The Orbitrap: a novel high-performance electrostatic trap

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Until recently, dynamic ion trapping in electrostatic fields has been regarded little more than a curiosity of doubtful analytical merit. This work describes a new type of mass analyser based on an electrostatic ion trap known as "ideal Kingdon" trap [1-3].

In the absence of any magnetic or RF fields, ion stability in this trap is achieved only due to the balance between centrifugal and electrical forces. The former requires ions to orbit around an axial electrode hence the name Orbitrap for the technique. At the same time, ions also perform harmonic ion oscillations along the electrode (Fig.1a). These oscillations are detected using image current detection and transformed into mass spectra using fast FT, like in FT-ICR.

a) **b)**

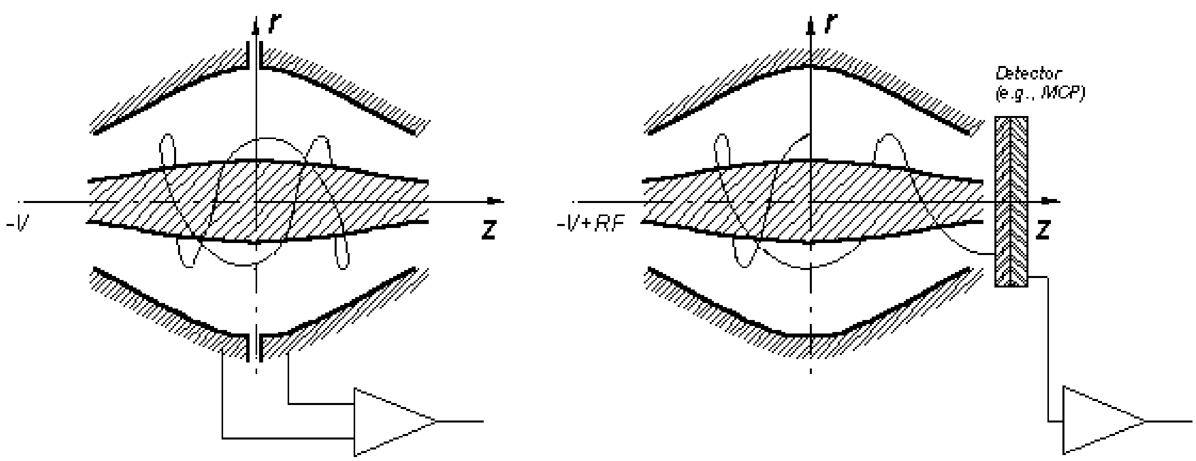


Fig.1. Mass analysis modes available in the Orbitrap: a) image current detection with FFT, b) mass-selective instability via parametric resonance

Alternatively, mass spectra could be acquired in mass-selective instability mode by applying RF-voltage of variable frequency to the central electrode. At low RF amplitudes (i.e. low q_z on Matheiu diagram), radial oscillations remain stable while axial oscillations experience parametric resonance and increase their amplitude until ions are ejected to the detector outside the trap (Fig.1b).

For ions with mass-to-charge ratio *(m/z)*, angular frequency ω_z of axial oscillations in the Orbitrap is $\omega_z \sim (m/z)^{-1/2}$. This dependence contrasts with $\omega \sim (m/z)^{-1}$ dependence in both FT-ICR and quadrupole ion trap. The slower decrease of frequency with the increase of *(m/z)* promises much better space-charge stability at *(m/z)*>500-1000 Th (Fig.2). Among other potential advantages, the following are to be noted:

- in a refined design, mass resolutions up to 100000 are predicted;
- due to high robustness to space charge, good mass accuracy is expected;
- energy acceptance spans up to several hundred volts;
- as all ions have been accelerated by several kV, high-energy collision-induced dissociation on background gas may be achieved automatically after appropriate waiting time;
- parametric resonance with low-voltage RF may be used for precursor ion selection, in addition to possibility of resonance excitation;

- in MS-only mode, all-mass excitation may be achieved just by off-centre pulsed injection of ion beam from an external ion source.

Ultra-high vacuum (below 10^{-9} mbar) is required for high mass ions however only within the small volume of the trap (<0.1 litre). No collisional cooling is possible inside the trap, so all cooling must be performed in the external ion source prior to ion injection.

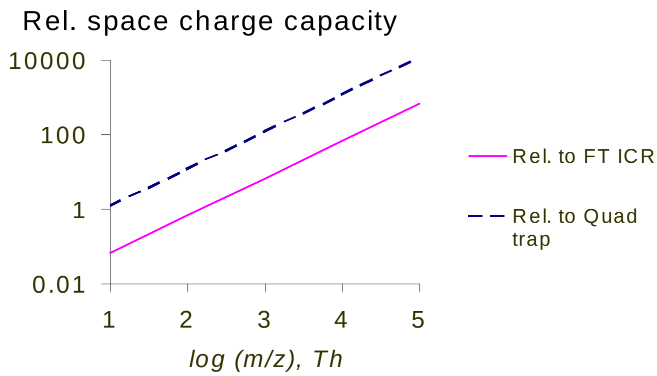
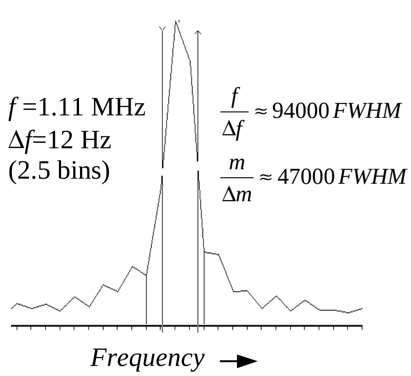


Fig.2. Expected performance of Orbitrap comparing to FT ICR (9.4 T) and Quad trap (10 kV RF p-p).

Initial experiments have been carried out on a compact bench-top experimental setup with a laser ablation ion source. Wide mass range detection for a pulsed laser source has been demonstrated- from ^{7}Li and ^{23}Na to PEG-1000. For alkali ions, mass resolution above 40000 is routinely achieved (Fig.3). In this case, mass resolution seems to be limited mainly by record length. No signal deterioriation has been observed even when ion energy was changed by 100 V. Mass peak position stays within 10 ppm even when the number of trapped ions is increased up to about 10^{6} ions (saturation of amplifier).

Trapping times for Cs exceed 0.2-0.5 seconds even for pressures above 10^{-7} mbar. However, much faster signal decay and therefore lower mass resolution has been observed for heavier organic molecules. Due to independence on pressure, the effect has been attributed to metastable fragmentation. Nevertheless, even under these conditions isotopic resolution of MALDI ions has been observed (Fig.4). Further effort is underway to add collisional cooling to the setup.



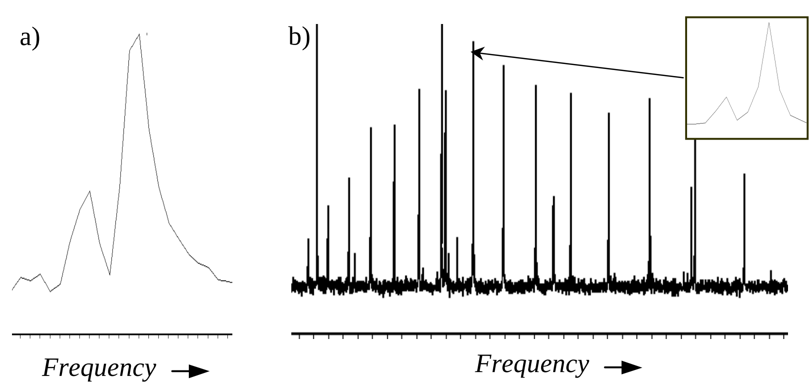


Fig. 3. Mass peak of $^{23}Na^{+}$

Fig. 4. Preliminary MALDI spectra: a) Angiotensin 2 (30 shots, 1 spot)
b) PEG-1000 (50 shots, 1 spot)

References:

1. K.H. Kingdon, Phys.Rev., 21 (1923), 408-418.
2. R.D. Knight, Appl. Phys.Lett., 38 (1981) 221-222.
3. L.N. Gall, Y.K. Golikov et al, USSR Inventor's Certificate #1247973 (1986).