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QUADRUPOLE – DETECTION FT – ICR MASS SPECTROMETRY

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^α) In partial fulfilment of doctoral thesis.

Quadrupole-Detection FT-ICR Mass Spectrometry

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A new detection scheme for Fourier Transform - Ion Cyclotron Resonance (FT-ICR) studies is proposed and initial experimental results are presented. While in conventional FT-ICR the difference of the transient signals from two opposite electrodes yields a signal at the reduced cyclotron frequency ν_+ , which depends on the applied trapping voltage and space charge, it is also possible to use the difference of the sum of these signals and the sum of a similar set of electrodes perpendicular to the first one. In this way resonances are observed at the harmonic of the reduced cyclotron frequency, $2 \cdot \nu_+$, as well as at $(\nu_+ + \nu_-)$. The latter is interesting in respect to accurate mass measurements, since $(\nu_+ + \nu_-)$ does not depend on the trapping voltage.

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INTRODUCTION

In the last few years different methods have been developed to extend the scope of observed resonance frequencies in Fourier Transform - Ion Cyclotron Resonance (FT-ICR) [1]. The trapping frequency has been observed by a Fourier Transform Mass Spectrometry (FTMS) method [2], the observation of harmonics has been suggested [3] and demonstrated [4] and the interharmonics ($\nu_+ - \nu_-$) [5], [4] and ($\nu_+ + \nu_-$) [4] have been investigated. The last one is of special interest, because in an ideal trap ν_+ and ν_- add up to ν_c , the cyclotron frequency of a free ion in a homogeneous magnetic field, undisturbed by the presence of an electrical field like, e.g., the trapping field. In contrast to all the eigenfrequencies of the ions in the trap, ($\nu_+ + \nu_-$) is independent of the trapping potential and therefore most suited for exact mass measurements. The experiments reported below are an extension and further development of the first investigations of the possibilities of the direct observation of ($\nu_+ + \nu_-$) reported in [4]. They are also closely related to investigations on the quadrupole excitation of the ion motion in Penning traps [6].

I. THEORETICAL CONSIDERATIONS

The aim of these experiments was to observe signals at frequencies other than the reduced cyclotron frequency ν_+ . For an ion of charge q and mass M in a Penning trap with a minimum radius of the ring electrode ρ_0 , a distance $2 \cdot z_0 = \sqrt{2} \cdot \rho_0$ between the endcaps, a magnetic field B and voltage difference U between the

ring and the endcap electrodes this frequency is given by

$$\nu_+ = \frac{\nu_c}{2} + \sqrt{\left(\frac{\nu_c}{2}\right)^2 - \frac{\nu_z^2}{2}} \quad (1)$$

with the cyclotron frequency

$$\nu_c = \frac{qB}{2\pi M} \quad (2)$$

and the trapping frequency

$$\nu_z = \frac{1}{2\pi} \sqrt{\frac{2qU}{M\rho_0^2}}. \quad (3)$$

The frequency of the magnetron motion is given by

$$\nu_- = \frac{\nu_c}{2} - \sqrt{\left(\frac{\nu_c}{2}\right)^2 - \frac{\nu_z^2}{2}}. \quad (4)$$

A detailed derivation of the equations of the motion of ions in a Penning trap can be found in the review by Brown and Gabrielse [7].

The method used in this work is shown schematically in Fig. 1. In the conventional configuration of FT-ICR detection [8], which in the following will be called dipole-detection FT-ICR, the observed signal is the difference of the signals from two opposite electrodes. This signal has the same frequency as the cyclotron motion of the ion in the trap. Using the new configuration (quadrupole-detection FT-ICR), however, the frequency of the signal is doubled, because the ions are seen twice by both sets of detection electrodes during one cyclotron revolution (Fig. 2).

The signals shown schematically in Fig. 1 are for the limiting case where the radius of the magnetron motion ρ_- is small compared to the radius of the reduced cyclotron motion ρ_+ . The top part of Fig. 2 shows a Fourier spectrum for this

situation. But already here a second resonance appears. A closer inspection of this resonance shows that it is at the frequency $(\nu_+ + \nu_-)$. The origin of this resonance can be explained with the help of Fig. 3. The cyclotron motion is superimposed onto the magnetron motion. Therefore the intensity of the pick-up signal at the frequency ν_+ increases and decreases at each detector electrode with the frequency of the magnetron motion. It has been shown [4] that this modulation can be described by a $\cos^2(\omega_-t/2 + \phi)$ modulation term of the signal of the reduced cyclotron frequency ν_+ . With this assumption the calculation of the total signal is straightforward. The pick-up signals of the four electrodes are described (using the appropriate relative phases) by

$$S_{Ia}(t) = S_{I,0} \cdot \cos(\omega_+t) \cdot \cos^2(\omega_-t/2) \quad (5)$$

$$S_{IIa}(t) = S_{II,0} \cdot \cos(\omega_+t + \pi/2) \cdot \cos^2(\omega_-t/2 + \pi/4) \quad (6)$$

$$S_{Ib}(t) = S_{I,0} \cdot \cos(\omega_+t + \pi) \cdot \cos^2(\omega_-t/2 + \pi/2) \quad (7)$$

$$S_{IIb}(t) = S_{II,0} \cdot \cos(\omega_+t + 3\pi/2) \cdot \cos^2(\omega_-t/2 + 3\pi/4) \quad (8)$$

The amplitudes $S_{I,0}$ and $S_{II,0}$ have been chosen differently to allow for different geometries of the pick-up electrodes used in set I and II. Hence, for the pick-up signals of the two sets of electrodes one gets

$$S_I(t) = S_{Ia}(t) + S_{Ib}(t) = \frac{S_{I,0}}{2} \{ \cos[(\omega_+ - \omega_-)t] + \cos[(\omega_+ + \omega_-)t] \} \quad (9)$$

$$S_{II}(t) = S_{IIa}(t) + S_{IIb}(t) = \frac{S_{II,0}}{2} \{ \cos[(\omega_+ - \omega_-)t] - \cos[(\omega_+ + \omega_-)t] \} \quad (10)$$

Therefore, by exciting the ions into the described kind of motion it is possible to observe signals at $(\nu_+ - \nu_-)$ and $(\nu_+ + \nu_-)$ by use of just one of the two sets of electrodes [4].

For an ideal Penning trap $(\nu_+ + \nu_-)$ is identical with $\nu_c = qB/2\pi M$, i.e. the unperturbed cyclotron frequency of a particle of mass M and charge q in a homogeneous magnetic field B . This frequency is independent of the trapping voltage applied to the electrodes. Furthermore, assuming the confined ion cloud can be approximated by a uniformly charged ellipsoid, the frequency shifts of ν_+ and ν_- due to this space charge cancel each other [9]. A direct observation of this frequency therefore eliminates the electric field effects without having to know what they are. Thus the observation of the sum frequency $\nu_+ + \nu_-$ is most interesting for precise mass measurements [10], [11].

It is evident from (9) and (10) that the signals of the two sets of pick-up electrodes cancel each other at $(\nu_+ - \nu_-)$ while they add at $(\nu_+ + \nu_-)$, if the detection is done differentially. The difference signal is given by

$$S_I(t) - S_{II}(t) = \frac{S_{I,0} - S_{II,0}}{2} \cos[(\omega_+ - \omega_-)t] + \frac{S_{I,0} + S_{II,0}}{2} \cos[(\omega_+ + \omega_-)t] . \quad (11)$$

For equal amplitudes $S_{I,0} = S_{II,0} = S_0$ the cancellation at $(\nu_+ - \nu_-)$ is complete and only the $(\nu_+ + \nu_-)$ resonance is seen in the Fourier spectrum with

$$S(t) = S_0 \cos[(\omega_+ + \omega_-)t] . \quad (12)$$

II. EXPERIMENTAL SETUP

An experimental proof of the new detection scheme has been performed by use of a FT-ICR system using a Penning trap with hyperbolically formed electrodes of $\rho_0 = 20 \text{ mm}$ and $z_0 = \rho_0/\sqrt{2}$. Fig. 4 shows the geometry and dimensions of this trap. For future developments and experimental flexibility endcaps and ring

have been split into segments, in total 12 pieces. This Penning is placed in the bore of a superconducting magnet at a magnetic field of $B = 5.00\text{ T}$.

Fig. 5 shows the electrical connections to and from the ring segments. The ring is on ground potential, segments I and V and segments III and VII are used for the quadrupole-detection mode described above. Segments II and IV are used to excite the magnetron motion, segments VI and VIII for the excitation of the cyclotron motion. The endcaps are connected to the trapping-voltage supply.

The experiments are performed with argon ions created by electron impact ionization (100 eV , 10^{-7} A) in the trap along the z -axis. Argon is supplied to the vacuum chamber by use of a UHV precision valve. The chamber is pumped by a cryo pump. Typical pressure during operation is $1 \cdot 10^{-7}\text{ mbar}$ measured by a Penning ionization gauge.

The time structure of the experiment is as follows: After a quench pulse to empty the trap by inverting the trapping voltage to about -13 V the ions are created and their motion is excited to larger magnetron radii. Afterwards their cyclotron motion is excited by a short pulse at the frequency ν_+ . The differential transient signal from segments I/V and III/VII is picked up by an amplifier, fed through a high-pass filter ($\nu > 100\text{ kHz}$), sampled by a CAMAC transient recorder and read out by a VME-bus system. The data are transferred to a VAX cluster where the fast Fourier transformation and the display of the spectrum takes place.

III. EXPERIMENTAL RESULTS

As described above the top part of Fig. 2 shows a Fourier spectrum where only the cyclotron, but not the magnetron motion has been excited. Therefore the

magnetron radius is much smaller than the cyclotron radius and the resonance at $2 \cdot \nu_+$ is large compared to that at $(\nu_+ + \nu_-)$. By excitation of both motions the intensity ratio between the two resonances can be reversed (Fig. 2, bottom). In the following only the frequency range near to ν_c will be discussed. In the top part of Fig. 6 this range of the Fourier spectrum is shown for different trapping potentials. Since the segments of the two sets of pick-up electrodes differ in size, the $(\nu_+ - \nu_-)$ resonance does not cancel completely. For comparison the bottom part of Fig. 6 shows a spectrum where the transient has been picked up in dipole-detection mode (using the differential signal from ring segments I and V). The ν_+ resonance of this detection mode falls as expected right into the center between the resonances at $(\nu_+ - \nu_-)$ and $(\nu_+ + \nu_-)$ measured at the same trapping potential.

Fig. 7 shows the dependence of the resonance frequencies on the trapping potential U for the range between $U = 10 \text{ V}$ and $U = 100 \text{ V}$. Whereas the signal at $(\nu_+ + \nu_-)$ is independent of the applied trapping potential U , $(\nu_+ - \nu_-)$ is shifted to lower frequencies with increasing U . The linear coefficient of a polynomial fitted to the $(\nu_+ - \nu_-)$ data is $\Delta\nu/\Delta U = 168(5) \text{ Hz/V}$ in agreement with what is expected if a small space charge is taken into account [9].

A linear fit to the $(\nu_+ + \nu_-)$ data yields a slope of $\Delta\nu/\Delta U = 2.6(6.1) \text{ Hz/V}$. The extrapolation to $U = 0 \text{ V}$ of the two sets of data yields almost the same value for ν_c ($1921.2(4) \text{ kHz}$ from the $(\nu_+ + \nu_-)$ data and $1921.1(3) \text{ kHz}$ from the $(\nu_+ - \nu_-)$ data).

The resolution of these measurements has been limited by both the relatively high pressure in the Penning trap and the limited sampling length of the transi-

ent recorder of only 8192 words. Nevertheless these first results show no slope within the experimental uncertainty and an upper limit of any possible slope of only about a tenth of the slope of the reduced cyclotron frequency (80 Hz/V) measured by conventional dipole-detection FT-ICR [12]. Therefore this detection-mode is most interesting for high-precision, direct mass measurements.

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FIGURE CAPTIONS

Fig. 1. Schematic experimental setup in the plane perpendicular to the magnetic field (left) and the transient signal observed at the output of the amplifier (right) neglecting the magnetron motion ($\rho_- = 0$). Top: Conventional dipole-detection FT-ICR. Bottom: Quadrupole-detection FT-ICR.

Fig. 2. FT-ICR spectra of argon ions. Top: For the case of a small magnetron radius ρ_- as compared to the cyclotron radius ρ_+ (excitation only at ν_+). Bottom: For the case of similar magnetron and cyclotron radii (excitation at both ν_+ and ν_-).

Fig. 3. Quadrupole-detection scheme of FT-ICR with ion motion in the plane perpendicular to the magnetic field for a magnetron radius ρ_- larger than the cyclotron radius ρ_+ .

Fig. 4. Geometry and dimensions of the Penning trap used for quadrupole-detection FT-ICR measurements. Left: Cut through ρz - plane. Right: Cut through xy - plane. The dimensions are given in *mm*.

Fig. 5. Electrical wiring of the ring segments for excitation of magnetron (II, IV) and cyclotron (VI, VIII) motion and quadrupole-detection FT-ICR (I, III, V, VII). The numbers refer to Fig. 4.

Fig. 6. FT-ICR spectra of argon ions in the region around ν_+ . Top: Quadrupole-detection mode for different trapping voltages (resonances at $(\nu_+ - \nu_-)$ and $(\nu_+ + \nu_-)$). Bottom: Dipole-detection mode for a trapping voltage of $U = 90$ V

(resonance at ν_+).

Fig. 7. Observed resonance frequencies of argon ions at $(\nu_+ + \nu_-)$ and $(\nu_+ - \nu_-)$ in dependence of the trapping potential U . The half width at half maximum was taken as error bars.

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Fig. 1

Fig. 2

Fig. 3

Fig. 4

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Fig. 5