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A NEW DETECTION SCHEME FOR FT – ICR SPECTROMETRY IN PENNING TRAPS

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A new detection scheme for FT-ICR spectrometry in Penning traps

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A new detection scheme for 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 is recorded and Fourier transformed, it is also possible to use the sum of these signals. In this way resonances are observed at the harmonic of the reduced cyclotron frequency $2 \cdot \nu_+$ as well as at $\nu_+ - \nu_-$ and $\nu_+ + \nu_-$, the latter being important for accurate mass measurements. The experiments were performed with a Penning trap in an electromagnet.

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INTRODUCTION

Since the first introduction of the Fourier Transform - Ion Cyclotron Resonance (FT-ICR) method in mass spectrometry [1] an impressive number of further developments have been carried out so that today a large variety of experimental schemes are applied: The geometry of the trap may be cubic, cylindrical or of Penning type. The excitation may be performed in narrow-band, sweep, or SWIFT modes. The amplified transient may be Fourier transformed immediatly, or, alternatively, many transients may be added before transformation. The signal may also be heterodyned to lower frequencies. However, the transient signal used is basically always the same; it is the difference of the signals of two opposite electrodes located in the plane, perpendicular to the magnetic field. Only very recently, new detection schemes have been suggested[2]. In this paper we report on the sum of the signals from two opposite detection electrodes. The signals observed are explained by taking into account the superposition of the harmonic motions of the ions in the trap.

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 e and mass M in a Penning trap with a minimum radius of the ring elctrode r_0, a distance $2 \cdot z_0 = \sqrt{2} \cdot r_0$ between the endcaps, a magnetic field B and voltage difference

U between the ring and the endcap electrodes this frequency is given by

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

where

$$\nu_c = \frac{eB}{2\pi M}$$

and

$$\nu_z = \frac{1}{2\pi}\sqrt{\frac{2eU}{Mr_0^2}}.$$

The frequency of the magnetron motion is given by

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

A detailed derivation of the equations of the motion of ions in a Penning trap giving the reduced cyclotron frequency ν_+, the magnetron or drift frequency ν_- and the trapping frequency ν_z can be found in the review by Brown and Gabrielse [3].

The method used in this work is shown schematically in Fig.1. In the conventional configuration of FT-ICR detection the observed signal has the same frequency as the cyclotron motion of the ion in the trap. The frequency of the signal of the new configuration is doubled however, because the ions are seen twice by the detection electrodes during one cyclotron revolution.

The signals shown in Fig. 1 are for the limiting case where the radius of the magnetron motion r_- equals zero or is at least small compared to the radius of the reduced cyclotron motion r_+. If the two radii are nearly equal, or if r_- exceeds r_+, the situation becomes slightly more complicated. This motion and the corresponding signal are shown in Fig. 2. Now, the magnetron motion is superimposed on the cyclotron motion. Therefore the intensity of the observed signal at the frequency ν_+ increases and decreases at each detector electrode with the frequency of the magnetron motion. This modulation can be described by a $\sin^2(\omega_- t/2)$ and $\cos^2(\omega_- t/2)$ modulation term of the signal of the reduced cyclotron frequency ν_+. With this assumption the calculation of the total signal is straight forward. The pick-up signals of the two electrodes are described by

$$\begin{aligned} S_1 &= S_0 \cos\omega_+ t \cdot \cos^2(\omega_- t/2) \\ S_2 &= -S_0 \cos\omega_+ t \cdot \sin^2(\omega_- t/2) \end{aligned}$$

Hence, observing the sum signal, one gets

$$S_1 + S_2 = (S_0/2)\left(\cos(\omega_+ - \omega_-)t + \cos(\omega_+ + \omega_-)t\right)$$

Hence, by exciting the ions into the described kind of motion it is possible to observe signals at $\nu_+ - \nu_-$ and $\nu_+ + \nu_-$. These signals have been seen before[4] but only as sidebands of the dominant signal at ν_+. With the suggested new detection scheme the signals at $\nu_+ \pm \nu_-$ can be observed without disturbance from the usually most intense signal at ν_+. For an ideal Penning trap $\nu_+ + \nu_-$ is identical with $\nu_c = eB/2\pi M$, i.e. the cyclotron frequency of a particle of mass M and charge e in a homogeneous magnetic field B. Since this true cyclotron frequency is independent of the trapping voltage applied to the electrodes and of space charge due to stored ions, the observation of the sum frequency $\nu_c = \nu_+ + \nu_-$ is most interesting for precise mass measurements[5,6]. It should also be mentioned that by including higher frequency components in the modulation, other sidebands may be produced, e.g. the $cos^4 \omega_- t$ term yields the sidebands $\nu_+ - 2\nu_-$ and $\nu_+ + 2\nu_-$.

II. EXPERIMENTAL SETUP

An experimental proof of the new detection scheme has been performed by use of a FT-ICR system and a Penning trap with hyperbolically formed electrodes[3] of $r_0 = 20\ mm$ and $z_0 = r_0/\sqrt{2}$. The magnetic field is provided by an electro magnet. The fields used for the experiments reported below range from 0.29 T to 0.66 T. The ions are created inside the trap by electron impact ionization of the residual gas. The reported experiments are performed with N_2^+ ions. Typical pressures range between 10^{-7} and 10^{-6}mb. The ions are excited by a frequency sweep using a frequency synthesizer controlled by CAMAC modules that also control the timing of the whole experiment. The transients are amplified by use of only one input channel of an amplifier[7]. The amplified signal is fed into a CAMAC transient recorder, read to an LSI computer and transferred to a microVAX cluster where the Fourier transformation takes place.

III. EXPERIMENTAL RESULTS

Fig. 3 shows the observed frequency spectra for the two limiting cases (r_- small and large compared with r_+) and a spectrum with intermediate conditions. It is possible to switch between these cases by varying the intensity of excitation of the two motions. As expected from the discussion in Chapter I, the harmonic signal $(2 \cdot \nu_+)$ is dominant for a small magnetron radius of the confined ions. Its signal height decreases drastically with increasing r_-, whereas the opposite holds for the signals at $\nu_+ - \nu_-$ and $\nu_+ + \nu_-$.

Fig. 4 shows the dependence of the spectra of N_2^+ on the the trapping potential U (the difference of the voltage applied to the end caps and to the ring electrodes) for the case $r_- \gg r_+$. Whereas the signal at $\nu_+ + \nu_-$ is independent of the applied trapping potential U, $\nu_+ - \nu_-$ is shifted to lower frequencies with increasing U.

Finally Fig. 5 shows dependence of the observed frequency on the trapping potential for a magnetic field of 0.37 T. As already noted from Fig. 4, the frequency of the $\nu_+ + \nu_-$ is constant and equals ν_c as expected for an ideal Penning trap. Hence, this signal is most suited for high-precision, direct mass measurements. The signals at $2 \cdot \nu_+$ and $\nu_+ - \nu_-$ vary linearly with the applied trapping potential. The observed slope is in agreement with theory.

It should be pointed out that the two resonances at $\nu_+ - \nu_-$ and $\nu_+ + \nu_-$ coincide at a trapping potential $U = 2$ V and not, as predicted by theory, at $U = 0$ V. This feature is observed at different magnetic fields (0.29 T to 0.66 T). The corresponding intersection potentials are found to vary between 1 V and 3 V. No clear correlation with the magnetic field is found. The descrepancy may be due to a rather large inhomogeneity of the magnetic field in the electro magnet used.

IV. CONCLUSION

It has been shown, from simple theoretical considerations and by experiment, that it is possible to easily observe interharmonic signals of the ν_+ and ν_- motions in a conventional Penning trap and to do this with virtually no interference from the ν_+ signal that is the strongest signal in conventional FT-ICR. In particular, the sidebands $\nu_+ - \nu_-$ and $\nu_+ + \nu_-$ are easily seen by a two-electrode detector system. The resonance at $\nu_+ + \nu_-$ is important for precise mass measurements.

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FIGURE CAPTIONS

Fig. 1. Schematic experimental setup in the plane perpendicular to the magnetic field (left) and of the transient signal observed at the output of the amplifier (right) neglecting the magnetron motion ($r_- = 0$). Top: Conventional FT-ICR with detection of the difference of the pick-up signals. Bottom: FT-ICR with detection of the sum of the pick-up signals.

Fig. 2. Schematic experimental setup in the plane perpendicular to the magnetic field (left) and the transient signals S_1, S_2 and S_1+S_2 (right) for the case of a magnetron radius r_- larger than the reduced cyclotron radius r_+.

Fig. 3. FT-ICR spectra for different kinds of motion of N_2 ions in the trap. Top: $r_- \simeq 0$; center: $r_- \simeq r_+$; bottom: $r_- \gg r_+$.

Fig. 4. FT-ICR spectra of N_2^+ in dependence of the trapping potential U. The frequency region around $\nu_+ - \nu_-$ and $\nu_+ + \nu_-$ is displayed.

Fig. 5. Observed frequencies $2 \cdot \nu_+$, $\nu_+ + \nu_-$ and $\nu_+ - \nu_-$ of N_2 ions in dependence of the trapping potential U.

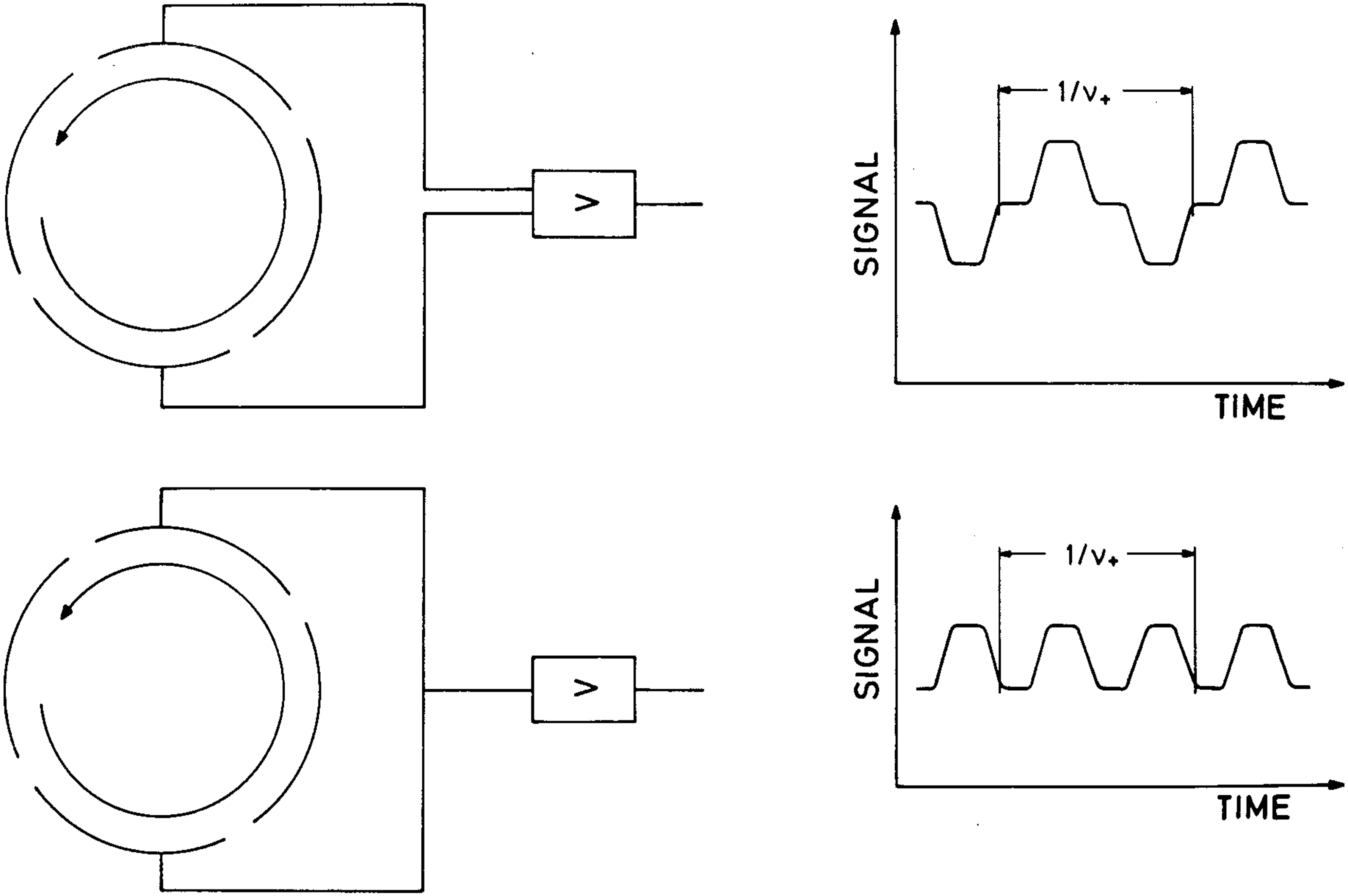

Fig. 1

88 664

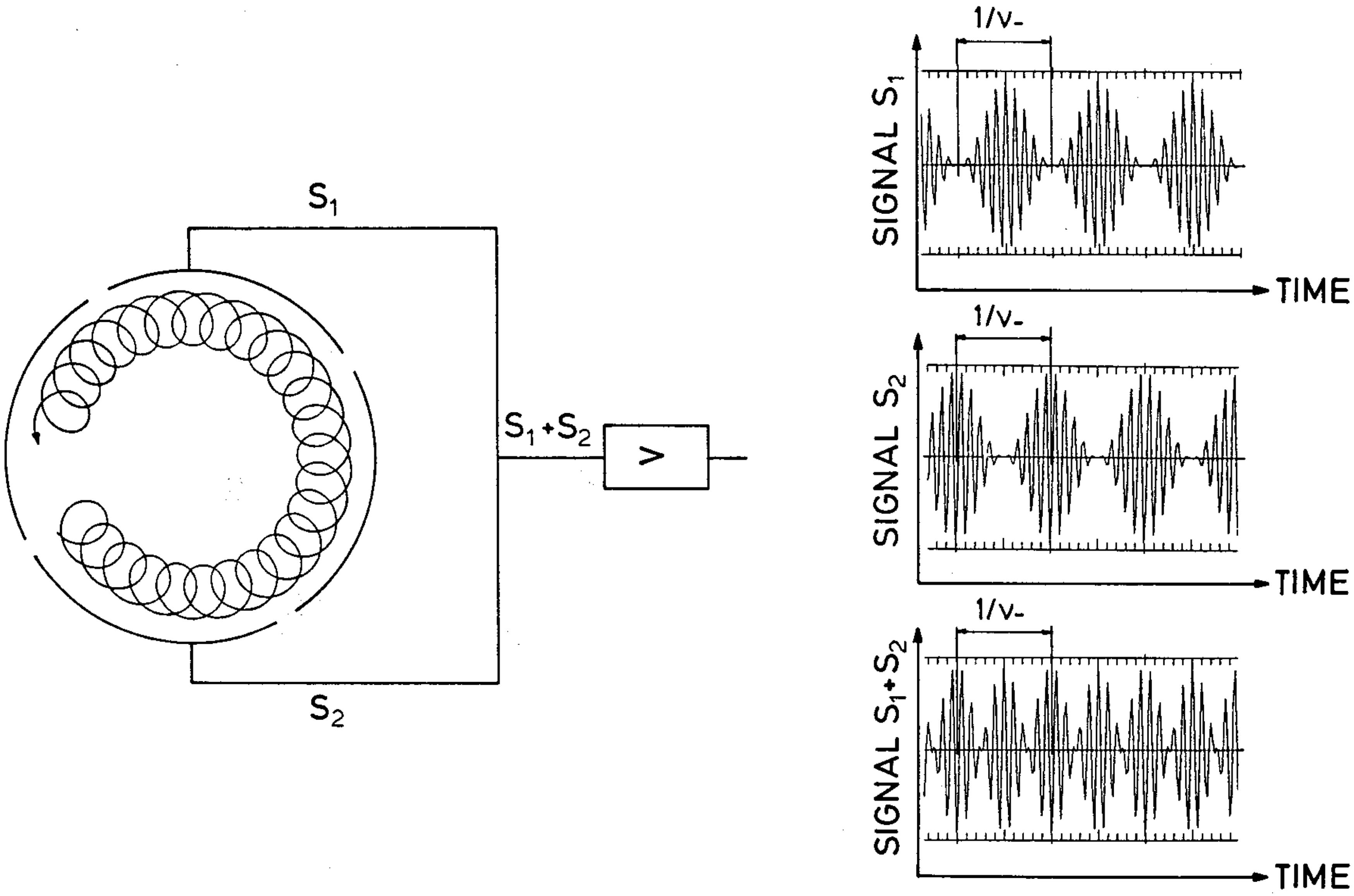
S_1
S_2
S_1+S_2
V
SIGNAL S_1
SIGNAL S_2
SIGNAL S_1+S_2
1/ν-
1/ν-
1/ν-
TIME
TIME
TIME

Fig. 2

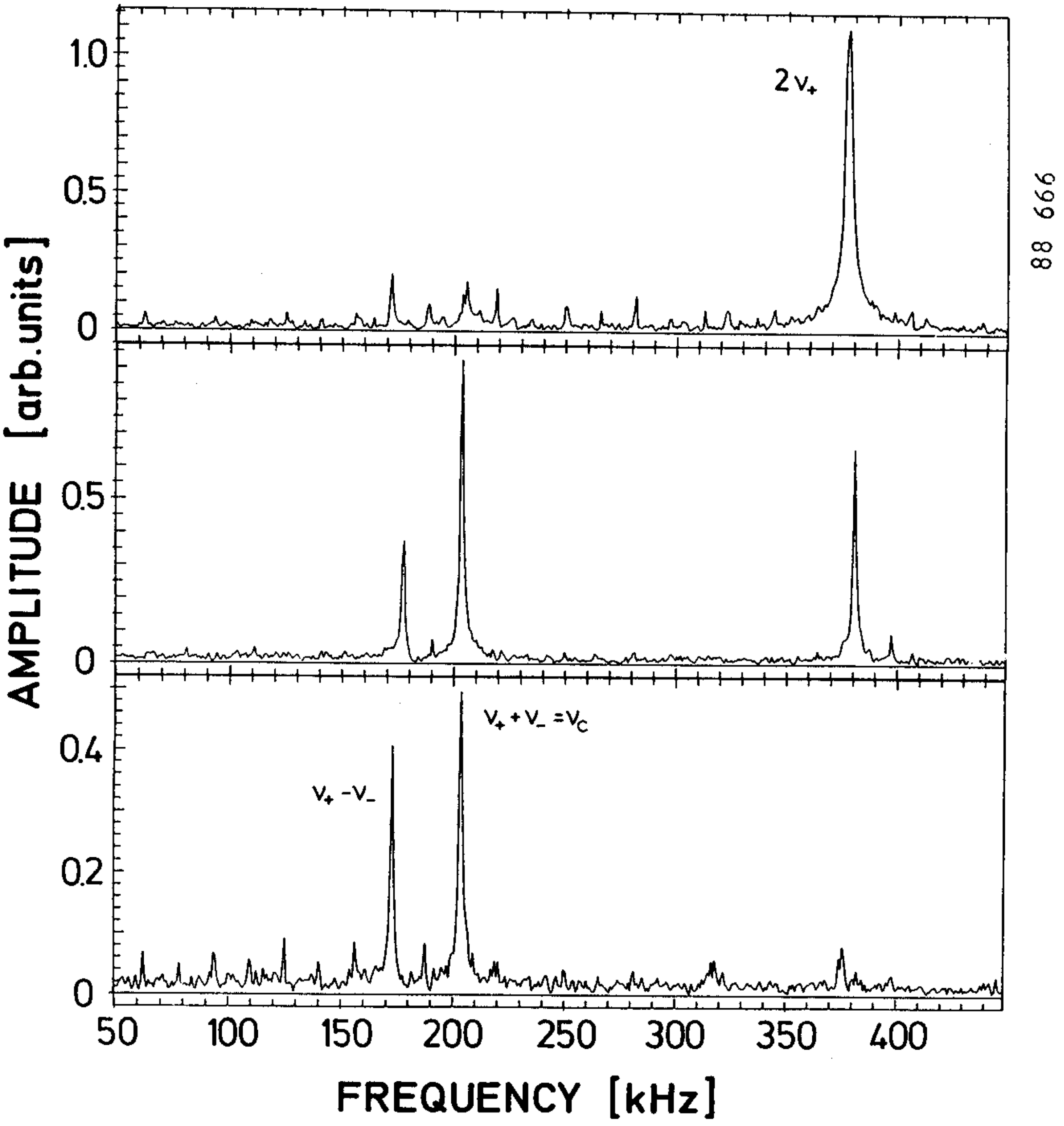
2ν₊
ν₊ + ν₋ = ν_c
ν₊ - ν₋
AMPLITUDE [arb.units]
1.0
0.5
0
0.5
0
0.4
0.2
0
50
100
150
200
250
300
350
400
FREQUENCY [kHz]
88 666

Fig. 3

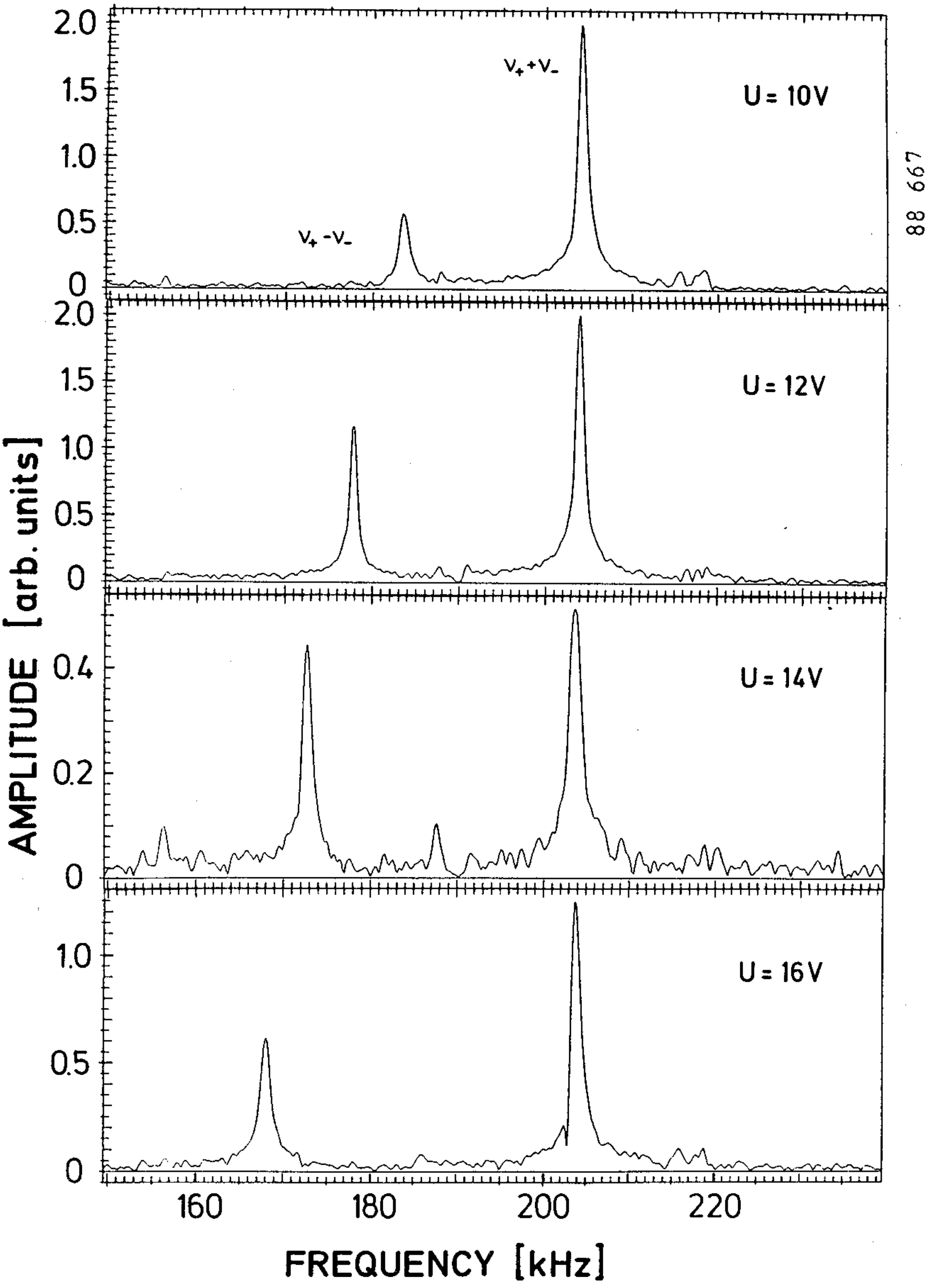
AMPLITUDE [arb. units]
FREQUENCY [kHz]
2.0
1.5
1.0
0.5
0
0.4
0.2
160
180
200
220
ν+ + ν-
ν+ - ν-
U = 10V
U = 12V
U = 14V
U = 16V
88 667

Fig. 4

88 663

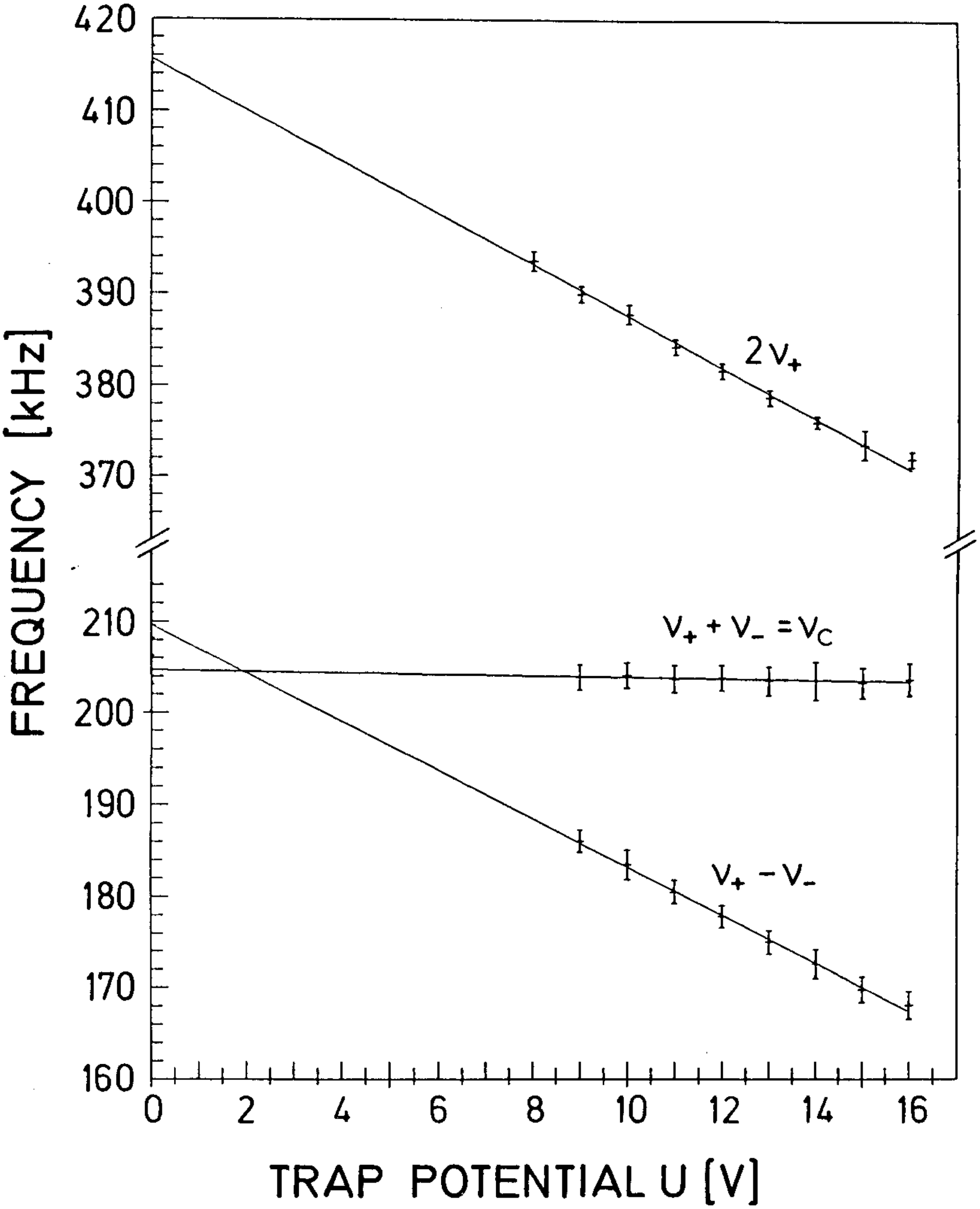
420
410
400
390
380
370
210
200
190
180
170
160
FREQUENCY [kHz]
$2\nu_+$
$\nu_+ + \nu_- = \nu_C$
$\nu_+ - \nu_-$
0
2
4
6
8
10
12
14
16
TRAP POTENTIAL U [V]

Fig. 5