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Time-dependent frequency of ion motion in Fourier transform mass spectrometry

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ABSTRACT

Recent experimental and theoretical findings suggest that the concept of time-dependent instantaneous frequency (IF) is required to comprehensively describe ion motion and mass spectra generation in Fourier transform mass spectrometry (FTMS). Here, we derive a set of differential equations describing ion motion in ion cyclotron resonance (ICR) and Orbitrap FTMS mass analyzers from the IF standpoint. A moving ion is represented by two 2D oscillators: first with oscillations coupled in the radius-azimuth, (r, φ), and second in the radius-z axis, (r, z), coordinate planes. The presented description is thus fundamentally different from a standard representation of ion motion in FT-ICR MS in a form of a superposition of cyclotron and magnetron radii. Analysis of ion motion with the developed theory validates the hypothesis that time-dependent IF is the most probable characteristic condition of ion motion in FTMS mass analyzers. Application of IF theory improves understanding of FTMS fundamentals and should advance FTMS implementation and practice. For instance, the obtained relations between an ion's IF values and mass-to-charge ratios may be used to refine calibration and frequency shift equations. Other envisioned benefits are improved descriptions of ion RF excitation and transient generation processes, as well as of an influence of a space-charge and of an image charge fields.

1. Introduction

Owing to highly accurate frequency measurements of multi-periodic ionic signals, Fourier transform mass spectrometry (FTMS) provides superior resolution and mass accuracy for molecular structural analysis compared to other MS techniques [1–8]. The periodic ion motion and generated time-domain signals (transients) in FTMS are traditionally described by components having static angular frequency $\omega = \text{const}$ and phase $\Phi(t)$ that depends on time linearly, i.e., $\Phi(t) = \omega \cdot t + \phi_0$ where ϕ_0 is an initial phase [9,10]. In case of a phase function $\Phi(t)$ non-linearly dependent on time, ion motion calculations require a novel description, based on time-dependent instantaneous frequency (IF) approach, where the corresponding IF is $\tilde{\omega}(t) = (d\Phi(t)/dt) \neq \text{const}$. Recently, it has been established that indeed there are components with time-dependent frequencies in both experimental and simulated transients in FT ion cyclotron resonance MS (FT-ICR MS) [11–14]. The mechanism of frequency variation in time has been explained by collisions leading to an increase in a space-charge field of ions with the same m/z value [15], and the space-charge field of ions with diverse mass-to-charge ratios [12,14,16,17], although other fundamental causes remain unclear [10]. Therefore, there is an incentive to develop a theory describing ion motion with time-dependent frequency for improved understanding of FTMS processes. Interestingly, the IF approach has been developed and applied in many application areas of signal processing [18–22], but not for ion motion in mass analyzers.

Historically, the ion motion equations were first developed for a single ion motion based on the Lorentz force law for various electromagnetic fields, particularly for the case of a constant uniform magnetic field and quadratic electrostatic potential in mass analyzers [23–30]. In parallel, charged particle motion analysis was developed in ion physics, vacuum electronics, plasma science, space science, and other scientific directions [31–38]. Some of these achievements have been adopted for the MS applications [39,40]. The non-linear solutions of ion motion equations in FT-ICR MS have been considered using a number of approaches, including variation of constants, Laplace transform, averaging in time, perturbation theory, and complex-variable oscillator with both cyclotron and magnetron radii oscillations [30,33,34,41–48]. Specifically, ion motion with a variable phase was considered in

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a non-linear approach with averaging in time [49,50]. A number of solutions were presented in terms of the cyclotron and magnetron radii complex oscillator [46,51]. Using Laplace transform, a superposition of cyclotron and magnetron radius-vectors in the linear approach was employed to describe ion radio frequency (RF) excitation [41]. Nevertheless, in the study of geometries for single-frequency resonant, in-phase excitation in FT-ICR MS it was assumed that each ion motion mode maintains a constant frequency during the excitation process [48]. Similarly, in the dipole RF excitation scheme for FT-ICR MS, analysis of ion motion equations was conducted using the constant frequency of ion rotation [52]. In an Orbitrap mass analyzer, solutions of z-axial ion motion with non-linear time-dependent phase have been obtained numerically with space-charge field consideration [53].

In that context, the aim of the current work is deriving a missing analytical description of ion motion with an IF $\tilde{\omega}(t)$ and non-linearly time-dependent phase $\Phi(t)$ for both ICR and Orbitrap mass analyzers. The paper is organized as follows. In Section 2.1, the description of the current analytical theories of ion motion in FTMS is given and their limitations are underlined. In Section 2.2, a first order ordinary differential equation is derived for both radial and azimuthal IF in the uniform magnetic field and any electric field. In Section 2.3, the derived differential equation is solved for ion trajectories in the uniform magnetic field for the case of a harmonic electric field with a quadratic potential distribution. In Section 2.4, ion axial oscillations in both ICR and Orbitrap FTMS analyzers are described. In Section 2.5 the general relations of mass-to-charge ratio and frequency shift with the IF value are presented. Further, Section 2.5 contains an overview of the developed IF approach as well as the utility of its application in FTMS.

2. Results and discussions

2.1. Limitations of the current FTMS theories of ion motion

Analytical theory of ion motion in FT-ICR MS is built around a classical equation, widely employed within Newton-Lorentz framework [25–40,54–56], see also Section SI in Supplementary Information:

$$\ddot{\vec{r}} - \dot{\vec{r}} \times \vec{\omega}_c + \eta \cdot \nabla U(\vec{r}, t) = 0 \quad (1)$$

In Eq. (1) the following parameters are employed: variable with a dot on the top describes, as usual, a full derivative in time, $\vec{r}$ is a radius-vector of a charged particle with a charge q and mass m, ion cyclotron frequency, $\vec{\omega}_c = \eta\vec{B}, \quad \eta = q/m$, U is an electric potential with the corresponding electric field $\vec{E} = (-\nabla U)$ around ion trajectory, and $\vec{B}$ is a magnetic field vector. At the present stage of ion motion consideration, we assume that the dissipative processes are absent. If both the radius-vector $\tilde{r}(t) = x + iy$ and the electric field vector $\tilde{E} = E_x + iE_y$ are complex variables in a plane transverse to the homogenous magnetic field $\vec{B} = [0, 0, B_z]$, Eq. (1) could be re-written as [27–30]:

$$\ddot{\tilde{r}} + i\omega_c\dot{\tilde{r}} - \eta\tilde{E}(\tilde{r}, t) = 0 \quad (2)$$

A linear (or harmonic), electric field, acting on the ion trajectory, can be described by the following relations in Cartesian coordinates $\tilde{E} = E_x + iE_y = C(x + iy)$, C = const. In a linear field, the well-known solution of Eq. (2) can be each of the two decoupled ion phasors, namely $\tilde{r}_+$ and $\tilde{r}_-$, rotating with different time-independent angular frequencies, ω_+ and ω_-, as well as their linear sum [25–30,54]:

$$\tilde{r} = \tilde{r}_+ + \tilde{r}_- = r_+ \exp[\pm i(\omega_+ t + \phi_{0+})] + r_- \exp[\pm i(\omega_- t + \phi_{0-})] \quad (3)$$

In the superposition, Eq. (3), r_+ and r_- are constants, and ϕ_0 is the initial angular phase correspondingly for $\tilde{r}_+$ and $\tilde{r}_-$. To analyze the transient generation it is required to determine ion trajectory $(r(t), \varphi(t), \dot{r}(t), \dot{\varphi}(t))$ with the initial parameters $(r_0, \varphi_0, \dot{r}_0, \dot{\varphi}_0)$. Upon calculation of Eq. (3) typically certain values of r_+, r_-, ϕ_{0+}, and ϕ_{0-} are taken as initial conditions. As a rule, it is assumed that radii are the real constants and both ϕ_{0+} and ϕ_{0-} are equal to 0. However, there is no known procedure for r_+, r_-, ϕ_{0+}, and ϕ_{0-} direct measurement. To calculate their values one must first obtain, experimentally or theoretically, a number of physical parameters, such as ion initial coordinates and velocities. Note, the ion trajectory can be calculated if the frequency of ion motion is found as a function of time and if the initial parameters are known.

The characteristic algebraic equation for the static, time-independent and constant along an ion trajectory, frequency ω = const of ion motion in linear constant electric field is usually derived by the substitution of a phasor $\tilde{r}$ into Eq. (2) [25–30,33,45–47,54]:

$$\omega^2 - \omega\omega_c + \eta\frac{\tilde{E}}{\tilde{r}} = 0 \quad (4)$$

The algebraic Eq. (4) is employed to describe ion motion during the ion detection event, when $\tilde{E}/\tilde{r}$ = const. The solution of Eq. (4) is a pair of spectral static partial ion motion frequencies: reduced cyclotron ω_+ and magnetron ω_- frequencies, which do not depend on ion coordinates and/or time on the trajectory:

$$\omega_\pm = \frac{\omega_c}{2} \pm \left(\frac{\omega_c^2}{4} - \eta\frac{\tilde{E}}{\tilde{r}}\right)^{1/2} = \frac{\omega_c}{2} \pm \left(\frac{\omega_c^2}{4} - \eta C\right)^{1/2} \quad (5)$$

Although solutions given by Eqs. (3)–(5) are useful and widely employed in FTMS theory, they do not explicitly present the IF $\tilde{\omega}(t)$ spectra of an ion's radius-vector $\tilde{r}(t)$ oscillations, and, importantly, are not applicable in the presence of non-linear fields.

Furthermore, Eqs. (2)–(5) were derived for FT-ICR MS in a typical approximation that ion motion both along magnetic field and transverse to it can be considered independently. However, this is possible only for a linear (harmonic) field along all three coordinates when components of this field are not coupled. Thus, 1D ion axial motion is typically described independently from a transverse (r, φ) motion by a differential equation of the second order, derived from Eq. (1):

$$\ddot{\tilde{z}} - \eta \cdot (E_{z0} + \tilde{E}_z) = 0 \quad (6)$$

In Eq. (6) variable $\tilde{z}$ is an ion coordinate along the z-axis (along the magnetic field in FT-ICR MS). In the quadratic potential distribution the harmonic electric field along the axis is given by $E_{z0} = -\partial U/\partial z = -2C\tilde{z}, \quad C = 2U_0/d_0^2 = \text{const}$. In this case, when the non-linear field $\tilde{E}_z = 0$, ion axial oscillations take place with a frequency not dependent with time: $\omega_{z0}^2 = -\eta(E_{z0}/\tilde{z}) = \eta(4U_0/d_0^2) = 2\eta C$. Solutions of Eq. (6) are thus harmonic oscillations with a constant frequency ω_{z0} [3,27–30,57]. In this exceptional case, formal relation $\eta C = (1/2)\omega_{z0}^2$ is typical for Eq. (5) in the FT-ICR MS literature [3]. However, frequency of axial oscillations in the presence of non-linear fields cannot be accounted for by this approach, vide infra.

In the environment of the ICR and Orbitrap cells non-linear fields include: the space-charge field, the RF excitation field, the image charge and induced current-generated field, the field distorted by the misalignment of the cell geometry, and the force field created upon ion collisions with neutrals, e.g., residual gases [25,41,44–48,52,54,58–60]. Importantly, non-linearity of an electric field should lead to a non-linear form of Eq. (6) [40]. However, Eq. (6) is not compatible with substitution of an axial electric field dependent on both coordinates, (r, z). To account for such fields, it is required to develop the theory of 2D ion oscillators in the r, z plane. Similarly, in the transversal plane, Eqs. (4) and (5) do not allow substitution of such non-linear fields as this would introduce frequency dependence on time, which contradicts the original approximations for derivation of these equations. For