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First investigation of phase-shifted Ramsey excitation in Penning trap mass spectrometry

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ABSTRACT

The excitation with time-separated oscillatory fields of the ion's cyclotron motion inside a Penning trap is used to improve the precision of mass measurements. In this work at TRIGA-TRAP the effect of a phase shift of the radio frequency field between the two Ramsey excitation pulses on the resulting ion-cyclotron-resonance time-of-flight line shape is investigated and compared with theoretical predictions.

1. Introduction

The mass and its direct connection to the binding energy reflects all forces between the nuclear constituents. Therefore, a precise knowledge of the mass is required in many physical applications with accuracies ranging from $\delta m/m = 10^{-5}$ down to $\delta m/m = 10^{-12}$ [1,2]. Penning trap mass spectrometers like TRIGA-TRAP [3] achieve high precision by converting the mass measurement into a frequency measurement of an ion's cyclotron frequency $\nu_c = qB/(2\pi m)$ with charge-to-mass ratio q/m, which is stored in the superposition of a strong homogeneous magnetic field B and a weak electrostatic quadrupole field V [4]. ν_c is in this case determined by the excitation of the ion's radial eigenmotions and the measurement of its time-of-flight to a detector outside the magnetic field [5]. The so-called time-of-flight ion-cyclotron-resonance (TOF-ICR) [6] is obtained by measuring the ion's time of flight as a function of the excitation frequency which is scanned around ν_c. The shape of the resonance curve depends greatly on time structure and phase between the excitation pulses. Thus, the influence of these parameters has to be examined systematically to optimize precision and to cancel out certain systematic errors.

In 1989, Ramsey received the Nobel Prize for the invention of the separated oscillatory fields method [7], which was used in Penning traps for the first time in 1992 for the excitation of the cyclotron motion [8,9]. Later on, the theoretical line shape of the corresponding TOF-ICR resonance was derived [10] and tested experimentally at different facilities with mass measurements of short-lived nuclides including a demonstration of an additional significant gain in precision compared to a continuous excitation, see, e.g. [11–14]. The effect of phase shifts in the oscillatory fields on molecular beams was already discussed by Ramsey in 1951 [15]. Experimental studies of the effect on ions in Penning traps and on the measured TOF-ICR line-shape which is theoretically addressed in [10] have not been performed yet. In this report, the results of experimental tests of the theory concerning phase shifts between the two rf pulses used to excite ions in a Penning trap are presented.

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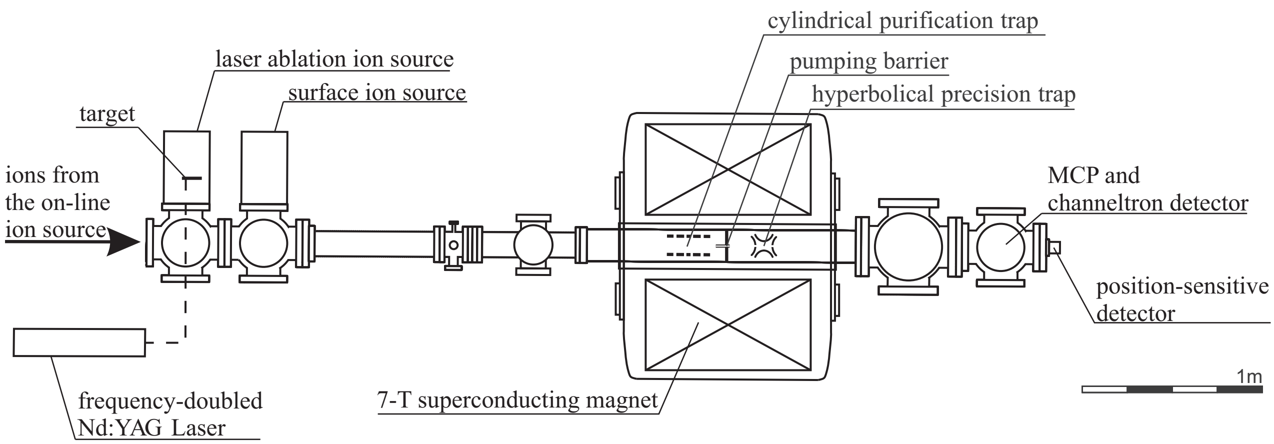

Fig. 1. Top view on the TRIGA-TRAP setup [3] with the ion sources on the left and the 7-T superconducting magnet with the two Penning traps in the middle. The detectors used for the time-of-flight ion-cyclotron measurement are on the right.

2. Experimental setup

The phase-shifted Ramsey excitation in a Penning trap was investigated at the double Penning trap mass spectrometer TRIGA-TRAP located at the research reactor TRIGA Mainz. TRIGA-TRAP is part of the TRIGA-SPEC experiment dedicated to determine ground-state properties of short-lived radioactive nuclides at the research reactor TRIGA Mainz [3]. A sketch of TRIGA-TRAP is presented in Fig. 1. The short-lived radionuclides are extracted from the reactor using a gas-jet system [16], which is connected to an ECR ion source [17]. Furthermore, two off-line ion sources are available: a surface ion source for alkali ions and a non-resonant laser-ablation ion source for the production of carbon cluster ions $^{12}C_n^+$ $(7 \le n \le 24)$ used for calibration purposes [18]. The latter was used for the studies presented here. Also other stable and sufficiently long-lived isotopes can be ionized with the laser-ablation ion source which was used for the first mass measurement at TRIGA-TRAP on ^{197}Au [19].

The ions are injected into the first trap placed inside a 7-T superconducting magnet where q/A selection is carried out by means of mass-selective buffer-gas cooling [20]. For this, the motional amplitude of all ions is increased with a mass-independent dipolar excitation of the magnetron motion. Subsequently, the desired ions are centered in the trap by a mass-dependent quadrupolar excitation and transported to the second trap through a differential pumping barrier [21]. The actual mass measurement is performed by the destructive TOF-ICR technique [6]. Therefore, the ions are resonantly excited by dipolar and quadrupolar rf fields inside the second trap to convert their magnetron motion into cyclotron motion. Afterwards, they are ejected to a microchannel plate (MCP) or channeltron electron multiplier detector (CEM) [22] outside the magnetic field. On their flight path to the detector, the ions are accelerated in axial direction due to the interaction of their motional magnetic moment with the magnetic field gradient.

3. The Ramsey excitation technique

In general the ion motion was excited continuously for a time τ with a constant amplitude (see Fig. 2a)(top). The conversion prob-

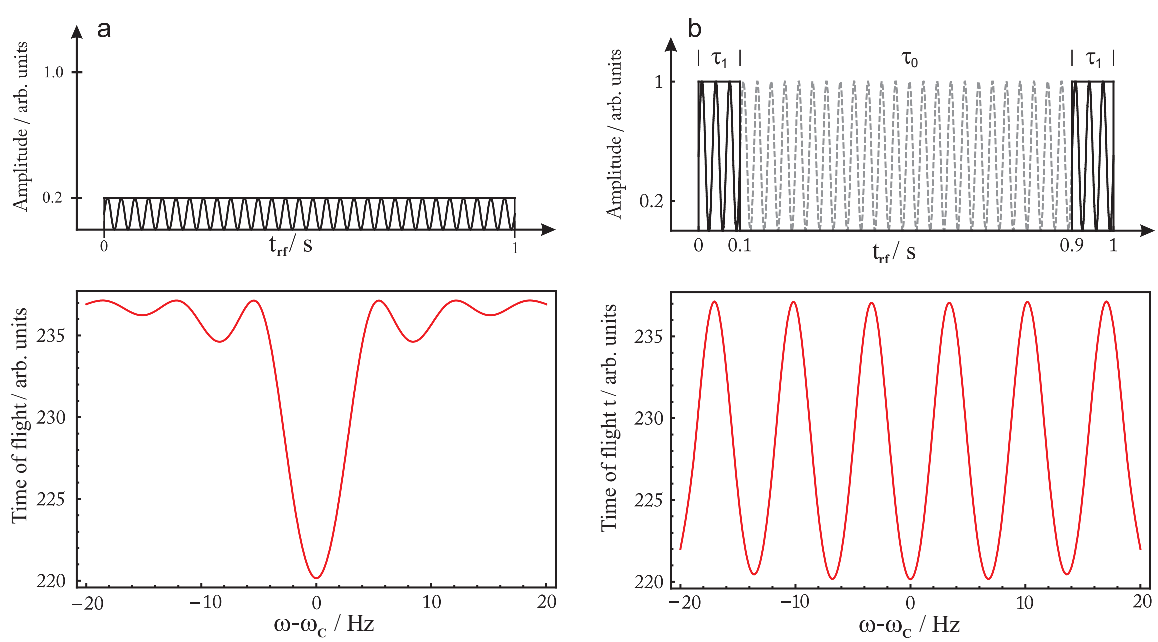

Fig. 2. Typical excitation schemes and the resulting time-of-flight resonances. (a) Continuous excitation for 1 s. (b) Ramsey excitation with τ_0 = 800 ms waiting time and two excitation pulses of τ_1 = 100 ms length. The dashed line between the pulses represents the time evolution of the rf signal during the waiting time. For details see text.

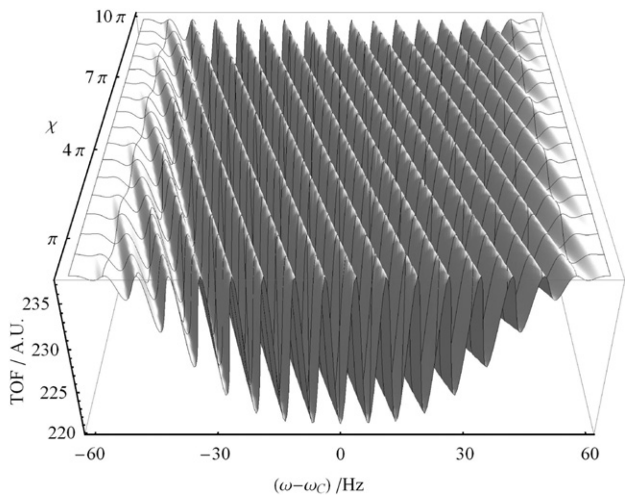

Fig. 3. Calculated time of flight as function of the detuning $\delta = \omega_c \pm 60$ Hz and the phase shift χ from 0 to 10π using Eqs. (2) and (3). For detailed discussion see text.

ability from a pure magnetron to a cyclotron motion is

$$F_1(\delta; \tau, g) = \frac{4g^2}{\omega_R^2} \sin^2\left(\frac{\omega_R \tau}{2}\right) \quad (1)$$

with the frequency detuning $\delta = \omega - \omega_c$, the Rabi-frequency $\omega_R = \sqrt{\delta^2 + 4g^2}$ and the conversion factor $g = \pi/(2\tau)$ [10]. Ramsey's method of time-separated oscillatory fields is realized by exciting the ion twice for a certain time τ_1 with a waiting time τ_0 in between (see Fig. 2b, top), keeping the total interrogation time $\tau = 2\tau_1 + \tau_0$ constant. It is also possible to excite the trapped ions several times, but since this does not increase the precision [12] it is not used at TRIGA-TRAP and therefore not considered here.

Assuming that the ion has no initial cyclotron motion, the conversion probability in the two pulse excitation scheme is

$$F_2(\delta; \tau_0, \tau_1, g, \chi) = \frac{4g^2}{\omega_R^2} \left\{ \cos\left(\frac{\omega_R \tau_0}{2} + \frac{\chi}{2}\right) \sin(\omega_R \tau_1) + \frac{\delta}{\omega_R} \sin\left(\frac{\omega_R \tau_0}{2} + \frac{\chi}{2}\right) [\cos(\omega_R \tau_1) - 1] \right\}^2, \quad (2)$$

where χ denotes the phase shift of the second excitation pulse relative to the first one [10]. Taking into account that the conversion from magnetron to cyclotron motion has to be completed after $2\tau_1$, the conversion factor is $g = \pi/(4\tau_1)$.

Finally, the time of flight of the ion from the trap at position z_0 to the detector at z_1 is given by [6]

$$T(\omega, \chi) = \int_{z_0}^{z_1} \sqrt{\frac{m}{2[E_0 - qV(z) - \mu(\omega, \chi)(B(z) - B(z_0))]}} dz \quad (3)$$

with the total initial ion energy E_0, the electric field $V(z)$ and the magnetic field $B(z)$. The magnetic moment of a rotating charge $\mu(\omega,\chi)$ contains the conversion probability and therefore the phase of the second Ramsey pulse relative to the first one. At resonance the magnetic moment is maximal and thus, the time of flight is minimal if one of the excitation schemes shown in Fig. 2 is used with $\chi = 0$. The time-of-flight resonances resulting from the continuous and the two-pulse Ramsey excitation are shown in Fig. 2. In Fig. 2(a) the ions are excited continuously (here: 1 s) and the cyclotron frequency manifests itself as a well-pronounced minimum in the time-of-flight spectrum. In Fig. 2(b) the Ramsey excitation is applied for typically two 0.1 s pulses interrupted by a 0.8 s waiting time. The damped sidebands in the continuous excitation scheme are more pronounced if the ions are excited with the Ramsey excitation and in addition, the full width at half maximum of the central fringe is about 40% smaller for the conditions used in Fig. 2(b), which results in a gain in precision of typically a factor of three with the same statistics [12] for the same interrogation time. Typical values for excitation and waiting times used at TRIGA-TRAP are $\tau_0 = 800$ ms and $\tau_1 = 100$ ms, respectively.

4. Influence of the phase

Already in 1951, Ramsey and Silsbee suggested changing the phase between the excitation pulses since this would increase the sensitivity of the measurement by increasing the effective intensity of their signal [15]. In these NMR experiments the ordinate between maximum and minimum increased by a factor of two by introducing a phase of π between the two excitation pulses. With a phase of $\pm\pi/2$ the curve passes through zero at resonance with a steep slope, which provides a sensitive mean to find the resonance frequency. In the following, we investigate the effect of phase-shifted Ramsey pulses on the time-of-flight spectra.

According to Eq. (2), the phase χ affects the conversion probability F_2 and therefore the magnetic moment of the ions. Thus, the fringes of the TOF spectrum move with the phase shift as shown in Fig. 3. The time of flight is minimal at the cyclotron frequency ν_c if the phase shift is 0 or an even multiple of π and maximal with odd multiples of π, whereas with a phase shift of odd multiples of $\pi/2$ the resonant frequency is at an inflection point of the spectrum.

The experimental result of the Ramsey excitation with a phase-shifted second pulse is presented in Fig. 4. While the phase between the excitation pulses is zero in Fig. 4(a), a phase shift of $\pi/2$, π and $3\pi/2$ is applied to the second excitation pulse used to record the resonance shown in Fig. 4(b)–(d), respectively. A comparison with Fig. 3 shows that the fringes move to the same position in the experimentally measured time-of-flight spectrum as predicted theoretically [10].

The extracted resonance frequencies of the measured resonances obtained from a fit of the theoretical line shape [10] to the data are presented in Table 1, where χ denotes the applied phase shift between the two excitation pulses and ν_c the determined cyclotron frequency. An upper limit of the uncertainty resulting from field fluctuations was estimated from long-term measurements of TOF resonances. Therefore, the cyclotron frequencies obtained in the long-term studies were corrected by the linear field drift published in [19]. The remaining uncertainty, mainly due to magnetic field fluctuations, is 20 mHz, which is added quadratically to the statistical error from the fit to calculate $\delta\nu_c$.

For each resonance in Table 1, the time of flight of about 2000 ions was recorded. The cyclotron frequencies match within 1σ at different phase shifts. This demonstrates, at the present precision level of TRIGA-TRAP, that the resonance frequency cannot be determined more precisely when a phase shift is applied, which was expected due to the fact that the theoretical function is fitted to all data points of the resonance curve whose shape does not change. In comparison with Ramsey's experiment it is clear that the sensitivity is not improved since the ordinate between maximum and minimum remains the same with a phase shift. To prevent systematic

Table 1
Resonance frequencies of the measured spectra using different phase shifts χ as presented in Fig. 4.

χ	ν_c/Hz	$\delta\nu_c$/Hz
0	639766.150	0.024
$\pi/2$	639766.175	0.024
π	639766.179	0.026
$3\pi/2$	639766.181	0.025

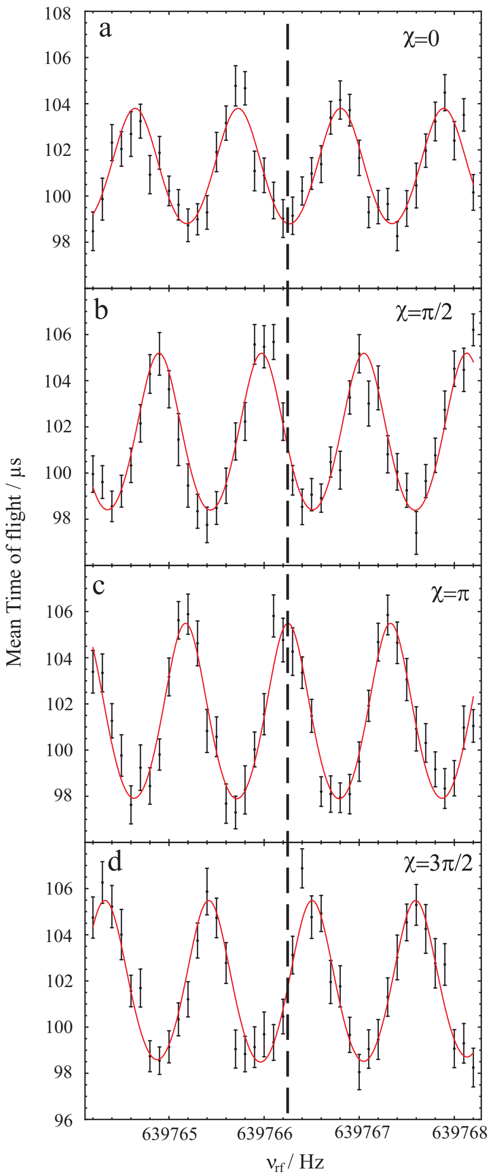

Fig. 4. Time-of-flight spectra of $^{12}C_{14}^{+}$ ions using the Ramsey technique applying phase differences of 0, $\pi/2$, π and $3\pi/2$ corresponding to the spectra in (a)–(d). The solid line is a fit of the theoretical line-shape to the data [10], the dashed vertical line marks the mean resonance frequency of all four resonances. For a more detailed description, see text.

errors when performing mass measurements with the two-pulse Ramsey excitation technique, a phase-locked excitation with a precisely known χ has to be ensured. According to Fig. 3, the Ramsey fringes shift linearly with χ. Thus, the systematic error from an unknown phase shift of $\Delta\chi$ is $\Delta\delta_{\text{phase}} = d \times \Delta\chi/(2\pi)$ with the frequency difference d between two minima in the time of flight. With $d = 1$ Hz one obtains an uncertainty of $\Delta\delta_{\text{phase}} = 2.8\,\text{mHz}/1^\circ$ whereas a phase stability below 1° can be reached easily.

5. Conclusions and outlook

Within the studies reported here, the effect of the phase between two rf pulses in the Ramsey excitation technique in high-precision Penning trap mass spectrometry was investigated with the carbon cluster ion $^{12}C_{14}^{+}$. By measuring time-of-flight ion-cyclotron-resonance (TOF-ICR) curves with phase shifts of 0, $\pi/2$, π and $3\pi/2$ between two Ramsey excitation pulses, the theoretical results have been confirmed experimentally. This includes the demonstration that the phase between the excitation pulses is an important parameter since it has to be well-known and kept constant during the measurement. These investigations are the first proof that the phase in present experiments is so well under control that it does not affect high-precision mass measurements at the present uncertainty limit of about 10^{-8} for radioactive isotopes.

Although the phase-shifted Ramsey excitation technique presented here does not directly result in a gain in accuracy, it could be used in the future for *B*-field stabilization exploiting the fact that if a phase shift of $\chi = \pi/2$ is applied the resonance frequency is at an inflection point of the resonance curve. Thus, little changes in the magnetic field resulting in a frequency shift would become more pronounced through deviations in the flight time as compared to the $\chi = 0$ pulse pattern.

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