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In order to study cluster beams, it is essential to measure their mass and velocity distributions as the fundamental characteristics. We demonstrate an experimental method to simultaneously measure both the mass spectrum and the beam velocities by the orthogonal acceleration time-of-flight mass spectrometer. The method is based on the ion-interruption effect of the electrode wire-mesh in the accelerator. The neutral clusters are photoionized in a small area in the accelerator, accelerated perpendicularly to the cluster beam axis, mass-analyzed and detected. Depending on the mass and the beam velocity, specific ions are interrupted by the wires arranged with a equal spacing and cannot reach the detector. This ion-interruption effect modulates the transmittance of the ions, yielding the apparent oscillations in the mass spectra. Unfolding these modulated mass spectra, we have successfully measured both the mass spectrum and the beam velocities as a function of the mass simultaneously.

1. Introduction

In order to study cluster beams, it is essential to measure their mass and velocity distributions as the fundamental characteristics. In our present experiments, the cluster beams have been generated by a laser vaporization and a nozzle technique and analyzed by time-of-flight (TOF) mass spectrometers (MS).

We have previously reported the mass and velocity measurements by a linear type TOF-MS.1) The TOF-MS is mounted parallel to the cluster beam axis. The clusters are ionized by a laser pulse at a sampling area of an accelerator. With an acceleration field, the ions are accelerated, mass-separated and reach a detector to obtain TOF mass spectra. On the other hand, without the acceleration field, the ions drift with initial beam velocities and reach the detector, yielding the TOF velocity spectra. However, this simple method has disadvantages of a low resolution and a low signal-noise ratio.

A TOF-MS, mounted perpendicular to the cluster beam axis, is called an “orthogonal acceleration” TOF-MS and one can attain a high mass resolution. Zimmermann et al introduced a method to perform the mass and velocity measurements by the TOF-MS.2) The clusters are ionized by a laser pulse between two skimmers of differential pumping stages (at Area-I in Fig. 1). After a certain delay-time, the acceleration field of the TOF-MS is switched on. Only the ions reaching the sampling area of the TOF-MS at this instant are mass-analyzed. A mass spectrum of the clusters with the specified beam velocity is obtained.

Recently we developed a reflectron TOF-MS mounted on a cluster experimental setup as shown in Fig. 1.3) The method developed by Zimmerman et al have introduced into our experimental setup. In the paper, we demonstrate another method to perform the beam velocity measurements combined with the mass spectrum measurements, which is based on the ion-interruption effect of electrode wire-mesh in the accelerator.

2. Experimental

Figure 1 shows a schematic view of the setup. The clusters were produced by a laser vaporization (ablation) technique in a low-pressure condensation cell.4) Solid targets were ablated by the 2nd harmonic wave of a Nd:YAG laser pulse. The vaporized atoms were cooled in a low pressure ambient helium gas (300 Pa) and aggregated to the clusters. The clusters flowed out with the helium carrier gas through a nozzle with a diameter of 2 mm and formed a cluster beam. The...
cluster beam passed through two skimmers of differential pumping stages and reached the accelerator of TOF-MS.

Although the cluster beams consisted of neutral and ions (positive and negative) clusters, we concentrate on the neutral clusters in the present paper. The neutral clusters were ionized by an ArF excimer laser pulse at the sampling area of the accelerator (Area-II in Fig. 1) and mass-analyzed by TOF-MS.

Figure 2 shows one of the typical examples of the mass spectra of photoionized tantalum clusters Ta$_n^+$. The Ta$_n^+$ of $n$ up to five hundreds (100,000 u) are observed. Because of the high mass resolution of our TOF-MS, it is possible to resolve the individual mass peaks in the expanded mass scales of Figs. 2(b) and (c). The satellite peaks just besides Ta$_n^+$ are due to the presence of small contamination of oxides Ta$_n^+$O$_y$ ($y=1,2,3,...$).

Mass spectra may provide valuable information on the size-dependent structure of clusters. It is well known that the shell structure (magic number) manifests as minima of oscillations in the photoionized mass spectra since closed-shell clusters have relatively larger ionization potentials.$^5$ In Fig. 2, we observe oscillations in the mass spectrum but the minima do not correspond to the closed-shell clusters. The feature of the oscillations are common to the pure Ta clusters and their oxides. The oscillations themselves are reproducible but do not reflect the existing mass-distributions of the cluster beams because the mass-position of the minima shift in accordance with the focus position of the ionization laser. These oscillations are clearly observed when the ionization laser pulse has a low-fluence and is well-focused onto the cluster beams, resulting in a small area of the ionization. It is shown below that the oscillations are spuriously introduced by the ion-interruption effect of the electrode wire-mesh in the accelerator and that it can be positively used for measurement of the velocity of the cluster beams.

3. Estimation of the Beam Velocity by the Ion-Interruption Effect of the Wire-Mesh

Figure 3 shows a schematic view of the accelerator. To generate a homogeneous acceleration field, it consists of two electrodes, a repeler plate at high voltage ($U_a$) and an exit-ring with a crossed wire-mesh (Buckbee-MN-17: wire spacing $a=0.36$ mm, wire diameter 0.018 mm) at a ground potential. The array of the square opening of the crossed wire-mesh is oriented along the cluster beam axis.

The neutral clusters are introduced in the accelerator with the beam velocity $v_C(m)$. They are ionized around $x=0$ and $y=y_0$ and accelerated perpendicularly to the beam axis, mass-analyzed and detected. We
consider an orbit of the ions with the mass of \( m \) and the charge of \( e \), which are ionized at the point \( x = 0 \) and \( y = y_0 \). Other parameters are also shown in Fig. 3.

The y-position of the ions at the wire-mesh plane \( (x = s) \) is given by,

\[
y = y_0 + v_c(m) \sqrt{\frac{2sL_a}{eU_a}} - m
\]

(1)

The ions, which are interrupted by the wires arranged with an equal spacing of \( a \) cannot reach the detector. In such a case, the following relation is satisfied,

\[
k = \frac{y_0}{\alpha} + \frac{v_c(m)\alpha}{\alpha} \sqrt{\frac{2sL_a}{eU_a}} - m (k = 1, 2, 3, \cdots)
\]

(2)

where \( k \) is an integer index and we neglected the wire diameter to simplify the notations.

In the practical measurements, the ionization area is not a point but has a finite source size. In the case of Fig. 2, the laser focus was estimated to be about 0.1 mm in diameter. The wire diameter has also a finite size. Furthermore, the beam velocity of the ions even with the same mass of \( m \) is distributed around the \( v_c(m) \). Therefore, the ion-interruption effect of the wires is not complete but causes the decrease in the transmittance at the specific masses, yielding the minima of the oscillation in the mass spectrum. The oscillations are clearly observed when the ionization laser pulse has a low-fluence and is well-focused onto the cluster beams, resulting in a small area of the ionization. With the laser focus diameter larger than the wire spacing, the oscillations smear in the mass spectra.

By using the Eq. (2) and the observed data, we can estimate the beam velocity \( v_c(m) \). The minima of the oscillations in the spectrum of Fig. 2 correspond to the tantalum clusters \( T_a \) with \( n = 33 \pm 1 \), \( 46 \pm 1 \), \( 63 \pm 1 \), \( 83 \pm 1 \), \( 109 \pm 1 \), \( 138 \pm 1 \), \( 172 \pm 1 \), \( 210 \pm 2 \), \( 253 \pm 3 \), \( 300 \pm 3 \), \( 355 \pm 5 \). The experimental parameters were \( U_a = 10 \text{kV}, \ s = 25 \text{mm}, \ L_a = 30 \text{mm} \) and \( \alpha = 0.36 \text{mm} \).

First, we assume that the \( v_c(m) \) is linearly distributed at the same mass of \( m \) and have the value of \( v_c \). In this case, \( k \) should be a linear function of \( m^{1/2} \). Figure 4 shows \( k \) vs. \( m^{1/2} \) plot and the observed data are plotted by closed circles. We use \( v_c \) and \( y_0 \) as adjustable parameters to fit the Eq. (2) to the observed data. We obtain \( v_c = 510 \pm 10 \text{m/s} \) and \( y_0 = 0.71 \pm 0.05 \text{mm} \). The fitting is represented by the solid straight line in Fig. 4 but can not reproduce the observed data well.

Next we take into account of the mass dependence of the \( v_c(m) \). It is known that the \( v_c(m) \) is slightly decreasing from the velocity of the helium carrier gas \( v_{\text{He}} \) with increasing mass (**velocity slip**). We estimate the values of the \( v_c(m) \) by two methods below.

- **[I]** By a simple model, a relation between the \( m \) and the \( v_c \) is given by

\[
m = \beta \left( \frac{v_c(m)}{v_{\text{He}} - v_c(m)} - \ln \left( \frac{v_c(m)}{v_{\text{He}} - v_c(m)} + 1 \right) \right)^{-3}
\]

where \( \beta \) is a constant. We use \( v_{\text{He}}, \beta, \) and \( y_0 \) as adjustable parameters to fit the Eqs. (2) and (3) to the observed data. We obtain \( v_{\text{He}} = 1.585 \pm 50 \text{m/s}, \ \beta = 140 \pm 20, \ y_0 = 0.16 \pm 0.05 \text{mm} \). The fitting with these values is represented by the dotted line in Fig. 4 and reproduces the observed data quite well.

- **[II]** From the Eq. (2), we have the following relation,

\[
v_c(m_{a+1})/v_c(m_a) = m_{a+1}/m_a - a \sqrt{2sL_a}/eU_a
\]

(4)

According to the Eq. (4), we can have all of the \( v_c(m_a) \) if we assume \( v_c(5,790 \text{u}) \) = 778 m/s and estimate the complete \( v_c(m) \).

The values of the \( v_c(m) \) are shown in Fig. 5, where the results obtained by the methods [I] and [II] are shown by a solid line and closed circles, respectively. They agree well each other and the values of the \( v_c(m) \) are reasonably consistent with the experimental conditions. We have, therefore, succeed in the measurements of the cluster beam velocities as a function of the mass.

4. Conclusions

We have demonstrated an experimental method to simultaneously measure both the mass spectrum and the beam velocities by the orthogonal acceleration time-of-flight mass spectrometer. The method is based
on the photo-ionization within the small focusing area of the low-fluence laser pulse and the ion-interruption effect of the electrode wire-mesh in the accelerator. This ion-interruption effect modulates the transmittance of the ions, yielding the apparent oscillations in the mass spectra. Utilizing the effect, we have successfully measured both the mass spectrum and the beam velocities as a function of the mass simultaneously.

References

Keywords: Cluster, Ion, Beam, Velocity, Mass, Wire, Mesh, Time-of-flight.