Eliminating mass-dependent inaccuracies in MRTOF-MS for the study of RI using arbitrary reference masses

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In high-precision mass spectrometry of radioactive isotopes, mass dependent inaccuracies are one of the major topics to be discussed, because the ionic mass (mass-to-charge ratio) of the rare isotopes to be studied can be distant from that of the reference ions used for calibration. In Penning-trap mass spectrometry, such effects have been studied extensively in the past using carbon cluster sources.[1)] For multi-reflection time-of-flight (MRTOF) mass spectrometry similar investigations are awaited, but are not completed yet. Other than in Penning traps, in electrostatic ion optics systems the trajectory of ions of equal energy but different mass is exactly the same, which comes from fundamental theorems. Following that, the detected TOF of any ion is obtained by $t_{\rm D} = \alpha\sqrt{m/q}$, with the characteristic device constant α and m, q as mass and charge. The mass can be calculated by use of a reference ion with m_1, q_1 and TOF $t_{\rm D1}$ by:

$$m = q\frac{m_1}{q_1}\left(\frac{t_{\rm D} - t_0}{t_{\rm D1} - t_0}\right)^2 , \qquad (1)$$

with t_0 being the offset time of the measurement (start of the TDC). However, mass-dependent inaccuracies can come from the acceleration process of the ions, which has been investigated in a new theoretical framework.[2)] The acceleration process of ions out of an ion trap happens with an electric field that is switched on with a transient in time with duration $t_{\rm T}$, and induces a mass-dependent dynamic process. We have found a solution to include such a field transition, and to calibrate masses far away from the reference mass despite this effect, while having only one reference ion species available during the online measurement. To this end, the system can be pre-calibrated once using two stable ion species before the online measurement according to the new equation $t_{\rm D} = \alpha\sqrt{m/q} + \beta\sqrt{q/m}$ having a second device constant β. During the online measurement, only one of the two reference species serves again as reference ion. Using a linear approximation of the acceleration field during the increase $\vec{E} = \vec{E}_{\rm max}\frac{t}{t_{\rm T}}$, a new equation has been found for the mass of the ions:

$$m = q\left(\frac{\widetilde{t}'_{\rm D}}{2\alpha}\frac{\widetilde{t}_{\rm D1}}{\widetilde{t}'_{\rm D1}} + \sqrt{\left(\frac{\widetilde{t}'_{\rm D}}{2\alpha}\frac{\widetilde{t}_{\rm D1}}{\widetilde{t}'_{\rm D1}}\right)^2 - \frac{\beta}{\alpha}}\right)^2 . \qquad (2)$$

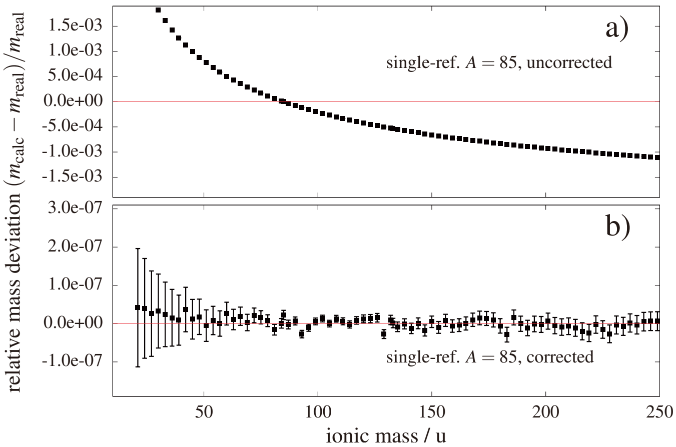

Fig. 1. Relative deviation from the real mass value (upon recalculation of the mass from the TOF data of the reflectron simulation) as a function of the mass number, using a transition time of 100 ns. a): Recalculation of masses using the usual approach without correction with mass $A = 85$ as reference ions. b): Recalculation with correction using Eq. (2). Note the different scales.

The times $\widetilde{t}'_{\rm D}$, $\widetilde{t}'_{\rm D1}$, and $\widetilde{t}_{\rm D1}$ are reduced detection times of the radioactive ion, the reference ion online, and the reference ion before the measurement, respectively. All times are reduced according to $\widetilde{t}'_{\rm D} = t'_{\rm D} - \frac{t_{\rm T}}{2} - t_0$, where $t_{\rm T}/2$ is a new correction for the switching transition emerging from the calculations. A simulation model for a simple TOF mass spectrometer with short TOF of only about 40 μs and a long switching time $t_{\rm T} = 100$ ns has been written to show amplified effects. The TOF of ions has been simulated including dynamic acceleration, and over a broad mass range while assuming that our reference ions have mass $A = 85$. The results using the mass equation of the electrostatic problem and the newly derived mass formula is shown in Fig. 1. It can be seen that, in our constructed example, the impact of such dynamic ion acceleration can be very significant if the switching is not fully considered. For MRTOF-MS, however, this effect is usually very small because of the fast switches (20 ns) and the very long TOF of 6 ms. It will become important for measurements of superheavy nuclei with large mass distances of reference to the SHE mass (depending on charge state), where the effects can become significant. The masses can then be accurately derived using the new correction.

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