# PRACTICAL ASPECTS OF TRAPPED ION MASS SPECTROMETRY

Volume V

Applications of Ion Trapping Devices

*Edited by* Raymond E. March John F. J. Todd



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# 10 Sympathetically-Cooled Single Ion Mass Spectrometry

Peter Frøhlich Staanum, Klaus Højbjerre, and Michael Drewsen

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## **10.1 INTRODUCTION**

Many mass spectrometry methods have been demonstrated, refined and applied since the first technique was introduced nearly a century ago [1]. As is documented, for example, by the previous contributions to the present series of books *Practical Aspects of Ion Trap Mass Spectrometry* [2], several of these techniques involve ion trapping. An obvious question to ask at this juncture is: do we need still more methods? We believe that the answer to this question is 'yes', and we hope that we are able to present a good case through this contribution to the current volume.

New mass spectrometric methods emerge typically when a higher precision in measurements is needed and when new experimental approaches become feasible. It is with respect to the latter circumstance that the present contribution should be viewed. Recently, we have been interested in exploring the possibilities of carrying out experiments with a single trapped molecular ion cooled sympathetically by a single laser-cooled atomic ion trapped simultaneously. The prospects for such single molecular ion experiments are manifold. First, this situation (to be described in more detail below) makes it possible to perform experiments with molecules one at the time, such that ensemble averaging is obviated. Second, due to the sympathetic cooling, the molecular ion can be translationally very cold as well as spatially localized. Third, under ultra-high vacuum (UHV) conditions, experiments can be carried out in the absence of perturbations of the internal state of the molecules. Consequently, the above features make such single molecular ions ideal targets for a wealth of investigations including coherent manipulations of single molecular ions by laser light. For the proposed investigations, the objective was to develop a simple in situ and non-destructive mass measurement method for the identification of a single trapped molecular ion.

In Section 10.2 is discussed the principal idea of our novel SCSI-MS (Sympathetically-Cooled Single Ion Mass Spectrometry) technique for performing single-ion mass measurements in the light of already well-established techniques. This discussion is followed by both a description of the current experimental arrangement, used for single molecular ion experiments (Section 10.3), and an account of the

present status of experiments with single molecules (Section 10.4). Thereafter, various issues that may limit the potential of this method are examined and the effects of these issues in practical applications (Section 10.5) are evaluated. This chapter concludes with a brief survey of experiments that may be facilitated through exploitation of this technique in the near future (Section 10.6).

# 10.2 SINGLE-ION MASS MEASUREMENTS

In this section, a brief discussion is presented of existing techniques for performing single-ion mass measurements. This discussion is followed by a description of the non-destructive SCSI-MS technique that has been developed recently in this laboratory [3], and a comparison of the SCSI-MS technique with methods established previously.

# 10.2.1 COMMON SINGLE-ION MASS SPECTROMETRY TECHNIQUES

Detection of a single ion is generally fairly easy, because the direct detection of a particle with a single elementary charge can be achieved with close to 100% efficiency, provided the particle is accelerated to an energy of a few electron-volts. This feature is used, for example, in more traditional mass spectrometers such as the quadrupole mass filter (QMF) [4,5] and the time-of-flight (TOF) instrument [4,6], where the ion in each case hits eventually an electron multiplier detector (for example, a channeltron detector). In the more recent technique of Fourier Transform Ion Cyclotron Resonance (FT-ICR) mass spectrometry [7], single ion sensitivity can again be obtained, but this time through a non-destructive measurement of cyclotron motion induced image charges in pick-up plates. While FT-ICR can be used to reach formidable accuracies in mass measurements through high precision frequency measurements (relative mass resolution [8]  $m/\Delta m = 10^{11}$  compared to  $10^2-10^6$  for QMF/ TOF measurements [5,6], where m is the mass of interest and  $\Delta m$  the uncertainty with which it can be determined), it is limited in its ability to make spatial and timeresolved measurements as compared to the QMF and TOF techniques. This ability to make spatial and time-resolved measurements means that the QMF and TOF mass measurement techniques are employed usually in fast dynamic experiments where the mass of the particles of interest may change due to reactions or photofragmentation, while FT-ICR is applied often in 'static' precision measurements and slower dynamics situations.

# 10.2.2 THE SCSI-MS TECHNIQUE

A schematic of the SCSI-MS technique is presented in Figure 10.1. The technique relies on the measurement of the resonant excitation frequency of one of the two oscillatory modes of a trapped and crystallized linear two-ion system consisting of one laser-cooled atomic ion of known mass and the *a priori* unknown atomic or molecular ion, whose mass is to be determined. From this measured frequency, the mass of the unknown ion can be deduced from a simple relation between the frequency and the relative masses of the two ions (see Section 10.3).



**FIGURE 10.1** Sketch of the SCSI-MS technique. Shown in the figure are the linear RF ion-trap electrodes, the cooling laser beams and the CCD camera used to monitor the fluorescence from the laser-cooled atomic ion. An image-intensifier-based shutter that can be gated phase-locked to a periodic driving force is installed in front of the camera. A driving force, for excitation of the ion motion along the *z*-axis, is applied either in the form of a sinusoidally-varying voltage applied to the end-cap electrodes of the ion trap or through modulation of the scattering force on the atomic ion by using an EOC for intensity modulation. (Reproduced from Drewsen, M.; Mortensen, A.; Martinussen, R.; Staanum, P.; Sørensen, J.L., *Phys. Rev. Lett.* 2004, *93*, 243201. With permission from the American Physical Society.)

The crystallization of the two-ion system results from the sympathetic cooling of the unknown ion through the Coulomb interaction with the laser-cooled ion. This crystallization can be observed by imaging the fluorescence light emitted by the lasercooled ion onto a charge-coupled device (CCD) camera chip. Here, a well-localized spot appears with the atomic ion displaced a specific distance away from the iontrap center when it is trapped together with a non-fluorescing unknown ion, see, for example, Figure 10.4b. In the linear RF trap used in these experiments (see Section 10.3), the two-ion system is aligned along the trap's main axis (the z-axis in Figure 10.1). The resonant excitation is promoted either by applying a sinusoidally-varying electric field along this axis (through sinusoidally-varying voltages applied to the end electrodes of the ion trap) that will exert a force on both ions, or by modulating periodically the laser intensity of at least one of the cooling laser beams propagating along the main axis; this latter action leads to a periodically-varying scattering force on the laser-cooled ion. The resonance frequencies are determined by monitoring the fluorescence light from the laser-cooled ion by the CCD camera while scanning the period of the applied driving force. When the period is equal to the period of one of the two oscillatory modes of the two-ion system (that is, the center-of-mass (COM) mode, where the ions move in phase, or the breathing (BR) mode, where the ions move with opposite phase [9,10]), the motion of the ions is most highly excited (neglecting damping exerted by the cooling lasers). For CCD camera exposure times larger than

the oscillation period of the ions, an enlarged axial extension of the fluorescence spot is observed close to these mode resonance frequencies. The simplest way to obtain an estimate for the mode frequency, and hence the mass of the unknown ion (see Section 10.3), is to look for a maximum amplitude in the motion of the laser-cooled ion while changing the period of the force. This detection method leads easily to a relative mass resolution below 10<sup>2</sup>, and can lead, for optimized conditions, to a resolution at the 10<sup>4</sup> level. However, when the phase of the motion of the laser-cooled ion is monitored over a longer period, a more precise measurement is expected (see Section 10.5.6.2). The phase of the motion is monitored by gating the CCD camera such that light emitted only at a certain phase of the motion with respect to the phase of the driving force is detected (see Section 10.3.4). Such measurements have been shown [3] to lead to relative mass resolutions,  $m/\Delta m$ , of about  $3 \times 10^4$ .

It is worth mentioning here that both detection methods are non-destructive, and that the ion of interest (the unknown ion) is translationally cold and extremely well-localized spatially both before and after each a mass measurement. This feature of the measurements is highly relevant to the successful achievement of several experiments proposed for the future (see Section 10.6).

#### 10.2.3 Advantages and Disadvantages of the SCSI-MS Technique

It is interesting first to note that in contrast to standard mass measurement techniques, a strong Coulomb coupling between ions (the ion of interest and the laser-cooled atomic ion) is essential, rather than being problematical. However, as is discussed in Section 12.5, the non-linear nature of the Coulomb interaction between the two ions can lead to unwanted systematic errors in the mass measurements.

While the relative mass resolution of ca 10<sup>4</sup> of the SCSI-MS technique can compete very well with standard QMF and TOF mass spectrometers, the mass accuracy of the SCSI-MS technique will probably never be able to challenge that of FT-ICR mass spectrometry; nevertheless, this shortcoming does not mean that the new technique is irrelevant. On the contrary, the SCSI-MS technique encompasses the advantages of high spatial and temporal resolution from QMF and TOF together with the ability to perform non-destructive detection from FT-ICR.

Due to the simple and open ion-trap structure, laser and molecular beams can be integrated more easily into the SCSI-MS technique (see Figures 10.2 and 10.3,[11]) than into a FT-ICR mass spectrometer with its large bulky super-conducting solenoid cooled cryogenically. Furthermore, because the SCSI-MS technique is compatible with micro-traps that are under development currently by the ion-trapping community (see for example Stick *et al.* [12]), this technique has the potential for possible future commercialization.

A limitation of the SCSI-MS technique in its present linear RF trap version is the requirement that the mass of the unknown singly-charged ion be within the range  $(ca \ 0.3-3)m_{at.ion}$ , where  $m_{at.ion}$  is the mass of the laser-cooled atomic ion, in order to achieve stable operating conditions with respect to the dynamical confining potential (see Section 10.3.1). With the availability of more atomic ion species that can be laser cooled, it will be possible to extend the range of masses that can be measured with the present complex experimental arrangement beyond the Mg<sup>+</sup> and Ca<sup>+</sup> ions that are



**FIGURE 10.2** (a) Sketch of the linear ion trap used in the experiments. The various parameters are defined in the text of Section 10.3.1. (b) Photograph of the actual ion trap used. As a scale, the center part of the electrode structure  $(2z_0)$  is 5.4 mm long. (Reproduced from Drewsen, M.; Jensen, L.; Lindballe, J.; Nissen, N.; Martinussen, A.; Mortensen, A.; Staanum, P.; Voight, D., *Int. J. Mass Spectrom.* 2003, 229, 83–91. With permission from Elsevier.)

investigated presently in Aarhus. In principle, singly-charged ions from 1 to *ca* 600 Th should be measurable.

Because the equilibrium position of the laser-cooled ion depends on the charge state of the unknown ion, the SCSI-MS technique measures both the charge and the mass of the unknown ion, and not merely the charge-to-mass ratio as do most mass spectrometers. This feature means that higher-charge states can be used, in some cases, to expand the measurable range of masses.

Recently, the axial alignment of two ions in a Penning trap has been demonstrated [13]. When a sufficiently general procedure can be realized such that any two simultaneously-trapped ions can be so aligned, the above-mentioned mass range for a single laser-cooled atomic ion species may be increased also.

# **10.3 EXPERIMENTAL REALIZATION**

In this section is presented the experimental arrangement for the experiments to be discussed in the succeeding sections.

## 10.3.1 THE LINEAR RF ION TRAP

The type of ion trap used in the experiments discussed below is a so-called linear RF(Paul) ion trap [14,15]. A schematic diagram of this ion trap is shown in Figure 10.2a



FIGURE 10.3 Photo of the linear RF ion trap inside the cylindrical vacuum chamber used in the experiments. The chamber has an inner diameter of 30 cm. The numbers in the picture indicate the essential components of the instrument. (1) The linear RF ion trap. (2) The magnesium and calcium ovens, which are the sources for the atomic beams passing through the center of the ion trap. (3) Oven shutter. (4) Skimmer plates, used to collimate the effusive beams from the ovens in order to avoid contamination of the ion-trap electrodes. (5) Electron gun including deflection plates installed to make an electron beam cross the atomic beams in the center of the ion trap for ion production. (6) One of two sets of oppositely-positioned window openings for sending in laser beams for laser cooling of the ions along the main ion-trap axis (the z-axis) and along an axis perpendicular to the z-axis. (7) A piece of optical fiber, with known diameter, that can be translated into the ion-trap center for calibration of the magnification of the lens system used to image the fluorescence of the laser-cooled ions. (8) One of two opposed window openings that permit a laser beam to cross the atomic beams nearly at right angles in the ion-trap center for producing ions by photoionization. Not seen in this picture is a CCD camera to monitor the fluorescence from the laser-cooled ions through a window in a top-flange of the vacuum chamber (not shown). Also not seen is a leak valve controlled inlet for the admission of various gasses into the ion-trap region. (Reproduced from Drewsen, M.; Jensen, L.; Lindballe, J.; Nissen, N.; Martinussen, A.; Mortensen, A.; Staanum, P.; Voight, D., Int. J. Mass Spectrom. 2003, 229, 83–91. With permission from Elsevier.)

while a photograph of the ion trap is shown in Figure 10.2b. The ion trap, similar to a standard QMF, consists of four electrodes with an RF voltage of the same phase applied to diagonally-opposed electrodes, but with a phase difference of 180° between the two sets of opposite electrodes. This arrangement leads to a near-ideal two-dimensional quadrupole field in the plane perpendicular to the direction defined by the electrodes (that is, the z-direction). Each electrode is divided into three parts such that a positive DC voltage, U, can be applied to the eight end-cap electrodes. While this DC voltage leads to static confinement along the z-axis of the ion trap, it gives rise to a defocusing force in the radial plane perpendicular to this axis. By appropriate choices of U, and the RF peak-to-peak voltage, V, as well as the RF frequency,  $\Omega$ , both axial and radial confinement can be obtained for the given ion-trap dimensions [16,17]. The confinement can be described in terms of the stability parameters

$$a_z \equiv \eta \frac{8neU}{m\Omega^2 z_0^2} \tag{10.1}$$

for the static confinement along the z-axis,

$$a_r \equiv -\frac{a_z}{2} = -\eta \frac{4neU}{m\Omega^2 z_0^2} \tag{10.2}$$

and

$$q_r \equiv \frac{2neV}{m\Omega^2 r_0^2} \tag{10.3}$$

for the motion in the radial plane, where *m* is the mass of the ion, *n* is the number of elementary charges, *e*, on the ion,  $z_0$  and  $r_0$  are the ion-trap dimensions as defined in Figure 10.2a, and  $\eta$  is a positive geometric parameter dependent on  $z_0$  and  $r_0$ . Whenever  $a_z > 0$  and  $a_r$  and  $q_r$  lie within certain stability regions [16], stable single-ion trajectories exist. The motion is generally complex but, when  $q_r < 0.4$ , a single ion not too far from the trap center will experience an effective harmonic potential,  $\varphi(z,r)$ 

$$\phi(z,r) = \frac{1}{2}m(\omega_z^2 z^2 + \omega_r^2 r^2)$$
(10.4)

where  $\omega_z$  and  $\omega_r$ , the oscillatory frequencies along the *z*-axis and in the radial plane, respectively, are given by

$$\omega_z = \frac{1}{2}\Omega\sqrt{a_z} \tag{10.5}$$

$$\omega_r = \frac{1}{2} \Omega \sqrt{\frac{q_r^2}{2} + a_r}$$
(10.6).

In the radial plane, the ions will be subject to the force from the effective potential above in addition to a fast oscillating force at the RF frequency; however, it can be shown that the amplitude of the corresponding motion (often named the micromotion) will be much smaller than the distance of the ion from the *z*-axis when  $q_r < 0.4$  [18]. In the experiments to be presented here, two ions are cooled such that both of them lie on the *z*-axis, hence we can neglect generally this rapid quiver motion.

The ion trap used in the experiments and shown in Figure 10.2b has the following dimensions:  $r_0 = 3.50$  mm,  $z_0 = 2.70$  mm,  $z_{endcap} = 20.00$  mm, and R = 4.00 mm; these values have been chosen in order to achieve a nearly perfect radial quadrupole RF field [19] and a near-harmonic DC-axial potential over a few millimeters. Numerical simulations show that these choices of ion-trap dimensions result in  $\eta = 0.248$ . The applied RF field is coupled resonantly to the ion-trap electrodes at a radial frequency

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 $\Omega = 2\pi \times 3.88$  MHz with a peak-to-peak amplitude *V* of typically 300–500 V. With a typical DC voltage of *ca* 1 V, Equation 10.4 gives rise to a potential-well depth of *ca* 1 eV. Because this energy is many orders of magnitude higher than the thermal energy of the cooled ions and the thermal energy of the background gas, the storage time of the ions can be hours or more at a typical vacuum of *ca* 10<sup>-10</sup> mbar. In Figure 10.3, a photograph of the ion trap (see also Figure 10.2b) and other important components in the experimental vacuum chamber are presented.

# 10.3.2 LASER-COOLING OF ATOMIC IONS

# 10.3.2.1 Loading of Atomic Ions

The atomic ions used in the experiments presented in Section 10.4 are created by crossing a skimmed atomic beam originating from an effusive oven with a photoionizing laser beam at the center of the ion-trapping region. This method has many advantages in comparison to the more usual electron impact ionization technique. First of all, resonance-enhanced photoionization is not only element selective but is isotope selective also [20,21]. Second, because photoionization is very efficient, these experiments may be carried out using low laser powers and low atomic beam fluxes. The adequacy of low atomic beam fluxes for these experiments means that ovens can be operated at relatively low temperatures with the accompanying benefit of a minimal pressure rise in the vacuum chamber. During ion loading, the pressure in the vacuum chamber increases by less than  $10^{-10}$  mbar above the base pressure of  $ca \ 2 \times 10^{-10}$  mbar. Lastly, but actually very importantly for the SCSI-MS technique presented in this contribution, the problem of electrical charging of the insulating parts near the ion-trapping zone is kept at a minimum because only one free electron is created for each atomic ion created. In our laboratory, both singly-charged magnesium and calcium ions can be produced currently by photoionization [20].

# 10.3.2.2 Cooling of the Atomic Ions

To laser-cool a trapped particle in an harmonic potential well characterized by three different oscillation frequencies, only a single laser beam propagating in a direction different from the three major axes of motion is needed. However, in our experiments to decouple the cooling along the *z*-axis from the cooling in the radial plane, as well as being able to establish a balanced force along the *z*-axis, the atomic ions produced are Doppler laser cooled [22] by two counter-propagating laser beams (of the appropriate wavelengths for the particular ion species in use) along the *z*-axis of the trap and by one beam propagating perpendicularly to this axis (see Figure 10.3). With this cooling configuration, the laser-cooled ion(s) can reach readily a temperature below 10 mK, a temperature at which the ions become spatially localized to *ca* 1 µm or less (see Figure 10.4a). Through the Coulomb interaction between the laser-cooled ion and a simultaneously-trapped unknown ion, both ions can be cooled. For appropriate trapping parameters, this sympathetic cooling [23] can lead to temperatures of a few milliKelvins and can bring into alignment the two ions along the *z*-axis (Figure 10.4b).



**FIGURE 10.4** Images of fluorescence from  ${}^{40}Ca^+$  ions. (a) Two  ${}^{40}Ca^+$  ions at thermal equilibrium in the trap. (b) A laser-cooled  ${}^{40}Ca^+$  ion trapped together with a sympathetically-cooled  ${}^{40}Ca^+O^+$  ion at thermal equilibrium. (c) The same two  ${}^{40}Ca^+$  ions as in (a) but with a modulation voltage applied at a frequency near the COM mode resonance frequency of 98.7 kHz. (d) The same ions as in (b) but with a modulation voltage applied at a frequency of 89.4 kHz. In all experiments, the radial trap frequencies were 380 kHz and the exposure time of the CCD chip was 100 ms. (Reproduced from Drewsen, M.; Mortensen, A.; Martinussen, R.; Staanum, P.; Sørensen, J.L., *Phys. Rev. Lett.* 2004, *93*, 243201. With permission from the American Physical Society.)

# 10.3.2.3 Fluorescence Detection

The fluorescence imaging system used in these experiments consists, briefly, of an imaging lens system that, with a magnification of typically  $\times$  10, images light from the central ion-trapping region to the surface of an image intensifier (the shutter in Figure 10.1) that is connected to a CCD camera *via* a relay lens of magnification  $\times$  2. During the laser-cooling process, the cooled ion emits typically *ca* 10<sup>7</sup> fluorescence photons per second. With a total photon detection efficiency of the imaging system of about  $10^{-4}$ – $10^{-3}$ , some  $10^3$ – $10^4$  photons per second are detected. Because typically a few hundred detected photons are needed for a satisfactory ion-position determination, camera integration times of the order of *ca* 100 ms are needed. Examples of fluorescence images are presented in Figure 10.4a for the case of two atomic ions in the ion trap and in Figure 10.4b for an atomic ion together with an unknown and non-fluorescing ion.

# 10.3.3 INDUCING FORCED MOTION OF THE IONS

The SCSI-MS technique relies on the determination of the common mode resonance frequencies for a two-ion system in which the mass is known for only one of the ions. In order to determine these resonance frequencies, the two-ion system is subjected to a periodic driving force. The forced motion of the ions can be induced in two ways: (1) by applying a sinusoidally-varying voltage to some of the end electrodes of the ion trap; and (2) by modulating the radiation pressure force from one of the laser beams propagating along the *z*-axis by chopping its intensity using an electro-optical chopper (EOC).

## 10.3.3.1 Electrical Forces

A sinusoidally-varying driving force can be obtained by applying a modulation voltage to some of the ion-trap end-cap electrodes (see Figure 10.2). The COM mode can be excited effectively by applying a time-varying homogenous electric field along the *z*-axis. This maneuver can be achieved easily by modulating the voltage applied to two diagonally-opposed end-cap electrodes at one end of the ion trap. In order to excite effectively the BR mode, a time-varying electric field that has a gradient along the *z*-axis is needed. This situation can be realized when a common modulation voltage is applied simultaneously to sets of end-cap electrodes at both ends of the ion trap.

Three potentials are combined in order to achieve the desired degree of control of the electrode potential; these potentials are (1) a constant DC potential for static trapping, (2) a modulation potential of *ca* 100 kHz for COM and BR mode excitation, and (3) an RF potential of *ca* 4 MHz for ion trapping in the radial plane. As indicated in the diagram shown in Figure 10.5, the modulation voltage is added to the DC voltage before it is combined with the RF voltage and led ultimately to the ion trap. The  $L_1, C_1$  filter suppresses the modulation voltage on the DC end; the  $R_1, C_3$  filter ensures a strong suppression of RF voltage at the DC end while allowing a fraction of the modulation voltage to pass the other way. The adjustable capacitor,  $C_5$ , is used for fine-tuning the RF voltage on the electrode.

A home-built programmable frequency synthesizer provides the modulation voltage for the COM and for the BR mode excitation. This synthesizer is able to step through a series of frequencies and, thus, to perform a scan across the expected resonance while delivering a trigger signal to the camera to ensure a well-defined frequency for each single image. In addition, the synthesizer outputs a short gating pulse with a variable phase delay that can be used to gate the image intensifier for phase measurements (see Section 10.3.4.2, below). The size of the frequency steps, the time between each step, and the modulation amplitude are adjustable and provide flexibility for the tailoring of scans. Furthermore, the synthesizer can hold in memory up to 10 predefined scans which, together with an option to loop when reaching the end of the last scan, permits repeated frequency scans of relevant masses.

## 10.3.3.2 Radiation Pressure Forces

Not only can the radiation pressure force lead to ion cooling through the Dopplereffect, but it can be used further to exert a periodic force on the atomic ions. By modulating the intensity of one of the two laser-cooling beams propagating along



**FIGURE 10.5** Electrical diagram showing how the modulation voltage is added to the ion-trap voltages.

the *z*-axis, the atomic ions can be induced to experience a periodic driving force. In these experiments, one axial laser-cooling beam is directed through an electro-optic modulator (EOM) and a linear polarizer in tandem. By appropriate adjustment of the polarization of the laser beam entering the EOM and the orientation of the polarizer, the two optical elements can together act as an EOC when the correct voltages are applied to the EOM. The programmable frequency synthesizer described in the previous section controls the shutter.

Test mass measurement experiments have shown that, at least at the level of  $m/\Delta m$  ca 10<sup>3</sup>, the two methods for introducing a periodic driving force do not lead to any systematic errors.

#### **10.3.4** DETECTION OF THE MOTION OF THE IONS

Before discussing the various ways of detecting the excited motion of the ions, first let us discuss briefly some basic theoretical issues of forced dynamics. For the linear RF ion trap described in Section 10.3.1, the potential energy for two singly-charged ions aligned along the *z*-axis is described well by the one-dimensional harmonic potential  $\Phi(z_1, z_2)$ 

$$\Phi(z_1, z_2) = \frac{1}{2}\kappa z_1^2 + \frac{1}{2}\kappa z_2^2 + \frac{e^2}{4\pi\varepsilon_0 |z_2 - z_1|}$$
(10.7),

where  $z_1$  and  $z_2$  are the positions of the two ions, respectively,  $\kappa$  is a spring constant, and  $\varepsilon_0$  is the permittivity of vacuum. The equilibrium positions of the ions when cooled to low temperatures are  $z_2 = -z_1 = \Delta z/2$  ( $z_2 > z_1$ ), with

$$\Delta z = \left(\frac{e^2}{2\pi\varepsilon_0\kappa}\right)^{1/3} \tag{10.8}$$

being the equilibrium ion distance.

Under such conditions, the strongly-coupled motion of the ions, mediated by the Coulomb interaction and for small excursions, gives rise to two axial normal motional modes. Using the fact that the spring constant  $\kappa$  can also be expressed in terms of the single ion oscillation frequency of the two ions  $\omega_i$  (*i* = 1,2) through

$$\kappa = m_i \omega_i^2 \tag{10.9}$$

the eigenfrequencies of these two modes can be found to be [10]

$$\omega_{+,-} = \left(1 + \frac{1}{\mu} \pm \sqrt{1 - \frac{1}{\mu} + \frac{1}{\mu^2}}\right) \omega_1^2$$
(10.10),

where  $\mu = m_2/m_1$ . The solutions  $\omega_+$  and  $\omega_-$  correspond to the mode with eigenvectors where the ions move in phase (COM mode) and out of phase (BR mode), respectively, with mass-dependent amplitudes.

Equation 10.10 displays the mass dependence of the oscillation frequency for the two normal modes that is essential for the non-destructive SCSI-MS technique. From a measurement of either  $\omega_+$  or  $\omega_-$  as well as  $\omega_1$  (the oscillation frequency of the known laser-cooled ion species), the mass ratio  $\mu$  and, hence, the mass  $m_2$  of an unknown ion species can be determined. Alternatively, by measuring the ratio between  $\omega_+$  and  $\omega_-$ , Equation 10.10 gives rise to an equation with solutions  $\mu$  and  $1/\mu$ . In such a case,  $\mu$  can be determined without measurement of  $\omega_1$ , provided that it is known that either  $\omega_+ > \omega_1$  or  $\omega_+ < \omega_1$ .

In the experiment, we try to determine  $\omega_1$ ,  $\omega_+$ , and  $\omega_-$  by resonant excitation of the ion motion through the application of a periodic driving force (see Section 10.3.3). In practice, the situation is complicated slightly by the fact that the lasercooled ion(s) is (are) subject to a damping force due to the laser-cooling process. In this case, the equations of motion read

$$\ddot{z}_1 - \frac{F_{Dopp,1}(\dot{z}_1)}{m_1} + \omega_1^2 z_1 = -\frac{e^2}{4\pi\varepsilon_0 m_1 (z_2 - z_1)^2} + \frac{F_{drive,1}}{m_1} \cos(\omega t)$$
(10.11)

and

$$\ddot{z}_2 - \frac{F_{Dopp,2}(\dot{z}_2)}{m_2} + \omega_2^2 z_2 = \frac{e^2}{4\pi\varepsilon_0 m_2 (z_2 - z_1)^2} + \frac{F_{drive,2}}{m_2} \cos(\omega t)$$
(10.12),

where  $F_{Dopp,i}$  denotes the Doppler cooling force applied to ion *i* and  $F_{drive,i}$  is the driving force applied to ion *i*. For two identical laser-cooled ions, one obtains  $F_{Dopp,1} = F_{Dopp,2}$ , while for two different ions where only ion 1 is assumed to be laser cooled, one obtains  $F_{Dopp,2} = 0$ . For end-cap electrode excitation, we choose  $F_{drive,1} = F_{drive,2}$  for COM mode excitation and  $F_{drive,1} = -F_{drive,2}$  for BR mode excitation. For excitation by laser modulation we have either  $F_{drive,1} = F_{drive,2}$  (identical ions) or  $F_{drive,2} = 0$  (different ions).

For small ion velocities the Doppler cooling force in Equations 10.11 and 10.12 can be approximated by a viscous damping force that is proportional to velocity,  $F_{Dopp,i} = -m_i \gamma_i \dot{z}_i$ , where  $\gamma_i$  is a constant that depends on the laser wavelength, intensity, detuning, and the ion mass [21]. Assuming small velocities and small excursions from the equilibrium positions, the motion for two identical ions can be described in terms of normal mode coordinates  $z_+ = (z_2 + z_1)/\sqrt{2}$  and  $z_- = (z_2 - z_1 - \Delta z)/\sqrt{2}$  for the COM and the BR mode, respectively, by the uncoupled equations of motion

$$\ddot{z}_{+,-} + \gamma_1 \dot{z}_{+,-} + \omega_{+,-}^2 z_{+,-} = \frac{F_{+,-}}{m_1} \cos(\omega t)$$
(10.13),

where  $F_{+,-} = (F_{drive,2} \pm F_{drive,1})/\sqrt{2}$ . Each of these equations of motion is that of a classical driven, damped harmonic oscillator with the solution leading to

$$z_{1}(t) = \frac{F_{+,-}}{\sqrt{2}m_{1}\sqrt{(\omega^{2} - \omega_{+,-}^{2})^{2} + \gamma_{1}^{2}\omega^{2}}}\cos(\omega t + \varphi) - \frac{\Delta z}{2} \equiv z_{0}(\omega)\cos(\omega t + \varphi) - \frac{\Delta z}{2}$$
(10.14),

where

$$\cos(\varphi) = \frac{\omega_{+,-}^{2} - \omega^{2}}{\sqrt{(\omega_{+,-}^{2} - \omega^{2})^{2} + \gamma_{1}^{2}\omega^{2}}}$$
(10.15).

For ions with different masses, the solution of the equation of motion for the 'detector' ion (ion 1) is much more complex [24] and reads as

$$z_{1}(\omega,t) = \frac{F_{drive,2}}{\kappa} \\ \left[ \cos(\omega t + \varphi)(2\omega_{2}^{2} - \omega^{2}) \sqrt{\frac{\left[ (2\omega_{1}^{2} - \omega^{2}) + \frac{F_{drive,1}}{F_{drive,2}} \omega_{1}^{2} \right]^{2} + \gamma_{1}^{2} \omega^{2}}{\left[ \omega^{4} - 2(\omega_{1}^{2} + \omega_{2}^{2})\omega^{2} + 3\omega_{1}^{2} \omega_{2}^{2} \right]^{2} + \gamma_{1}^{2} (2\omega_{2}^{2} - \omega^{2})^{2} \omega^{2}} - \cos(\omega t) \right] - \frac{\Delta z}{2}$$
(10.16).

where

 $\cos(\phi) =$ 

$$\frac{\left[(2\omega_{1}^{2}-\omega^{2})F_{drive,2}+\omega_{1}^{2}F_{drive,1}\right]\cdot\left[\omega^{4}-2(\omega_{1}^{2}+\omega_{2}^{2})\omega^{2}+3\omega_{1}^{2}\omega_{2}^{2}\right]+F_{drive,2}\gamma_{1}^{2}(2\omega_{2}^{2}-\omega^{2})\omega^{2}}{\left[(2\omega_{1}^{2}-\omega^{2})F_{drive,2}+\omega_{1}^{2}F_{drive,1}+i\gamma_{1}\omega F_{drive,2}\right]\cdot\left|\omega^{4}-2(\omega_{1}^{2}+\omega_{2}^{2})\omega^{2}+3\omega_{1}^{2}\omega_{2}^{2}+i\gamma_{1}(2\omega_{2}^{2}-\omega^{2})\omega^{2}\right|}$$
(10.17)

with  $\omega_i (i = 1, 2)$  defined through  $\kappa = m_i \omega_i^2$ .

The amplitude of the laser-cooled ion is enhanced resonantly near  $\omega_+$  and  $\omega_$ with maxima shifted from  $\omega_+$  and  $\omega_-$  by an amount that increases with  $\gamma_1$ . The resonance width is approximately  $\gamma_1$ . The in-phase amplitude has a dispersive shape, as for identical ions, and when only the laser-cooled ion is subject to a driving force (excitation by laser modulation) the amplitude has a zero-crossing at  $\omega_+$  and  $\omega_-$ . For electrode excitation, where both ions are driven, the zero-crossing is offset from  $\omega_+$  or  $\omega_-$  by an amount that, for  $\gamma_1/\omega_{+-} \ll 1$  is of the order of  $(\gamma_1/\omega_{+-})^2$ . Intuitively, such an offset is present because, when both ions are driven, the driven motion of the non-cooled ion perturbs the phase of the laser-cooled ion. In contrast, when only one ion is driven, the other ion is 'pulled' or 'pushed' into phase with the driven ion.

## 10.3.4.1 Amplitude Detection

In the amplitude method, the motion of the ions over many oscillation periods (typically 10<sup>4</sup> periods) is integrated such that it is the modulation frequency-dependent amplitude that is observed. The most precise determinations of the normal mode frequencies are found through fitting the relevant expression for  $z_1(\omega)$  (that is Equation 10.14 for identical ions and Equation 10.16 for non-identical ions) to the measured amplitudes of the laser-cooled ion as a function of the drive frequency, as shown in

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Figure 10.6a for two identical ions. For many purposes, however, it is sufficient simply to determine the modulation frequency where the amplitude is maximal, which occurs at

$$\omega_{\max} \approx \omega_{+,-} \tag{10.18},$$

because  $\gamma/\omega_{+,-}$  is typically *ca* 10<sup>-3</sup>–10<sup>-2</sup>. The relative error in the measurement of  $\omega_{+,-}$  is thus often smaller than 10<sup>-4</sup>.

In Figure 10.4c and d, images of two laser-cooled atomic ions and one atomic and one molecular ion (CaO<sup>+</sup>) are presented when applying a driving force of a frequency close to  $\omega_+$ . The smearing of the fluorescence as compared to Figure 10.4a and b, shows clearly that the ions are excited motionally.

#### 10.3.4.2 Phase Detection

In the phase-detection method, the image intensifier is gated such that the camera integrates only light emitted in a short time interval in phase with the driving force. Hence it is the amplitude of the component of the ion motion which is in phase with the driving force that is recorded, that is,  $z_1(\omega)\cos(\phi)$ . This in-phase amplitude shows the characteristic dispersive profile observed in Figure 10.6c and g and features a sharp zero-crossing of the in-phase amplitude near or at  $\omega_{+-}$ .

With laser light modulation, the voltage pulse for the gating signal can be overlapped temporally with the light pulse by detecting the latter with a photo diode. The adjustment of the detection phase is slightly more difficult when using the electrode excitation driving force, because the circuit used to couple the driving voltage to the electrodes leads to a frequency-dependent phase shift of the signal originating from the frequency synthesizer.

## **10.4 EXPERIMENTAL RESULTS**

In this section, some recent experimental results obtained in this laboratory using the SCSI-MS technique are described.

In the first part, Section 10.4.1, experiments with atomic ions involving either two laser-cooled <sup>40</sup>Ca<sup>+</sup> ions or one laser-cooled <sup>40</sup>Ca<sup>+</sup> ion trapped together with another Ca<sup>+</sup> isotope or a Mg<sup>+</sup> ion are considered. These experiments serve to test the accuracy of the SCSI-MS technique. In Section 10.4.2, experiments performed with single molecular ions are presented: (1) the reaction Ca<sup>+</sup> + O<sub>2</sub> $\rightarrow$ CaO<sup>+</sup> + O; (2) the reaction Mg<sup>+</sup> + HD $\rightarrow$ MgD<sup>+</sup>(MgH<sup>+</sup>) + H(D), in which a strong isotope effect was observed; and (3) experiments that demonstrate trapping and sympathetic cooling of single more complex ions, namely aniline ions, together with a study of their consecutive photofragmentation.

As explained in Section 10.2, a non-destructive mass measurement can be performed by measuring the characteristic oscillation frequencies of the COM and/or the BR mode of a two-ion crystal. These frequencies can be determined by exciting the COM and the BR mode motion with a periodic driving force (see Section 10.3.3). In Figure 10.6 are shown the detected amplitude and the in-phase amplitude signals



as a function of drive frequency for electrical excitation of the COM mode as well as the BR mode of two <sup>40</sup>Ca<sup>+</sup> ions. While the amplitude and the in-phase signals are well described by the basic theory given in Section 10.3 (Equations 10.13 and 10.14) for the COM mode, the BR mode signals show strong asymmetries. The origin of this latter asymmetry is discussed further below as well as in Section 10.5 [25].

# **10.4.1** EXPERIMENTS WITH ATOMIC IONS

# 10.4.1.1 Two Calcium Ions

Because the amplitude of the driven COM mode motion observed in Figure 10.6a is well described by Equation 10.14,  $\omega_+$  can be determined accurately from a fit to the data. Equation 10.13 is exact for the COM mode in the sense that no expansion of the Coulomb interaction term was needed for identical ions; hence, the solution in Equation 10.14 should be valid for arbitrary amplitudes. In order to verify this condition, the amplitude was recorded as a function of drive frequency for different driving forces. All of the amplitudes could be fitted to Equation 10.14 and, as shown in Figure 10.7, the center frequencies near 95.625 kHz are identical within 20 Hz, thus showing good agreement with the basic theory.

In contrast, Equation 10.13 for the BR mode is correct for small amplitudes only. As shown in Figure 10.8, even at moderate amplitudes a significant asymmetry of the amplitude profile is evident with a sharp drop in amplitude on the high frequency side of the resonance. As discussed in more detail in Section 10.5, the shape of the amplitude profile is caused by a non-linear response ('frequency-pulling' [26]) because the oscillation frequency is increasing with the amplitude. While frequency-pulling is an interesting non-linear phenomenon, in the present context it leads, unfortunately, to difficulties in making an accurate determination of the 'true' BR mode frequency, that is, the eigenfrequency at small amplitudes.

# 10.4.1.2 One Calcium and One Magnesium Ion

For the case of two non-identical ions, the COM mode frequency is also amplitude dependent. In order to investigate this effect, the amplitude was recorded as a function of drive frequency for one <sup>40</sup>Ca<sup>+</sup> ion and one <sup>24</sup>Mg<sup>+</sup> ion. As shown in Figure 10.9,

**FIGURE 10.6** (Opposite) The position-resolved ion fluorescence along the ion-trap axis as a function of the drive frequency of the modulation voltage. Each gray scale contour plot is composed of axial projections of the ion fluorescence intensity in images recorded during the frequency scans (step size: (a,c) 25 Hz/image, (b,d) 100 Hz/image). (a) and (c) show an excitation of the COM mode with the image intensifier in normal and gated modes, respectively, while (b) and (d) show an excitation of the breathing mode (BR) also with the image intensifier in normal and gated modes, respectively. The dark lines in the fluorescence track in (a) and (c) are due to shelving of the <sup>40</sup>Ca<sup>+</sup> ion in the non-fluorescing 3d <sup>2</sup>D<sub>5/2</sub> state [24]. (e through f): Amplitude of the ion motion as a function of the drive frequency. The amplitude is found from (a through b) as the difference between the HWHM of the fluorescence signal at a given drive frequency and the HWHM of the non-excited ion (that is, at a far-off resonant drive frequency). (g through h): In-phase amplitude of the ion motion as a function dive frequency. The in-phase amplitude is found from (c through d) as the center of the ion fluorescence track.



**FIGURE 10.7** Measured oscillation frequency for the COM mode of two laser-cooled  ${}^{40}Ca^+$  ions at different amplitudes. The dotted line indicates the mean value of 95.625 kHz.



**FIGURE 10.8** Amplitude *vs.* drive frequency for the BR mode of two laser-cooled <sup>40</sup>Ca<sup>+</sup> ions at different driving forces. The vertical line indicates the expected BR resonance frequency assuming no non-linear frequency pulling.

only at large amplitudes can a significant asymmetry of the amplitude profile be observed. The small asymmetry observed at low amplitudes can be explained by the slightly asymmetric shape of the amplitude predicted by Equation 10.16; such an asymmetry is predicted also by Equation 10.14 where it can be recognized as being due to the damping coefficient  $\gamma$ . The BR mode motion for two non-identical ions shows an asymmetry similar to that shown in Figure 10.7 for two identical ions. Figures 10.6 through 10.9 indicate that the 'true' COM mode frequency can be determined more easily and more accurately than the 'true' BR mode frequency. While this statement is true generally, there may be, on occasion, good reason to make use of the BR mode as is discussed further in Section 10.5 [27].



**FIGURE 10.9** Amplitude *vs.* drive frequency for the COM mode of one laser-cooled  ${}^{40}Ca^+$  ion and one  ${}^{24}Mg^+$  ion at different driving forces. The solid lines indicate fits to a model similar to that developed by Evoy et al. [27]. The fits yield the same resonance frequency for all of the five scans.



**FIGURE 10.10** Measured oscillation frequencies for three combinations of Ca<sup>+</sup> isotopes. The stated resonance frequencies are the statistical averages of the respective data points [3]. The horizontal position of the data points reflects the time order of the experiments. (Reproduced from Drewsen, M.; Mortensen, A.; Martinussen, R.; Staanum, P.; Sørensen, J.L., *Phys. Rev. Lett.* 2004, *93*, 243201. With permission from the American Physical Society.)

#### 10.4.1.3 Precision Mass Measurements of Calcium Isotopes

In order to test the accuracy of the SCSI-MS technique, the masses of the calcium isotopes  ${}^{42}Ca^+$  and  ${}^{44}Ca^+$  were measured with reference to the mass of the  ${}^{40}Ca^+$  ion; one of the isotopes was trapped together with a  ${}^{40}Ca^+$  ion and the COM resonance frequency was determined by the phase-detection method (see Ref. [3]). As a reference, the COM frequency for two  ${}^{40}Ca^+$  ions was determined also by the phase-detection method. The experimental oscillation frequencies from a series of measurements

are presented in Figure 10.10. Using Equation 10.10, mass ratios of  $\mu_{40/42} = 0.9526(3)$ and  $\mu_{40/44} = 0.9095(3)$  can be deduced from the results. Within the uncertainties of  $3 \times 10^{-4}$  these results are in agreement with the expected values of  $\mu_{40/42} = 0.952441$ and  $\mu_{40/44} = 0.909174$  [28].

## **10.4.2** EXPERIMENTS WITH MOLECULAR IONS

Molecular ions can be produced, trapped and cooled by the application of a variety of techniques. Within this laboratory, we can use essentially three methods: (I) reaction of trapped and laser-cooled atomic ion species with neutral molecules in a gas leaked into the vacuum chamber of the ion-trap apparatus; (II) electron impact ionization, using an electron gun, of neutral molecules leaked into the ion-trap center (see Figure 10.3); and (III) photoionization of leaked-in neutral molecules.

In the following discussion, attention is focused on experiments using methods I and III only, because method II in our current experimental arrangement leads to unwanted high charging of insulating material close to the ion-trapping zone. This problem could be solved, however, by utilizing a more complex linear ion-trap configuration that permitted the movement of ions from an 'ion production-region' to a 'mass-spectrometry-region'.

Alternatively, a molecular ion could be introduced from an ion beam either by opening and closing rapidly the trapping potential along the *z*-axis or by introducing temporarily a buffer gas into the ion-trapping region while loading a molecular ion [29].

## 10.4.2.1 CaO + lons

As a simple test of reaction method I, the reaction  $Ca^+(4p) + O_2 \rightarrow CaO^+ + O$ , was chosen because it gives rise to a relatively large mass difference between the reactant atomic ion and the product molecular ion. Upon application of the amplitude detection method together with on-line monitoring of the amplitude of the ions' motions on the CCD images when scanning the frequency in steps of 100 Hz, it was possible to obtain not only a mass resolution better than 10<sup>2</sup> but to distinguish that the CaO<sup>+</sup> ion shown in Figure 10.4b and d was, indeed, a <sup>40</sup>Ca<sup>16</sup>O<sup>+</sup> ion [3].

Furthermore, this reaction made it possible to monitor a subsequent  $CaO^+ + CO \rightarrow Ca^+ + CO_2$  reaction by leaking CO gas into the chamber. This latter reaction was observed readily by fluorescence from the Ca<sup>+</sup> ion appearing as the product ion outcome of the reaction [30].

## 10.4.2.2 MgH<sup>+</sup> and MgD<sup>+</sup> lons

In another series of experiments, the reaction between Mg<sup>+</sup> ions in the 3p excited state and hydrogen molecules and its isotopologues was studied [31,32]. Attention was focused specifically on the outcome of the reaction between Mg<sup>+</sup>(3p) ions and HD molecules. From only *ca* 250 single reaction events, the branching ratio between MgD<sup>+</sup> and MgH<sup>+</sup> formation was found to be greater than five [32]. The results are illustrated in Figure 10.11 where the ratio of the numbers of MgD<sup>+</sup> ions and MgH<sup>+</sup> ions observed is plotted as a function of the pressure ratio between HD and the unavoidable H<sub>2</sub> in the vacuum chamber. At high values of this ratio, where reactions with HD dominate, a clear preference for MgD<sup>+</sup> formation is seen. The solid line in



**FIGURE 10.11** The ratio of the number of MgD<sup>+</sup> and MgH<sup>+</sup> ions produced in reactions Mg<sup>+</sup> + HD/H<sub>2</sub> $\rightarrow$ MgD/H<sup>+</sup> + H/D at different ratios of the pressures of HD and H<sub>2</sub>, ( $P_{HD}/P_{H2}$ ) where each P is italized but not emboldened. The solid line indicates a fit to the model described in Ref. [32]; the dashed line indicates the prediction of the model in the absence of isotope effects. (Reproduced from Staanum, P.F.; Højbjerre, K.; Wester, R.; Drewsen, M., *Phys. Rev. Lett.* 2008, *100*, 243003. With permission from the American Physical Society.)

Figure 10.11 indicates the fit to a simple model that is described in Ref. [32], while the dashed line indicates the prediction of the model in the absence of isotope effects. The observation of this strong isotope effect provides insight into the details of the reaction dynamics in a reaction that should be a simple test case for theoretical modeling. Further insight was gained from additional measurements with  $H_2$  and  $D_2$  ions, which showed that the probability of forming either a MgH<sup>+</sup> or a MgD<sup>+</sup> ion from any of the intermediate MgH<sub>2</sub><sup>+</sup>, MgHD<sup>+</sup>, or MgD<sub>2</sub><sup>+</sup> complexes is the same [32].

## 10.4.2.3 The Aniline Ion and its Photofragments

A series of experiments with the aniline ion  $(C_6H_5NH_2^+)$  illustrates the application of the SCSI-MS technique to complex molecular systems and demonstrates that it is possible to study consecutive photodissociation of molecular ions at the single ion level in an ion trap [33]. In addition to providing detailed information on fragmentation processes, such consecutive dissociation processes provide also a probabilistic way of preparing a wealth of single molecular ions that could be objects for further study or serve as reactant ions in other experiments.

The aniline ion was formed through photoionization into a series of ro-vibrational states. From certain states further dissociation is possible through absorption of a single photon from the cooling laser [33]. By continuously scanning a broad range of masses, such consecutive dissociation reactions were detected. A reaction sequence where the ions  $C_6H_6^+$ ,  $C_6H_5^+$ , and finally,  $C_3H_3^+$  were produced and detected consecutively is presented in Figure 10.12 [33]. Identification of the fragment ions was facilitated by a complementary set of experiments with fully deuterated aniline. Furthermore, it was found that the  $C_3H_3^+$  ion was produced in its cyclic configuration,



**FIGURE 10.12** A consecutive photodissociation sequence observed in an experiment with a single aniline molecular ion being the initial reactant. (Reproduced from Højbjerre, K.; Offenberg, D.; Bisgaard, C.Z.; Stapelfeldt, H.; Staanum, P.F.; Mortensen, A.; Drewsen, M. *Phys. Rev. A.* 2008, *77*, 030702(R). With permission from the American Physical Society.)

that is, the cyclopropenium ion, as tested through a series of reaction experiments between  $C_3H_3^+$  ions and  $C_2D_2$  molecules [33].

# 10.5 ACCURACY OF THE SCSI-MS TECHNIQUE

In this section, various effects that can limit the accuracy of the SCSI-MS technique are considered. In particular, deviations from the idealized case considered in Section 10.3.4, due to finite size motional amplitudes and the effects of the Doppler cooling force will be discussed.

## 10.5.1 LASER-COOLING FORCE

Doppler laser-cooling is an essential ingredient in the SCSI-MS technique. First, it provides the necessary damping force to cool directly and sympathetically the atomic and molecular ions, respectively, such that a cold and strongly-coupled twoion system is formed. Second, it gives rise to the fluorescence photons used in the detection process. Third, the radiation pressure force can be modulated to excite the common motion of the ions.

In Section 10.3.4, the Doppler cooling force was approximated by a frictional force characterized by a friction (or cooling) rate  $\gamma_1$ . This approximation can be shown to be valid whenever the velocity *v* of the cooled ion is much smaller than the absolute value of the detuning of the laser cooling light,  $|\delta|$ , divided by the wavenumber  $k = 2\pi/\lambda$  of the light driving the cooling transition [22].

For the experiments involving <sup>40</sup>Ca<sup>+</sup> and <sup>24</sup>Mg<sup>+</sup>, the cooling rate  $\gamma_1$  needed was as low as  $2\pi \times 100$  Hz when applying a strong radial cooling. This condition required

detunings of the order of  $ca -10 \Gamma$ , where  $\Gamma$  is the cooling transition linewidth; such detunings can be applied readily but they lead to constraints on the velocity, v, of the ion such that  $v_{\text{max}} ca 80 \text{ m/s}$ .

For typical COM or BR mode resonance frequencies of  $\omega_{+,-}$  of  $ca 2\pi \times 100$  kHz and excitation amplitudes of  $ca 10 \,\mu\text{m}$ , the maximal ion velocity is ca 6 m/s, and hence is much smaller than the value for  $v_{\text{max}}$  stated above. Because the ion velocity is less than  $v_{\text{max}}$ , the frictional force approximation can be met readily.

For the results presented in Figure 10.7 with large excitation amplitudes, the magnitude of the laser detuning was only 1–2  $\Gamma$ , and so the frictional force approximation was fulfilled for over only part of the ion trajectory. The measured oscillation frequency was (within the error of the measurements), however, essentially independent of the maximum amplitudes because the  $\gamma_1$  dependence of the amplitude is weak for  $\gamma_1 \ll \omega_z$  (see Equation 10.14). By taking measurements while using larger detuning, the relative shift in the resonance frequencies due to the non-linear friction force can be expected to be smaller than 10<sup>-5</sup>.

For measurements with non-identical ions, another laser-cooling related effect to be considered is the intensity imbalance of the counter propagating beams. Such an imbalance, which gives rise to a constant force induced by the radiation pressure, will push the laser-cooled ion away from its equilibrium position established with balanced beams; in addition, the imbalance will lead to a shift in the mass-dependent trap frequency used in Equation 10.10 [24]. For presently typical parameters ( $\omega_1 = 2\pi \times 100$  kHz,  $\gamma_1 = 2\pi \times 100$  Hz,  $\delta = -\Gamma$ ) and a very conservative assumption of 10% intensity imbalance, the relative frequency shift is, at most,  $1 \times 10^{-5}$  for the COM mode motion of a <sup>40</sup>Ca<sup>+</sup> ion trapped together with an ion that is up to three times lighter or heavier. For the BR mode, the shift is much higher but less than  $4 \times 10^{-4}$ . By minimizing the difference between the resonance frequencies for the two possible ion configurations (that is, with the laser-cooled ion located either to the left or to the right of the ion-trap center), the intensity imbalance effect can probably be reduced to a level of <  $10^{-6}$ .

#### **10.5.2** Non-Linearity in the Coulomb Interaction

In Section 10.3.4, the dynamics were treated of two harmonically-confined ions having small amplitudes of oscillation around the equilibrium positions of the ions. More specifically, in deriving Equations 10.10 and 10.13 (for  $z = z_{-}$ ) it was assumed that the change of the ion distance is small compared to the equilibrium distance  $\Delta z$ , such that the Coulomb interaction energy can be approximated by a harmonic potential. For large changes in the ion–ion distance, additional terms in the Coulomb energy lead to an anharmonic interaction and, hence, to an amplitude-dependent oscillation frequency.

For the COM mode oscillation of *identical* ions, the ions move in the same direction with the same amplitude, corresponding to a normalized eigenvector [9,10] of  $(1,1)/\sqrt{2}$ , which means that the inter-ion separation is always equal to the equilibrium distance. Therefore, the Coulomb interaction energy is simply a constant term in the potential and cannot give rise to an amplitude dependence for the oscillation frequency. Indeed, Figure 10.7 above shows that the oscillation frequency is independent of amplitude. For the BR mode, in contrast, the ions move away from each



**FIGURE 10.13** The ratio between the difference of the eigenvector coordinates and the amplitude of coordinate 1 for the laser-cooled ion as a function of mass ratio,  $\mu$ . The larger relative difference for the breathing mode leads to a larger amplitude dependence of the oscillation frequency.

other (the eigenvector is now  $(1,-1)/\sqrt{2}$ ) such that the inter-ion separation is different generally from the equilibrium distance. Hence, for amplitudes that amount to a significant fraction of the equilibrium distance, the higher-order terms of the Coulomb interaction give rise to an amplitude-dependent oscillation frequency. In Figure 10.8, the shape of the amplitude as a function of drive frequency is, indeed, a result of an amplitude-dependent oscillation frequency as is discussed in more detail below.

For *different* ions, the two coordinates of the eigenvector of the COM mode generally have a different magnitude. Therefore, even for the excitation of the COM mode, the ion distance differs from the equilibrium distance. Hence, for both COM and BR mode motion, higher-order terms of the Coulomb interaction give rise to an amplitude-dependent oscillation frequency. The two coordinates of the eigenvectors,  $q_1$  and  $q_2$ , are mass dependent [10]. In Figure 10.13, the quantity  $|q_2-q_1|/|q_1|$ , that is, the change in ion distance relative to the amplitude of ion 1, which is the observed laser-cooled ion, is shown as a function of the mass ratio  $\mu$ . Clearly, the change in ion distance is much smaller for the COM mode than for the BR mode and, consequently, the COM mode oscillation frequency is much less amplitude dependent than is the BR mode frequency. In the limit of  $\mu \rightarrow 1$  (identical ions), the amplitude dependence vanishes completely for the COM mode.

In a harmonic potential where  $\omega_z = 2\pi \times 100$  kHz for a <sup>40</sup>Ca<sup>+</sup> ion, the equilibrium distance,  $\Delta z$ , equals 26.0 µm, while typically applied amplitudes in the experiments described in Section 10.4 are about 5 µm. In this case, it is necessary to consider the effect of higher-order terms in the Coulomb interaction for the BR mode and, in some cases, also for the COM mode for two different ions. This effect could be reduced, but not eliminated, if much smaller amplitudes could be detected by using a state-of-the-art imaging system with almost diffraction-limited resolution

of  $ca \ 1 \ \mu m$ ; however, there is the cost of additional experimental complexity to be considered because lenses must be mounted inside the vacuum chamber [34].

An amplitude-dependent oscillation frequency implies that the frequency dependence of the driven ion motion becomes non-linear because the resonance condition for the frequency of the driving force is amplitude dependent. The effect of this non-linearity is seen most clearly in Figure 10.6b and d and in Figure 10.8. When one follows the amplitude from the low-frequency side in Figure 10.8, the amplitude continues to rise even after the 'true' small-amplitude resonance frequency has been passed. This behavior is an example of frequency pulling where the effective resonance frequency gets shifted to higher values due to the increased amplitude. Jumps between large and small amplitudes appear around the point where the drive frequency is so far from the small-amplitude resonance frequency that the driving force is able, only marginally, to sustain non-linear oscillations.

As indicated in Figure 10.8, the small-amplitude BR mode frequency is found on the low frequency side of the resonant structure. A 'trained eye' may be able to estimate this frequency with *ca* 1 kHz precision from a series of scans with varied driving force, such as are presented in Figure 10.8. For the COM mode excitation of different ions, such non-linear effects at 5  $\mu$ m amplitude are not seen; only for very large amplitudes can be observed the effect of an amplitude-dependent oscillation frequency, as is shown in Figure 10.9.

In conclusion, at practically-applied amplitudes of *ca* 5  $\mu$ m, the breathing mode oscillation frequency is perturbed significantly by higher-order terms in the Coulomb interaction. Although the amplitude dependent shift prevents very accurate mass measurements based on the BR mode frequency, a measurement of the BR mode frequency can be useful in some situations, as is discussed in Section 10.5.7 below. In contrast, the amplitude-dependent shift of the COM frequency is much smaller than that for the BR mode and, at *ca* 5  $\mu$ m amplitude, will lead typically to a relative shift in the resonance frequency of about 10<sup>-4</sup> or less. For ions of almost the same mass, the shift is particularly small.

## **10.5.3** ION-TRAP IMPERFECTIONS

So far we have considered the one-dimensional motion in a perfectly-harmonic potential. In this section, the various unavoidable effects that give rise to deviations from the ideal case will be discussed.

#### 10.5.3.1 Anharmonicity

In reality, the trapping potential contains terms other than the harmonic one. Higher order even terms ( $z^4$ ,  $z^6$ , etc.) in the potential are unavoidable for practically-feasible shapes of the electrodes. Although odd terms are absent in a perfectly-symmetric trap, the symmetry is, in practice, broken by contact potentials [35] due to material deposited on the electrodes, by surrounding conductive or dielectric elements as well as by small misalignments and imperfections of the electrodes. Hence odd terms proportional to z,  $z^3$ , etc., can be expected to be present also.

A term linear in *z* leads only to a change in the equilibrium positions of the ions but not in oscillation frequency. All terms higher than second order will, however, influence the oscillation frequency. The effect of the *n*th higher-order term can be estimated by assuming the trapping potential to be of the form  $\frac{1}{2}m\omega_{+,-}^2 z^2[1 + (z/z_0)^{n-2}]$ , and by calculating the oscillation period for a given amplitude by integration of the instantaneous velocity. We have carried out such an estimation for n = 3 and n = 4 with  $z_0$  equal to the half-length of the center electrodes (2.7 mm). This choice of  $z_0$  is a worst-case scenario; in reality, higher-order terms are significantly smaller and, in fact, the fourth-order term cancels when the center electrode length is chosen appropriately [24]. We find that for both n = 3 and n = 4 the relative change of the oscillation frequency is less than 10<sup>-5</sup> for amplitudes up to 5 µm and less than 10<sup>-4</sup> for amplitudes up to 20 µm. Hence, at a relative frequency accuracy of 10<sup>-5</sup>, anharmonic effects can be neglected completely.

The effects of anharmonic terms have been sought experimentally by measuring the COM mode frequency at different amplitudes for two  $^{40}Ca^+$  ions. Because the non-linearity of the Coulomb force does not affect the oscillation frequency in this case, any amplitude dependence should be due to either anharmonicity or the non-linear velocity dependence of the Doppler cooling force as discussed in Section 10.5.1. As shown in Figure 10.7, at amplitudes between 15 µm and 35 µm, the measured COM frequencies near 95.625 kHz differ by less than 20 Hz and are equal within the error bars. Hence, at least at the level of  $2 \times 10^{-4}$  anharmonic effects can be ignored. Furthermore, if anharmonic effects were significant, a frequency-pulling effect should have been apparent, but no such effect was observed.

#### 10.5.3.2 Trapping Field Imperfections

The three-dimensional harmonic potential  $\frac{1}{2}m(\omega_x^2 + \omega_y^2 + \omega_z^2)$  gives rise to six normal modes for two ions [36]; the purely axial COM and BR modes, two purely radial modes, and two mixed modes that involve both radial and axial motion. Because the modes are normal at small amplitudes, it is justifiable to consider separately the axial modes, the COM and the BR mode. If, however, the potential contains undesired terms which couple the axial and the radial coordinates, that is to say, *xz* or *yz* terms, the coupling will change the axial eigenfrequencies when the ions are not confined to the *z*-axis. For  $\omega_{x,y} > \omega_z$ , two ions are aligned, on average, along the ion-trap axis [16], however, due to the finite ion temperature (*ca* 5 mK), they will move slightly off the ion-trap axis by up to *ca* 1 µm. Furthermore, when the ions move off the ion-trap axis, heating of the radial motion due to micromotion may be transferred to the axial motion either due to coupling terms in the potential or due to the mode mixing.

Spurious RF fields along the ion-trap axis (for example, due to slightly different RF amplitudes on the 12 electrodes) can give rise to an unwanted confining potential along the ion-trap axis. By minimizing the micromotion along the ion-trap axis, the RF voltages can be matched to within about one percent by adjusting individually the capacitive loads of the electrodes (see Figure 10.5). Let us consider the magnitude of a residual effective RF voltage equal to one percent of a typical applied V of 400 V at  $\Omega = 2\pi \times 4$  MHz. The value of the  $q_z$  parameter is 0.004 for <sup>40</sup>Ca<sup>+</sup> and the corresponding secular frequency is  $2\pi \times 6$  kHz which should be added to the axial ion-trap frequency in quadrature to obtain the total ion-trap frequency. Thus, for a

typical value for  $\omega_1$  of  $2\pi \times 100$  kHz, the axial frequency is changed by a few parts in a thousand. Because the secular frequency is mass dependent, this small change of axial frequency can lead to a correspondingly small error in the mass measurements when the mass is derived from  $\omega_1$  and  $\omega_+$  (see Equation 10.10). For ions with masses close to that for the laser-cooled ion, the systematic relative error may be as small as  $10^{-4}$ .

Finally, the stability of the source for the DC voltage U applied to the end-cap electrodes is obviously an important parameter because the ion-trap frequency is related directly to U through Equations 10.1 and 10.5. With the DC supply at hand, the relative drift of the ion-trap frequency is below  $10^{-4}$  over approximately 15 minutes (see Figure 10.15 below). As discussed in Section 10.5.7, a slow drift is non-critical for many experiments where a reference measurement and a measurement of  $\omega_{+}$  can be made within a short time interval.

#### 10.5.3.3 Residual Magnetic Fields

Residual magnetic fields with a component in the radial plane will couple the radial and axial motions of the ions. The effect of the cyclotron motion on the resonance frequencies  $\omega_{+,-}$  can be judged by considering the simpler single-ion situation. Here, the coupled equations of motion read

$$\ddot{z} + \omega_z^2 z - \omega_c \dot{r} = 0 \tag{10.19}$$

$$\ddot{r} + \omega_r^2 r + \omega_c \dot{z} = 0 \tag{10.20}$$

with  $\omega_z$  and  $\omega_r$  being the axial and radial ion-trap oscillation frequencies, respectively, and with  $\omega_c$  being the cyclotron frequency. In the limit where  $\omega_c \ll \omega_z$  and  $\omega_c \ll \omega_r$  and  $\omega_c \ll |\omega_z - \omega_r|$  the modified axial frequency  $\omega'$  is given by

$$\omega_{z}^{'} \approx \omega_{z} + \frac{1}{2} \frac{\omega_{c}^{2}}{\omega_{z}}$$
(10.21).

For a 'typical' residual magnetic field of *ca* 1 Gauss (if, for example, the Earth's magnetic field is not compensated for), the corresponding cyclotron frequency  $\omega_c$  of the ions is  $ca 2\pi \times 100$  Hz. Hence, with  $\omega_c/2\pi$  being typically of the order of 100 kHz, the relative change in frequency is only of the order of  $10^{-6}$ . A similar result can be found for  $\omega_{+-}$ .

In this laboratory, the amplitude of the residual magnetic field can be reduced readily to 0.1 Gauss, meaning that the effect of the magnetic field can be reduced to a level of  $10^{-8}$ .

#### 10.5.4 ION LOADING

When loading the ion trap with atomic ions, at least two undesirable effects may lead to uncontrolled changes in the trapping frequencies and, hence, may compromise the mass measurements. The effects are, (1) creation of contact potentials [35]



**FIGURE 10.14** Relative shift of the measured ion-trap frequency in a longer series of scans for a single <sup>40</sup>Ca<sup>+</sup> ion. For each scan, the shift is defined as  $\omega/\omega_0$ -1, where  $\omega$  is the trap frequency measured in the scan and  $\omega_0 = 2\pi \times 95.51$  kHz is the frequency measured in the first scan of part (a). (a) A series of scans where the neutral calcium beam is blocked (white background columns) and unblocked (gray background columns) sequentially. (b) Trap frequency measurements where the UV photoionization beam is blocked (white background columns) and unblocked (gray background columns) sequentially. The change of trap frequency when the UV beam is 'on' is most likely due to charging of insulating parts near the ion-trap region.

due to contamination of the ion-trap electrodes by neutral atoms from the effusive atomic beam (see Section 10.3.2), and (2) charging of insulating parts close to the ion-trapping region through photoelectron emission due to stray UV light. In order to investigate the possible influence of the atomic beam, a series of single Ca<sup>+</sup> ion oscillation frequency measurements was carried out while the atomic beam was blocked and unblocked sequentially by a shutter (see Figure 10.3). During these measurements, the UV photoionization beam was blocked. Similarly, the influence of the photoionization beam was investigated in another series of measurements where the UV photoionization beam was blocked and unblocked sequentially while the atomic beam was blocked. The measured single ion oscillation frequencies are shown in Figure 10.14 for both series of measurements. While no evidence for a systematic effect was found due to the atomic beam flux, the UV photoionization beam gives rise to oscillation frequency changes in the 100 Hz range. The rapid initial rise in the oscillation frequency followed by a slower rise in subsequent 'on' periods indicates that the charging of the affected insulating parts reaches a steady state eventually. The source of the "problematic" UV light is currently unknown, but it is likely either weak reflections from the exit window in the vacuum chamber (even though it is anti-reflection coated at 272 nm) or weak halo-like structures surrounding the main ionization beam. When the source is identified, its effect can probably be reduced dramatically by proper beam shaping and positioning. The effects observed here for calcium will most likely be observed also for other ions such as beryllium, magnesium, and mercury, which can be laser cooled; for these ions, photoionization requires UV light at 235, 285, and 185 nm, respectively. Furthermore, the laser cooling light at 313, 280, and 194 nm for beryllium, magnesium, and mercury, respectively, may cause charging effects. To avoid the charging problem in the special case of calcium, photoionization can be achieved using two lasers in succession at the wavelengths 423 nm and 390 nm, respectively [37]. This arrangement would probably significantly reduce the problem observed in the experiments with light of 272 nm. Another more complex, but general, solution to the photoionization loading problem, would be to employ a linear ion trap with multiple trapping zones, loading ion(s) into one zone, a 'loading zone', and transferring the trapped ion(s) into another 'experiment zone' [38].

## 10.5.5 BACKGROUND GAS

The main effect of background gas (residual gas or reactant gas) is due to ion/neutral collisions of background gas with the cold atomic and molecular ions. Some collisions are manifested by a sudden disappearance of fluorescence light because the ions acquire sufficient kinetic energy to move away from the ion-trap axis. They are, however, typically not expelled from the pseudo-potential well of depth *ca* 1 eV and, after a while, they become laser-cooled sufficiently to be re-aligned along the ion-trap axis and they resume fluorescing.

In this laboratory, the base pressure in the vacuum chamber is  $ca \ 10^{-10}$  mbar, at which collisions are extremely rare, that is to say about one in several minutes. For reaction studies, a gas pressure up to  $10^{-9}-10^{-8}$  mbar is applied typically. In these cases, it is possible to carry out scans of the drive frequency wherein few, if any, ionheating events occur. At much higher pressure, collision events can be observed so frequently that the analysis of a scan becomes unfeasible.

Another potential effect issuing from the introduction of a gas is the creation of contact potentials due to contamination of the electrodes. As a test of this effect, the COM mode frequency was measured for two <sup>40</sup>Ca<sup>+</sup> ions, before and after O<sub>2</sub> gas was leaked into the vacuum chamber at a pressure of  $10^{-7}$  Torr for a few minutes. Between the measurements, <sup>40</sup>Ca<sup>+</sup> ions were reloaded. Only a small shift at the level of  $1 \times 10^{-4}$  in the COM mode frequency was observed; this shift may be related to the reloading procedure (see Section 10.5.4).

Finally, it can be speculated as to whether there are other pressure-related effects, such as damping introduced by close or distant collisions that may influence the mass determination. However, the oscillation frequency of two <sup>40</sup>Ca<sup>+</sup> ions has been measured at pressures up to 10 times higher than the base pressure without observing any systematic effects.

## 10.5.6 PHOTON DETECTION

#### 10.5.6.1 Spatial Resolution

The position of a laser-cooled ion is measured by imaging the fluorescence light emitted during the Doppler laser-cooling process onto a CCD camera. There are two fundamental factors that limit the resolution: the spatial resolution of the imaging system and the finite ion temperature. While the resolution of the imaging system is independent of the trapping parameters, the thermal excursion of the laser-cooled ion at a fixed temperature scales as  $\omega_z^{-1}$ . From the simple physics point of view of being able to monitor small motional energy excitations, one would choose typically an ion-trap frequency  $\omega_z$  such that the thermal excursions of the ion are roughly the same as the spot size resolution of the imaging system. The better the resolution of the imaging system, the higher can be the ion-trap frequency, and the more precise can be the measurements expected. However, for a particular experimental arrangement, the effect of the non-linearity in the Coulomb interaction (see Section 10.5.2) must be taken into account when choosing  $\omega_z$ .

In this laboratory, the resolution is dominated by the spot size resolution of the imaging system which is about 3  $\mu$ m HWHM, while the amplitude for a <sup>40</sup>Ca<sup>+</sup> ion is less than 2  $\mu$ m at a temperature of 5 mK and an ion-trap frequency of 2 $\pi$  × 100 kHz.

## 10.5.6.2 Scattering Rate and Collection Efficiency

The number of collected photons from an ion is proportional to the photon scattering rate, the collection efficiency, and the CCD exposure time  $T_{exp}$ . Through the imaging system, the number of collected photons is converted to a digital signal for each pixel on the CCD chip. In Figure 10.6a through d, these pixel values are projected onto the z-axis for each drive frequency and the projected value is indicated by the grey scale coding. In the following discussion, the (z-dependent) projected value of the signal is termed S. The signal-to-noise ratio, S/N, that is, the signal divided by its standard deviation, limits the precision with which the frequency  $\omega_{+}$  can be determined. In order to determine  $\omega_{\perp}$  with a precision  $\Delta \omega$  from either the amplitude or the in-phase amplitude as a function of drive frequency (see Figure 10.6e and g), the uncertainty of the measured amplitude must be less than the variation of the amplitude over the frequency interval  $\Delta\omega$ . For the amplitude method, this variation is simply  $\Delta\omega^2$  times the curvature  $ca A_0/\gamma_1^2$ , where  $A_0$  is the maximal amplitude. The uncertainty on the amplitude is of the order of  $A_0(S/N)^{-1}$ , from which it follows that  $\Delta \omega \approx \gamma_1 / \sqrt{S/N} \propto$  $T_{\rm exp}^{-1/2}$ . For the phase method, the variation of amplitude over  $\Delta\omega$  is  $\Delta\omega$  times the slope  $A_0/\gamma_1$  which implies that  $\Delta \omega \approx \gamma_1/(S_g/N_g) \propto T_{exp}^{-1}$ , where the subscript 'g' indicates the S/N ratio when the image intensifier is gated.

In Figure 10.15 are shown the running average and its statistical uncertainty for a series of measurements of the COM mode frequency for two <sup>40</sup>Ca<sup>+</sup> ions where either the amplitude method (Figure 10.15a) or the phase method (Figure 10.15b) is applied. The statistical uncertainty for each measurement is in reasonable agreement with the estimates of  $\Delta \omega$  given above. The limiting value of the average, with a statistical uncertainty of only *ca* 2 Hz, is reached with fewer phase-method measurements than with the amplitude method measurements. The limiting value is reached, however, in approximately the same measurement *time*, because the amplitude method scans were five times faster than were the phase method scans.

In the estimates of  $\Delta\omega$  above, it has been assumed tacitly that the damping coefficient  $\gamma_1$  is much larger than is the inverse exposure time that, indeed, is the case in these experiments. When this assumption is not fulfilled, the width of a resonance has an additional contribution from the inverse integration time. In the extreme case of  $\gamma_1 \ll 1/T_{\rm exp}$ , it is found that  $\Delta\omega \propto T_{\rm exp}^{-3/2}$  for the amplitude method and  $\Delta\omega \propto T_{\rm exp}^{-2}$  for the phase method.



**FIGURE 10.15** Running average and statistical uncertainties of the COM mode frequency for two <sup>40</sup>Ca<sup>+</sup> ions obtained (a) with the amplitude method and (b) with the phase method. For the amplitude method, the CCD exposure time was 100 ms and *S/N ca* 17, while for the phase method the exposure time was 500 ms and  $S_g/N_g ca$  6.  $\gamma_1$  is  $2\pi \times 113$  Hz in both cases, yielding  $\Delta \omega ca 2\pi \times 27$  Hz for the amplitude method and  $\Delta \omega$  is  $ca 2\pi \times 19$  Hz for the phase method. These values are in reasonable agreement with the statistical uncertainty of about  $2\pi \times 7$  Hz for both methods. The total measurement times for the amplitude measurements and the phase measurements were 13 minutes and 23 minutes, respectively.

## **10.5.7** Reference Measurements

In order to determine the mass of an unknown ion from a measurement of the COM mode frequency using Equation 10.10, a reference measurement of  $\omega_1$  is needed. Alternatively, from a measurement of  $\omega_+$  and  $\omega_-$ ,  $\mu$  can be determined provided that  $\omega_1$  is known sufficiently well to determine whether  $\omega_+ < \omega_1$  or  $\omega_+ > \omega_1$ . The best choice of the reference measurement depends on the specific use of the SCSI-MS technique as well as the uncertainty on the mass derived from the frequency measurements.

In reaction experiments as described in Section 10.4.2.2, where two laser-cooled ions are trapped and one of them reacts to form an unknown molecular ion species, a reference measurement of  $\omega_1$  with two laser-cooled ions can be carried out easily in appropriate time intervals before the reaction occurs. In this way,  $\omega_1$  is measured shortly before  $\omega_+$  such that a slow drift of  $\omega_1$ , due to changing DC voltage for example, has negligible influence. Similarly, in experiments where a single lasercooled ion is trapped and a second unknown ion is loaded, a fragment of a complex molecular ion [33] or a super-heavy ion species for example [39–41], a reference measurement of  $\omega_1$  can be made with the single ion.

In a longer reaction sequence, for example either of bi-molecular reactions as described in Section 10.4.2.1, or photoreactions as described in Section 10.4.2.3, or a combination thereof, a drift of the ion-trap frequency would compromise the mass measurements for the different reaction steps. A linear drift can be corrected for by measuring the ion-trap frequency before and after the reaction sequence, provided that the necessary trap loading after the sequence does not give rise to significant shifts of the ion-trap frequency. Measurement of  $\omega_+$  and  $\omega_-$  during the

reaction sequence can effect a supplementary, self-referenced mass measurement. Since  $\omega_{+}$  and  $\omega_{-}$  can be measured within a short time interval, the self-referenced measurement is unaffected by slow drifts. The main drawback of this measurement is the reduced precision with which  $\omega_{-}$  can be determined due to the strong amplitude dependence. In combination, the two measurements should enable accurate mass measurements over long time scales even in the presence of a small drift of the ion-trap frequency.

Finally, we recall from Section 10.5.3.2 that, in case there is a significant induced secular potential due to an RF field along the ion-trap axis, the mass determination from  $\omega_1$  and  $\omega_+$  will contain a small error, while the mass determined from  $\omega_+$  and  $\omega_-$  will not be influenced by this error source.

The uncertainties on the measured frequencies, either  $\omega_1$  and  $\omega_+$  or  $\omega_+$  and  $\omega_-$ , translate to an uncertainty on the mass  $m_2$  of the unknown ion determined from Equation 10.10. As shown in Figure 10.16, the relative uncertainty depends on the chosen reference measurement as well as the mass ratio  $\mu$ . For a mass ratio larger than 1.25, it appears to be advantageous to determine the mass from  $\omega_+$  and  $\omega_-$ , however, the difficulties in making a precise determination of  $\omega_-$  are sufficiently severe that a mass measurement based on  $\omega_1$  and  $\omega_+$  is generally preferable, provided that error sources, which are more severe for mass measurements based on  $\omega_1$  and  $\omega_+$ , for example, drift of the ion-trap frequency and RF-induced secular potentials, are sufficiently small.



**FIGURE 10.16** The ratio between the relative uncertainty on the unknown ion mass and the relative uncertainty of the frequency measurement  $(\Delta\omega/\omega = \Delta\omega_1/\omega_1 = \Delta\omega_+/\omega_+ = \Delta\omega_-/\omega)$  as a function of mass ratio  $\mu$ . The two curves represent only COM mode measurements (One reference measurement of  $\omega_1$  and one measurement of  $\omega_+$ ) and combined COM and BR mode measurements, respectively.

#### **10.5.8** Choice of Parameters

Regardless of whether the COM mode frequency or the BR mode frequency is measured by either the amplitude or the phase method, it is advantageous to be able to measure low amplitudes in order to reduce, as much as possible, amplitudedependent shifts due to the Coulomb interaction. Furthermore, a weak cooling force along the ion-trap axis (z-axis) leads to a narrow resonance and, hence, to a more precise frequency determination. Because a strong radial cooling force is advantageous, the optimum situation is to be able to change the detunings independently of the radial and axial laser beams. However, as proven by the experimental results presented in this chapter, an acceptable compromise can be found normally using fixed detuning and different light intensities. The choice of ion-trap frequency is a compromise between several requirements: on the one hand a high relative precision  $(\omega_{\pm}/\Delta\omega)$  and a small ion spot width requires a large ion-trap frequency; on the other hand amplitude-dependent frequency shifts are reduced for a large equilibrium ion distance, that is, for a small trap frequency. It was found that with the relatively poor image resolution (spot size of ca 3  $\mu$ m HWHM) in our setup  $\omega_{\pm}$  ca  $2\pi \times 100$  kHz and  $\gamma_1 ca 2\pi \times 100$  Hz is a convenient set of parameters that enables accurate mass determination at the level of  $10^{-4}$ .

From the discussion in Section 10.5.6, it is clear that the amplitude method and the phase method have their advantages and disadvantages. The phase method features a sharp zero crossing which enables an accurate frequency determination. The price to pay is the long integration time required in order to obtain an adequate *S/N* ratio, because light is collected only during a fraction of the oscillation period. The amplitude method is much faster, but the profile of the amplitude is not so sharp. Ultimately, for large  $S_g/N_g$ , the phase method is, therefore, the more accurate one but, with the present error sources at the level of a few times  $10^{-4}$ , the amplitude method is superior owing to the shorter measurement time.

#### **10.6 CONCLUSION AND OUTLOOK**

In this Chapter, we have presented a mass spectrometric technique, the SCSI-MS technique that relies on the measurement of the normal mode frequencies of strongly-coupled two-ion systems. The strongly-coupled regime is reached by sympathetic cooling of the ion of interest (the unknown ion) through the Coulomb interaction with a simultaneously-trapped and laser-cooled atomic ion. The technique is inherently a single ion mass spectrometric technique, utilizing a non-destructive detection step. This latter feature of the SCSI-MS technique is suitable particularly for monitoring mass changes by, for example, either photofragmentation (see Section 10.4.2.3) or multiple-step reactions. The single ion aspect of such studies enables one not only to obtain an ensemble-averaged result, but presents the opportunity for comparing individual ion "histories". In particular, in experiments that involve complex molecular ions with complex internal structures, such individual ion "histories" may be essential for the identification of important processes.

Though our current experimental arrangement has not been optimized for SCSI-MS, we have proven that a mass resolution of  $m/\Delta m$  of  $ca \ 10^4$  can be obtained (see Section 10.4).

Based on the discussion in Section 10.5 of the various effects that can limit the mass resolution, there seems to be room for improvement in the measurement accuracy by a factor of 10–100 and, hence, mass measurement with an accuracy of  $m/\Delta m \approx 10^5-10^6$  should be within reach. In this respect, the main error sources to be minimized are charging effects during loading of ions (Section 10.5.4) and imperfections in the RF-field configuration (see Section 10.5.3.2). By a modest optimization of our current experimental arrangement, we expect to be able to achieve a relative mass measurement accuracy of < 10<sup>-4</sup>, and thus be able to discriminate between various mass doublets (for example, <sup>24</sup>MgH<sup>+</sup> and <sup>25</sup>Mg<sup>+</sup>).

In the future, we are also planning to exploit other advantageous features of SCSI-MS, namely, the excellent optical access to the ions in the trap and the fact that the ion of interest is both translationally cold and spatially very well localized. Currently, we plan to cool MgH<sup>+</sup> ions rotationally by irradiating the molecular ion with infrared light that drives a single vibrational transition [42,43]. This experiment can serve as a preparation step for doing cold chemistry. It is, furthermore, very compelling to exploit the extreme spatial localization of a molecular ion to study phase-sensitive coherent processes induced by laser light [44,45].

Finally, as mentioned briefly also in Section 10.5.7, the SCSI-MS technique may possibly find applications in the studies involving exotic ions, such as superheavy element ions [39] or rare isotope elements, because the technique can lead to quantitative results using only a relative small number of ions as is illustrated in Section 10.4.2.2.

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