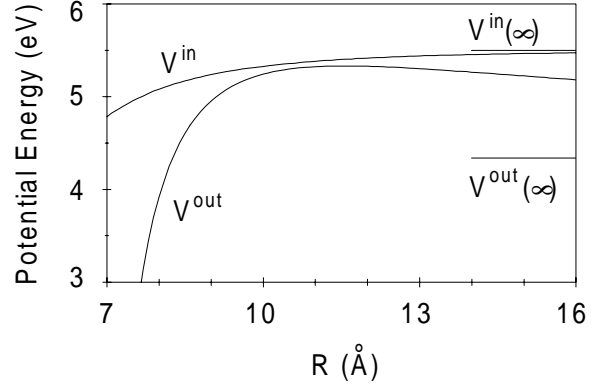
Fig. 4. Interaction potential curves for the input and output channels of reaction $\mathrm{Na}_{31}^{++} + \mathrm{Cs} \longrightarrow \mathrm{Na}_{31}^+ + \mathrm{Cs}^+$, *versus* the interparticle distance R, when $\alpha(\mathrm{Na}_{31}^{+*}) = 430$ Å^3.

interparticle distance R, the potential energy curves for the input and output channels are given respectively by

$$V^{in}(R) = \mathrm{IP}(\mathrm{Na}_{31}^+) - \frac{1}{2}\frac{(2e)^2\alpha(\mathrm{Cs})}{R^4} \tag{6}$$

$$V^{out}(R) = \mathrm{IP}(\mathrm{Cs}) - \frac{1}{2}\frac{(e)^2\alpha(\mathrm{Na}_{31}^{+*})}{R^2(R^2 - R_a^2)} + \frac{e^2}{R} + \delta E. \tag{7}$$

We consider for the output channel that the cluster is left in an electronically excited state of energy δE with a polarizability $\alpha(\mathrm{Na}_{31}^{+*})$. R_a is the radius of Na_{31}^{+}. In the right side of Eq. (7), the second term takes into account the polarization of a metal sphere having a radius R_a, and the third term is the Coulombic repulsion energy between Na_{31}^+ and Cs^+. $\mathrm{IP}(\mathrm{Na}_{31}^+)$ is taken as 5.5 eV, and $\alpha(\mathrm{Cs}) = 59.6$ Å^3 [20]. In a first step, one assumes that the polarizability of the cluster fragment in its excited state equals that of the fundamental state, 430 Å^3, which is deduced from reference [21]. $R_a = r_s n^{1/3} = 6.5$ Å, where r_s is the Wigner-Seitz radius of bulk sodium [20]. The corresponding level scheme is shown in Fig. 4. There is an R-domain where the energy separation $|V^{in} - V^{out}|$ is very small. In this domain exists an efficient coupling between input and output states. The Olson model [18] can be applied for the evaluation of σ. In this model, the coupling is efficient around R_c such that

$$H_{12} = \frac{1}{2}|V^{in} - V^{out}|_{(R_c)} \tag{8}$$

where the coupling matrix element $H_{12}(R)$ is written as $H_{12}(R) = AR\exp{-(\lambda R)}$. The constants A and λ are deduced from the IP values [22]. The model predicts a collision velocity dependence of σ with a maximum given by

$$\sigma_{max} = 1.08\frac{\pi}{2}R_c^2 \tag{9}$$

at the velocity

$$v_{max} = 3.1\frac{\pi|V^{in} - V^{out}|_{(R_c)}}{2\hbar\lambda}. \tag{10}$$

Numerical calculations lead to $R_c = 11$ Å, $\sigma_{max} = 250$ Å^2 and $v_{max} = 2.2 \times 10^5$ m/s. The value of σ_{max} is comparable to the measured one. However the measurements show a decrease of σ with increasing collision velocity, suggesting a value of v_{max} lower than the calculated one. The calculated value is very sensitive on the cluster fragment polarizability, that can be different for the excited and the ground state. A better agreement is found when taking for the cluster polarizability a lower value. Moreover, the two level model is a rough picture for the complex systems. At this point, more refined theoretical calculations are needed.

5 conclusion

The use of doubly charged species in a charge transfer experiment allows to determine easily the mass composition of the CCE products. In the present case, beyond the determination of σ which appears unusually large, showing evidence of large interparticle distance interaction, one demonstrates the existence of an energy transfer during the collision, implying the role of an excited state of the cluster. To a large extent these features result from the effect of the repulsive Coulombic term in the output channel potential interaction.

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