PRODUCTION OF MASS-SELECTED NEUTRAL CLUSTERS OF RUBIDIUM

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Charge neutralization of rubidium cluster ions (Rb_N^+) by Rb atomic vapor is reported. The cluster ions are generated by a liquid metal ion source (LMIS). The ions and the neutrals are detected directly without any photoionization step. The extent of dissociative neutralization is negligible. This results in intense, mass-selected neutral cluster beams. The charge exchange cross sections for Rb_2^+ and Rb_3^+ with Rb, are 9.3×10^{-15} and 3.1×10^{-15} cm^2 respectively.

1. Introduction

The structure and stability of different types of clusters (metallic, semiconductor, van der Waals, etc.) is currently a subject of intense interest. The dependence of these properties on the size of the cluster is a central aspect of these investigations. Several excellent review articles [1] discuss in depth the current status of theoretical and experimental research in this field. A number of important observations regarding the structure and stability of clusters have been made from the relative abundances in the mass spectra. Particularly noteworthy among them are

(a) observation of electronic shell structure in alkali metal clusters [2],

(b) magic numbers and close packing effects in inert gas van der Waals clusters [3].

The most widely used experimental method for producing a beam of metal clusters that exhibits a wide range of masses is the supersonic expansion of a mixture of the metal vapor and an inert gas such as He. However, the direct isolation of neutral clusters of a specific size is not feasible with this technique. Information concerning neutral structure and stability is obtained only in an indirect fashion: A subsequent photoionization step is used to generate detectable cluster ions. This indirect inference raises many issues regarding the fidelity of observed neutral cluster ion size distributions. The subject has been discussed quite extensively by a number of authors [4]. Furthermore, results that appear to unravel the size dependence of cluster properties may actually be complicated by the simultaneous presence of clusters of a wide range of sizes. Consequently, the generation of a beam of neutral clusters of a specific size or a narrow distribution of sizes is a goal of considerable importance. Only then can a fundamental understanding of the properties of clusters be achieved.

One potential means of producing a mass-selected, neutral beam is the application of charge neutralization to a mass-selected ionic cluster beam [5]. Of course, the neutralization process, itself, may smear the cluster mass distribution if dissociative neutralization and unimolecular decomposition are potential reaction channels. A careful study of the neutralization process is a necessary step towards the production of a mass selected neutral beam. Recently, Bréchignac et al. [6] addressed this issue elegantly in the reported experiments on the charge exchange of mass selected Na_N^+ with Cs atoms. In that experiment a supersonically expanded neutral cluster beam was photoionized, mass selected, charge neutralized, and then photoionized to allow mass analysis. In this communication, we report on our preliminary experiments on the charge neutralization of Rb_N^+ with Rb atoms. The present experiment is quite simple with a multi-kilovolt ionic cluster beam being directly produced by a liquid metal ion source (LMIS). After charge exchange the high energy neutral clusters are directly detected at an ion multiplier. Time-of-flight analysis yields the cluster

mass distribution. From these measurements we obtain cluster charge exchange cross sections and insights into processes which can alter the cluster mass distribution.

2. Experiment

Our approach for producing mass-selected neutral clusters of Rb is based on the charge neutralization of mass-selected Rb cluster ions with atomic Rb vapor,

$$Rb_N^+ + Rb \rightarrow Rb_N + Rb^+ .$$

The experimental apparatus is shown in fig. 1. A beam of Rb cluster ions is generated by a capillary-type liquid metal ion source. The source consists of a tungsten capillary needle welded to a stainless steel reservoir into which is loaded several grams of metallic Rb. Inside a high vacuum system the reservoir is heated to about 300°C for several hours. This results in the accumulation of liquid Rb in the tip of the capillary. The temperature of the tip is maintained higher than the melting point of Rb. A stainless steel extraction electrode (a circular disc with a 1 mm diameter hole in the center) is securely positioned near the tip of the needle. Ion emission from the liquid tip occurs when the potential difference between the tip and the extractor exceeds the threshold voltage of 2 kV. Typical positive ion emission from the tip is 30–50 μA. For a potential difference of a few hundred volts in excess of the threshold, emission current as large as 160–180 μA is observed. Under this condition, in addition to Rb^+, a copious amount of Rb_N^+, $N=2$–9 is generated. Although we easily observe Rb_N^+ up to $N=41$, these clusters are far less abundant than Rb_N^+ with $N=1$–9. The relative abundances of cluster ions as a function of N show sudden steps at $N=9$, 19, 21, etc. This is interpreted in terms of the electronic shell structure, according to which cluster ions with 8, 18, 20, 34, ... valence electrons form closed electronic structure which results in enhanced stability [7]. This type of ion source is generating considerable interest in the area of focused ion beam micro-lithography in integrated circuits [8].

The cluster ion beam is collimated by an electrostatic lens system and enters a Rb charge exchange heatpipe oven [9]. The heatpipe oven consists of a 2.5 cm diameter stainless steel pipe, about 30 cm long with water-cooled end caps with 3 mm entrance and exit holes for the ion and the neutral beams to pass through. Several grams of metallic Rb are loaded in the central reservoir of the heat pipe and are heated to about 200°C to produce a substantial vapor density of Rb. A stainless steel mesh rolled inside the tube acts as a capillary wick for the recirculation of liquid Rb. Several sets of electrostatic deflecting plates are positioned in the vicinity of the entrance and the exit apertures of the heatpipe. The ion source–charge exchange assembly is located inside a vacuum chamber maintained at 4×10^{-7} Torr of residual gas pressure.

The mass spectra of Rb_N^+ and the charge neutralized species are obtained by the time-of-flight technique. A potential difference of about 100 V applied between the A plates causes sufficient transverse deflection to sweep the ions off of the entrance aperture of the charge exchange oven. A pulse of cluster ions of different masses enter the charge exchange oven

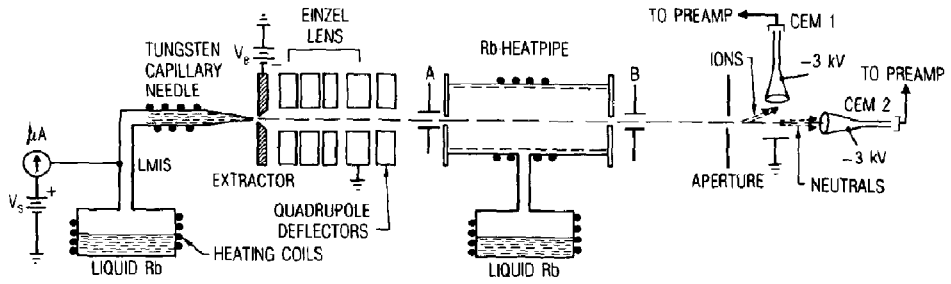

Fig. 1. Experimental apparatus used in the study of charge exchange of Rb_N^+ with Rb atomic vapor. The aperture in front of the detector (CEM2) limits the acceptance angle.

when there is 0 V between plates. Inside the charge exchange oven some cluster ions are charge neutralized. The ions and the neutrals that emerge from the charge exchange oven travel a distance of about 2 m before reaching the detector assembly. The typical background pressure in the drift region is about 4×10^{-8} Torr. The detector system consists of two continuous dynode electron multipliers (channeltrons) one mounted along the beam axis (CEM2), and other transverse to the beam axis (CEM1). The ions are drawn into CEM1 and the energetic neutrals are detected by CEM2. This enables us to simultaneously obtain the mass spectra of cluster ions and the neutral clusters.

The typical continuous ion beam current at the detector end is 1 nA. In fact, during the first few days of the operation of the LMIS ion currents as large as 30–40 nA at the detector end were observed. To obtain the mass spectrum of the cluster ions and the neutrals the voltage between the A plates is repetitively switched on and off (*off* for ≈ 2 μs and *on* for ≈ 250 μs). The start of the time-of-flight is defined by the leading edge of the on pulse. Cluster ions of different masses have the same kinetic energy only if they originate from the liquid tip at the source. The time-of-flight for a cluster ion containing N atoms is $D(NM/2eV_S)^{1/2}$ where V_S is the potential of the tungsten needle relative to ground, D is the drift distance, which is 2 m, and M is the mass of the Rb atom. A commercial amplifier/discriminator and a signal averager/multichannel scalar is used for data acquisition.

3. Results and discussion

A typical mass spectrum of cluster ions of Rb with essentially room temperature Rb vapor density inside the heatpipe is shown in fig. 2. Cluster ions up to Rb_9^+ are easily observed with an oscilloscope without requiring signal averaging. Atomic ions form a large fraction of the total ion beam. Ion currents of Rb_2^+ and Rb_3^+ are about 20% and 7–8% respectively of the Rb^+ current. Mass spectra of neutral Rb clusters emerging from the charge exchange oven are shown in fig. 3. The data shown in fig. 3 correspond to an ion kinetic energy of 2.0 keV and the average Rb vapor density in the heatpipe is about $10^{13}/cm^3$

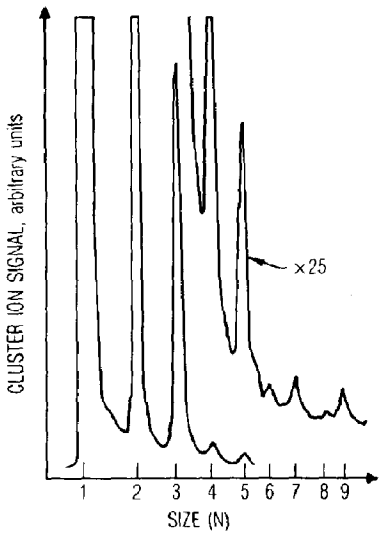

Fig. 2. Mass spectrum of Rb_N^+ ($N=1\rightarrow9$) generated by Rb liquid metal ion source (LMIS). For emission currents larger than 60 μA copious production of clusters up to $N=50$ is observed. The Rb heat pipe is at 25°C.

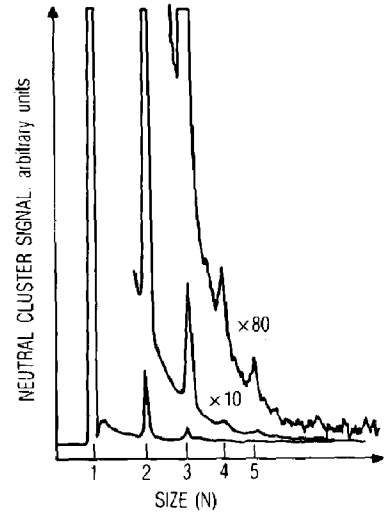

Fig. 3. Mass spectrum of neutral clusters (Rb_N) emerging from the Rb heat pipe–charge exchange region which is heated to about 200°C. The large attenuation of the Rb_N^+ beam is measured with CEM1 and the neutralized clusters are detected directly with CEM2. The aperture in front of CEM2 limits the acceptance angle.

with the effective vapor column of about 15 cm. As expected, one observes very efficient neutralization of the Rb ions resulting in the production of the fast (2.0 keV) Rb neutral beam. The resonant charge exchange process is known to be very efficient with peak charge exchange cross section being as large as a few hundred Å^2. Under these conditions we observe more than 80% attenuation of the Rb ion beam. In the resonant charge exchange process very little transverse momentum is imparted to the energetic neutrals. As a result of this a highly collimated intense beam of fast Rb atoms is generated. The neutral mass spectra show peaks corresponding to Rb_2, Rb_3, ..., Rb_7. The cluster ions emerging from the charge exchange oven are deflected away from the neutral detector by the negative bias voltage applied to CEM1. A pair of deflecting plates located at the exit aperture of the heat-pipe oven is also used for separating the ions from the emerging beam. In fig. 3 the signal due to the atomic neutrals is very much larger than the signals due to neutralized clusters. Under these conditions the relative mass distribution of the neutrals is substantially different from that of the cluster ions emerging from the charge exchange oven. We find substantial attenuation of the cluster ions by the Rb atomic vapor in the charge exchange oven. The charge exchange of alkali ions with alkali atoms has been studied extensively [10]. The symmetric charge exchange between an alkali atom and the corresponding alkali ion is a very efficient process. The total cross section for this process in the few keV energy regime is about 2×10^{-14} cm^2 [11]. For the single collision conditions that prevail in our experiments the attenuation of the atomic ions is entirely due to charge exchange. The scattering of the ions or resulting neutral clusters by the atomic vapor will be insignificant. This implies that the entire attenuated fraction of the Rb ions is converted to Rb neutrals. A direct comparison of the amplitudes of the ion signals with those of the neutral cluster signal can lead to erroneous conclusions due to possibly different detection efficiencies of the ions and the neutrals [12]. Typically the ions are extracted with kinetic energy of 2 keV. The energetic Rb atoms generated in the charge exchange region will also have the same kinetic energy. The cones of the electron multipliers are biased at -3 kV. Therefore the ions get an additional kinetic energy of 3 keV and impact the secondary emitting surface with a net kinetic energy of 5 keV. The neutrals do not get the additional kinetic energy and their energy of impact is much less than the ions. We observe a marked dependence of the detection efficiency of the neutrals on the impact energy. The ions are detected with nearly unit efficiency. Using our experimental data and assuming that the attenuation of the Rb ions is entirely due to charge neutralization, we estimate that relative to the ions the energetic atoms are detected with an efficiency of 0.6 for a kinetic energy of 1 kV. At 2 keV of kinetic energy the detection efficiencies for the atomic ion and the energetic neutral atom are very nearly the same.

The interpretation of the attenuation of the cluster ions requires caution. We will discuss the various factors that affect our interpretation. The charge exchange of molecular ions is a subject of considerable interest. Charge exchange of simple molecular ions has been experimentally investigated in detail by a number of research groups [12]. In many of the molecular ions investigated charge neutralization results in the dissociation of the neutralized molecule. The spectra of the released kinetic energy of the fragments give a deep insight into the molecular dynamics. In our experiments dissociative neutralization of cluster ions is a possibility which requires further discussion. The neutral fragments will in general acquire transverse momentum. For 1 eV of transverse kinetic energy the angular deviation of the neutral fragment relative to the direction of the cluster ion velocity is of the order of a few degrees which is over ten times the acceptance angle of our detector. By and large the neutral fragments resulting from the dissociative charge exchange will miss the detector. However, it must be pointed out that the time-of-flight of the neutral fragments will be very nearly the same as that of the parent cluster ion or the undissociated neutral cluster. Therefore in interpreting our data shown in fig. 3 we cannot unambiguously establish the size identity of the mass peaks based on the times of flight. Similar studies on the charge exchange collisions of Na_N^+ with Cs indicate, though, that for small cluster ions collisional and dissociative fragmentations are relatively weak channels of interaction. Based on these arguments we interpret our neutral mass spectra data as due entirely to charge neutralized clusters. This implies that the attenua-

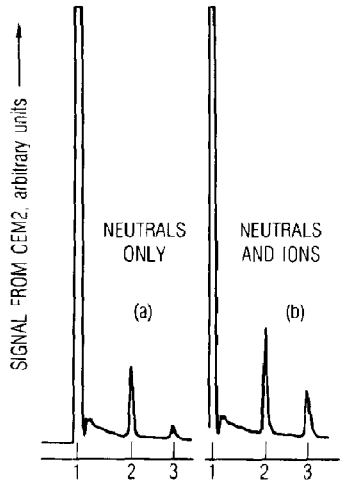

Fig. 4. Comparison of the signals with and without deflecting off the cluster ions. From this type of data we measure the charge exchange cross sections.

tion of the Rb_2^+ and Rb_3^+ is all due to the conversion of the cluster ions to the corresponding neutrals.

The neutralization efficiency is found to decrease rather sharply with the size of the cluster ions. This is brought out quite clearly in the data shown in fig. 4. The signal from the longitudinally positioned detector (CEM2) consists of both the neutrals and the ions when the latter are *not* swept off of the detector. Whereas CEM1 detects only ions CEM2 can detect either neutrals alone or neutrals and ions. We compare the signals of ions plus neutrals with the neutrals only signal. Since we known the attenuation of the respective ion currents from the CEM1 signals we can estimate the detection efficiency of neutrals relative to their ionic counterparts. In the CEM2 signal, for $N=1$ there is very little contribution from the Rb ions. In other words, there is nearly total conversion of the atomic ions to energetic Rb atoms. Comparing this with the case when there is very little neutralization (room temperature Rb vapor density in the charge exchange oven) we find that the atomic neutrals are detected with very nearly the same efficiency as the atomic ions. For typical data the attenuation of the atomic ions as measured by CEM1 is 92%. The attenuation of the Rb_2^+ by the Rb atomic vapor is 69% and for Rb_3^+ it is about 33%. From the direct measurements of cluster ion attenuation together with the corresponding neutral cluster signals we infer that the detection efficiencies of Rb_2 and Rb_3 with 2 keV are very nearly the same as that of Rb with the same kinetic energy. This allows us to estimate the charge neutralization cross sections for Rb_2^+ and Rb_3^+ in terms of the charge neutralization cross section for Rb^+ which has been measured quite accurately [11]. From the attenuation of Rb^+ we estimate the target thickness in the charge exchange oven to be $1.2\times10^{14}/cm^2$. Using Beer's law dependence of the transmission to the cross section,

$$I(Rb_N^+)=I_0(Rb_N^+)\exp(-[Rb]L\sigma_{CE}),$$

where $I(Rb_N^+)$ and $I_0(Rb_N^+)$ are the transmitted and incident currents of cluster ions of size N, L is the effective target thickness of the Rb vapor and σ_{CE} are the total charge neutralization cross sections, we find the charge neutralization cross sections for Rb_2^+ and Rb_3^+ to be 9.3×10^{-15} and 3.1×10^{-15} cm^2, respectively. These estimated total cross sections are of the same order of magnitude as measured by Bréchignac et al. [6] in the charge exchange collisions of Na_N^+ with Cs. Due to inadequate signal-to-noise ratio in our experimental data we cannot at present deduce with confidence the cross sections for cluster ions of larger sizes. Several modifications are in progress to improve the accuracy of our measurements. One of the difficult problems in our experiment is maintaining a stable cluster ion beam over periods of several hours which is the typical time it takes for the charge exchange oven to reach thermal equilibrium. The performance of our ion source deteriorates rather rapidly due to the deposition of Rb vapor on critical insulators.

The simplicity of our experimental method needs special emphasis. First of all our LMIS produces copious amounts of cluster ions of a wide range of sizes. It is fairly easy to operate. Ions are produced rather directly, quite unlike the commonly used methods where laser ionization of the neutrals are used for generating ions. Subsequent to charge neutralization the neutrals produced in our experiment are detected directly by the electron multiplier without converting the neutrals to ions by a second photoionizing laser. The photoionization process is completely eliminated thereby eliminating the use of lasers. This undoubtedly makes the entire experi-

mental approach very simple. On the other hand our interpretations will get considerably complicated if the electron multiplier introduces additional neutral mass discrimination effects. The mass discrimination effects are marginal for 2 keV kinetic energy and for the limited small sizes investigated here. A careful study of the multiplier mass discrimination effects is in progress. Finally, as no independent identification of the post-charge exchange neutrals is performed we are relying heavily on detector acceptance angle considerations and the results of ref. [6]. Further study in this area would be of value.

4. Summary and conclusions

We have made preliminary measurements of the total cross sections for charge exchange in collisions between thermal Rb atom and Rb_2^+ and Rb_3^+ relative to the charge exchange cross section of Rb^+ and Rb. The charge neutralization cross sections for Rb_2^+ and Rb_3^+ are smaller than that of Rb^+. With our limited data the general trend appears to be decreasing cross section as size increases. Our measured cross sections are of the same order of magnitude as those reported by Bréchignac et al. [6]. Since our cluster ion source produces μA of current of small cluster ions this efficient charge exchange scheme results in intense beams of neutral clusters. Mass selection prior to neutralization could be conveniently performed on the cluster ion beam. This would ultimately result in the generation of a mass selected neutral cluster beam. In our present experimental arrangement pulsed or cw mass selection of ions would require extensive modifications. As a result cluster ions of many different sizes entered the charge exchange region. Our experimental apparatus is being modified to enable us to mass select ions prior to charge exchange. Experiments are in progress to extend these measurements to a wide range of sizes.

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