Sympathetic cooling and detection of molecular ions in a Penning trap

M. A. van Eijkelenborg, M. E. M. Storkey, D. M. Segal, and R. C. Thompson
Blackett Laboratory, Imperial College of Science, Technology and Medicine, Prince Consort Road, London SW7 2BZ, United Kingdom
(Received 29 April 1999)

We have trapped and sympathetically cooled the molecular ions HCO$^+$ and N$_2$H$^+$ in a Penning trap. Through their Coulomb interaction with laser-cooled Mg$^+$ ions the molecules were sympathetically cooled to cryogenic temperatures. We identify the molecules through a measurement of their characteristic mass-dependent breathing mode frequencies. From a measurement of the temperature of the Mg$^+$ ions we estimate that the final temperature of the sympathetically cooled molecules is 4 K. [S1050-2947(99)04611-9]

PACS number(s): 32.80.Pj, 33.80.Ps, 52.70.−m, 52.65.–y

I. INTRODUCTION

Laser cooling of trapped ions has led to a multitude of high-precision experiments. Atomic and molecular ions can be stored for long periods of time in a nearly perturbation free environment, which is ideal for high-resolution spectroscopy. Convontional Doppler cooling requires a near two-level system such that shortly after laser excitation the atom will return to the initial state for the cooling cycle to be repeated. Unfortunately, laser cooling of molecules is not possible; due to the complicated vibrational-rotational level structure one cannot find an appropriate near-two level system to use as a cooling transition [1–3]. Sympathetic cooling offers a solution to these problems.

Simultaneous trapping of more than one molecular ion species and a study of ion/molecule reactions has been reported [4]. Further, sympathetic cooling of one species of atomic ions by another has been achieved [1,5–10], and it has recently been shown that a single laser cooled ion can maintain the crystalline order of a crystal of 15 ions through sympathetic cooling [11]. The sympathetic cooling of molecules was recently studied in a linear rf trap [3]. Penning traps have some advantages over rf traps, the most important of which is the absence of rf heating. Penning traps allow trapping of large numbers of ions at very low temperatures. Ion crystals of up to $10^6$ ions have recently been observed in a Penning trap by optical Bragg diffraction, confirming the bcc ion crystal lattice [12,13].

We have simultaneously trapped laser cooled Mg$^+$ ions and the molecular ions HCO$^+$, N$_2$H$^+$, and NH$^+$ in a Penning trap. The molecular ions are identified by a measurement of their breathing mode frequency: a characteristic mass-dependent motional frequency [14,15]. By exciting the motion of a particular ion species with an external drive, the ion cloud as a whole absorbs energy and changes size, which we observe by a change in the fluorescence rate from the laser cooled Mg$^+$ ions [16]. Using this technique we have detected the atomic ions $^{40}$Ar$^+$, $^{24,25,26}$Mg$^+$, $^{24}$Mg$^{2+}$, and $^9$Be$^+$, and, more importantly, the molecular ions HCO$^+$, N$_2$H$^+$ and NH$^+$, which are of spectroscopic interest in astrophysics [17–20] and chemistry [21].

Further, we present the results of numerical simulations of sympathetic cooling in a Penning trap [22]. We calculate the spatial distribution of an ion cloud consisting of two or four different ion species, only one of which is laser cooled. Our simulations indicate that the temperature difference between the sympathetically cooled ions and the laser cooled ions is small when the difference between the $mlq$ ratios is small [22]. Therefore we can estimate the temperature of the HCO$^+$ molecules ($mlq=29$) from a measurement of the temperature of the laser cooled Mg$^+$ ions ($mlq=24$), and we find a temperature of 4 K.

II. EXPERIMENT

The Penning trap used in this work has been described in detail elsewhere [23]. It consists of two endcaps separated by $2z_0=7$ mm and a ring electrode with an internal diameter of $2r_0=10$ mm. A conventional electromagnet provided a magnetic field $B=0.968$ T aligned with the axis of the trap, i.e., along a line between the endcaps. The trap was enclosed in an ultra-high vacuum system kept at around $3\times10^{-10}$ mbar. Two atomic beam ovens (containing Be and Mg at natural abundances) are situated between the endcaps and the ring electrode. Ions were created by directing an electron beam through the center of the trap with a kinetic energy of 15 eV. To study sympathetic cooling of different ion species, we either ran the Be oven in conjunction with the Mg oven, or leaked some air, N$_2$, CO$_2$, or Ar into the vacuum system using a leak valve, to a pressure of about $4\times10^{-8}$ mbar.

A few hundred microwatts of uv radiation at 280 nm, which is required for cooling and detection of $^{25}$Mg$^+$, was generated by intracavity frequency doubling in a Coherent CR699 ring dye laser running on Rhodamine 560 Chloride. The uv beam was sent through two diametrically opposing holes in the ring electrode and was focused to a waist of about $40\times80$ μm at the center of the trap. The solid pole pieces of the electromagnet do not allow optical access along the direction of the field, so that we are restricted to laser cooling in a direction almost perpendicular to the z axis. Light scattered by the ions is detected through a third hole in the ring electrode at right angles to the laser beam. A two-lens system images the ion fluorescence onto the photocathode of a photon-counting photomultiplier.

The motion of an ion in a Penning trap is well understood, and we refer to a recent review article by Peurrung et al. [15] for details. The motional frequencies have been calculated for a single ion (or the center-of-mass for an ion cloud) and measured in various different situations [15,16,24–28]. The...
motional frequencies relevant for the present paper are the axial frequency, \( \omega_z \), and the so-called breathing mode frequency, \( \omega_r \). These motions are of a very different nature. The axial motion corresponds to an oscillation of the center-of-mass of the ion cloud in the axial direction. The breathing mode is a motion in the radial plane, related to the ion motion towards and away from trap center as a result of the combination of cyclotron and magnetron motions [15]. The axial frequency \( \omega_z \), the magnetron frequency \( \omega_m \) and the breathing mode frequency \( \omega_r \) are given (in angular frequency units) by [15,24,25]

\[
\omega_z = \sqrt{\frac{4q(V_0 - V_c)}{m(r_0^2 + 2z_0^2)}}
\]

(1)

\[
\omega_m = \frac{1}{2}(\omega_z - \sqrt{\omega_z^2 - 2\omega_r^2}),
\]

(2)

\[
\omega_r = \omega_z - 2\omega_m = \sqrt{\omega_z^2 - 2\omega_r^2},
\]

(3)

with \( V_0 \) the dc trapping potential, \( V_c \) an effective trap voltage offset caused by the possible presence of contact potentials from a partial Mg coating of the electrodes, and \( \omega_c = qB/m \) the cyclotron frequency with \( q \) and \( m \) the charge and mass of the ion.

The ions' motional oscillation frequencies are measured by monitoring the response of the ions to an external drive in the form of a small oscillating voltage applied to the endcaps. Since the drive voltage is very small compared to the voltages applied for trapping, appreciable effects are only expected when the drive frequency is resonant with one of the ions' motional frequencies. At a resonance the ion cloud absorbs energy and changes shape, which can be detected as a change in the level of fluorescence emitted by the laser cooled Mg\(^+\) ions [16].

III. USE OF THE AXIAL MOTION FOR MASS SPECTROMETRY

The axial motional frequency \( \omega_z \) has been used for the analysis of single trapped ions [29,30] and one component plasmas [31]. The cloud's center-of-mass axial motion is easily excited by applying an oscillating voltage of a few millivolts to the endcaps in an out of phase manner [14]. To determine various trap parameters we first measured \( \omega_z \) as a function of \( V_0 \) with only Mg\(^+\) in the trap. By fitting Eq. (1) to the data we find the trap parameters \( r_0^2 + 2z_0^2 = 5.30(7) \times 10^{-5} \) m\(^2\) and a contact potential of \( V_c = +0.08(2) \) V. By measuring \( \omega_c \) as a function of \( V_0 \) we have determined the magnetic field strength in the center of the trap to be \( B = 0.968(5) \) T.

For detection and identification of the trapped molecules we need to measure a mass spectrum in a non-destructive manner. The mass dependence of the axial frequency has been used for mass spectrometry in the case of a single ion or a one component plasma [15,31]. To test whether it can also be used with more than one ion species in the trap we performed some experiments with a mixture of Mg\(^+\) and Be\(^+\) ions. The Be\(^+\) ions were sympathetically cooled through their Coulomb interaction with the laser cooled Mg\(^+\) ions. Subsequently, the axial motions were excited by scanning an external drive frequency from 0 to 500 kHz and back in 32 seconds. The point at which the drive frequency is resonant with an axial frequency is indicated by a sudden rise in the fluorescence level from the Mg\(^+\) ions [14,16].

Figure 1 shows the observed axial response frequencies as a function of \( V_0 \). The solid curves correspond to the calculated axial frequencies for Mg\(^+\) and Be\(^+\) (upper curve for Be\(^+\)) in the absence of other ions. The measurement in Fig. 1 is merely given as an example; the data are not reproducible. There appears to be a strong dependence of the axial frequencies on the relative Mg\(^+\) and Be\(^+\) ion densities (which are hard to control and may even vary during a measurement). In general the measurements of the axial frequencies show the following behavior. At low \( V_0 \) only one axial frequency is observed, in between the "unperturbed" Mg\(^+\) and Be\(^+\) frequencies. At intermediate \( V_0 \) three responses are observed, and at high \( V_0 \) one finds the unperturbed Be\(^+\) and Mg\(^+\) responses, but sometimes this is accompanied by another frequency somewhere in between the two. Due to these complications we conclude that the axial motion is not suited for mass spectrometry when different ion species are simultaneously present in the trap.

To gain some insight into the behavior of the axial motional frequencies with different ion species we have performed numerical simulations of sympathetic cooling [22]. We start with random positions and velocities for all ions. The ions are propagated by numerical integration of the equations of motion, taking the Coulomb interaction between all the ions into account at each integration step. The integration is performed in a frame rotating with a frequency \( \omega_c/2 \). This means that ions of different \( m/q \) ratio are propagated in frames with different rotation frequencies, since \( \omega_c \) is mass dependent. The use of the rotating frame increases the numerical accuracy, and, more importantly, it allows for an easy implementation of the laser cooling [32]. The laser cooling is modelled by a continuous damping force in three dimensions, applied to the set of laser cooled ions only [33]. This is a crude simplification of laser cooling in a Penning trap, neglecting that the ions are only laser cooled when they pass through the laser beam, and that the interaction with the laser light depends on both the laser intensity profile and the frequency shifts due to the Doppler effect. Also, the effect of
the photon recoil is not taken into account. However, since we are mostly interested in the spatial distribution of the different ion species we feel that this approximation of laser cooling is sufficient to this purpose. We have compared the outcome of our simulations with previously reported calculations [8,34–36] and found good agreement in all cases with one possible exception [37].

It is well known that the presence of the magnetic field leads to a centrifugal separation of ions with different $m/q$ ratios into rings or shells [1,6–8,38,39]. Our numerical simulations presented in Fig. 2 clearly show this behavior. We have calculated the radial distance to the trap center, $r = \sqrt{x^2 + y^2}$ and the axial position $z$ of Mg$^+$ and Be$^+$ ions after a few ms of laser cooling. In all cases the heavier Mg$^+$ ions (closed squares) form ring-like shapes around the lighter Be$^+$ ions (open circles). The results for high and low values of $V_0$, however, show a different spatial distribution. At low $V_0$, as in Fig. 2(a), the ions are in an elongated shape, the Mg$^+$ ions forming a long hollow cylinder around the Be$^+$ ions. Nearly every Be$^+$ ion will have a Mg$^+$ ion in its direct vicinity and vice versa. Moreover, near the edges of the cloud, at $z \sim \pm 150$ $\mu$m an axial motion of for instance the Be$^+$ ions (open circles) would take the ions in and out of the Mg$^+$ cylinder. As a consequence, excitation of the center-of-mass motion of one of the two ion species will have an influence on the other. We therefore expect that at low $V_0$, the axial motional frequencies will be modified from their unperturbed values. When this coupling if sufficiently strong we expect the axial frequencies of the two species to reduce to one frequency, corresponding to a center-of-mass motion of the entire cloud at a frequency somewhere in between the two individual frequencies. This corresponds to what was observed in the axial frequency measurements in Fig. 1. The spatial distribution of the ions for large values of $V_0$ is shown in Fig. 2(d). The interaction region between the two ion species is now much smaller and the effect at the edge of the cylinder in not present. The ions have more freedom to move independently of the other species, and they will respond at (nearly) the same frequencies as when there are no other ions present. Again, this corresponds to what was observed at high $V_0$ in Fig. 1.

IV. USE OF THE BREATHING MODE FOR MASS SPECTROMETRY

Various radial motional frequencies have been successfully used as a diagnostic tool for trapped single ions and one component plasmas [14–16,40,41]. The breathing mode has received particular attention [42–44] since it has the great advantage that it is excited by a simple modulation of the quadrupole trap potential. This eliminates the need for a split ring electrode as is often needed for the other radial motions [15]. It can be excited by applying a small driving voltage to both endcaps in phase [14,15]. The breathing mode allows for a relatively non-invasive measurement of the mass spectrum, and the relatively large frequencies involved permit a high accuracy [15]. However, this may no longer be true when different ion species are simultaneously present in the trap. We therefore ran some tests experiments detecting $^{40}$Ar$^+$, $^{24}$Mg$^+$, and $^9$Be$^+$ in the presence of the laser cooled $^{24}$Mg$^+$ ions. We found, as the results below will show, that the breathing mode frequencies are virtually unaffected by the presence of another ion species, in contrast to the axial mode frequencies. Further, these tests provide us with reference points with both higher and lower $m/q$ ratios compared to Mg$^+$. These preliminary measurements enable us to use the breathing mode for identification of the trapped molecular ions.

We have loaded the trap with Mg$^+$ ions at an elevated air pressure of a few times $10^{-8}$ mbar. The cloud is laser cooled for a few minutes while the laser is repetitively scanned over a 2 GHz range to the red detuned side of the cooling transition of Mg$^+$. Then the detuning is set to $\sim 700$ MHz and the drive frequency is scanned from 200

![](image.png)

FIG. 2. Positions of 70 Mg$^+$ and 30 Be$^+$ ions in the $(r,z)$ plane, showing the spatial distribution of the two ions species for different values of the trapping voltage $V_0$. At low $V_0$, as in (a), the heavier Mg$^+$ ions (closed squares) form an elongated cylinder around the sympathetically cooled Be$^+$ ions (open circles), whereas at high $V_0$, as in (d), they form a set of thin rings around the Be$^+$. The simulations were performed for $B = 1$ T and $r_0^2 + 2z_0^2 = 5.30 \times 10^{-3}$ m$^2$. 

The calculations were performed for 20 N$_2$H$^+$, Mg$^+$, NH$^+$, and Mg$^{2+}$ ions. The scan time is 16 s, the trap voltage $V_0=6.00$ V and the laser detuning is set at $\sim -700$ MHz.

to 1700 kHz. By monitoring the Mg$^+$ fluorescence we find four breathing mode resonance frequencies, as shown in Fig. 3. No response was found at higher or lower driving frequencies. As is explained below, we can ascribe these breathing frequencies to the presence of N$_2$H$^+$, Mg$^+$, NH$^+$, and Mg$^{2+}$ ($m/q$ of 29, 24, 15 and 12, respectively, in units of $ue$). The response at $m/q=15$ only occurs in the presence of N$_2$ molecules which rules out the possibility of the ionized background molecule CH$_3^+$ [45]. A separate study of the response over a small range around the $^{24}$Mg$^+$ frequency and with a six times increased driving amplitude showed two much weaker neighboring responses, corresponding to the $^{25}$Mg$^+$ and $^{26}$Mg$^+$ isotopes (with natural abundances of 10 and 11 % respectively). When necessary, the trap could be selectively “cleaned” by driving the breathing mode frequency of an unwanted ion with very high amplitude (up to 0.4 V on the endcaps). This will temporarily cause a strong change in Mg$^+$ fluorescence, until the unwanted ion species has been driven out of the trap. Using this technique we can clean the trap, so that only the molecules of interest and the laser cooled ions remain in the trap. We applied this technique to remove the NH$^+$ and Mg$^{2+}$ ions from the ion cloud that was detected in Fig. 3, leaving only the responses at N$_2$H$^+$ and Mg$^+$. Usually, some N$_2$H$^+$ would be lost in the process however, which is indicated by a lower amplitude of the response at that frequency after cleaning.

With our computer simulation program we have calculated the spatial distribution of a cloud with four different ion species, consisting of N$_2$H$^+$, Mg$^+$, NH$^+$, and Mg$^{2+}$ ions. Figures 4(a) and 4(b) show the spatial separation of the four ion species in the x, y and r, z planes respectively. The calculations were performed for 20 N$_2$H$^+$, 120 Mg$^+$, 20 NH$^+$, and 20 Mg$^{2+}$ ions. We have chosen these numbers, which are probably about ten times lower than in the experiments, to keep the computing time manageable.

In different measurements of the breathing mode frequency we have detected Ar$^+$, HCO$^+$, N$_2$H$^+$, Mg$^+$, NH$^+$, Mg$^{2+}$, and Be$^+$(m/q of 40, 29, 29, 24, 15, 12, and 9, respectively). All ions were identified by their characteristic motional frequency, using the measurement of $^{24}$Mg$^+$ as a calibration. The measured breathing mode frequencies as a function of $V_0$ are shown in Fig. 5. Note that these were not all measured simultaneously. The curves have been calculated by fitting Eq. (3) to the data points for each ion species with the mass-to-charge ratio acting as the only fitting parameter. We find the values 40.2 for $^{40}$Ar$^+$, 29.0 for $^{1}$H$^{12}$C$^{16}$O$^+$, 29.1 for $^{14}$N$_2$H$^+$, 15.1 for $^{15}$N$^1$H$^+$, 12.0 for $^{24}$Mg$^{2+}$ and 8.9 for $^{9}$Be$^+$, with an uncertainty in the determination of m/q of less than 1 %. The slope of each curve confirms that we excite the breathing mode, since the measurements are in perfect agreement with the calculated slope (which is not a fit parameter and is only determined by the trap parameters that were measured independently in Sec. III).

We found the presence of HCO$^+$ and N$_2$H$^+$ surprising at first, expecting to find N$_2^+$ and CO$^+$. However, the proton affinity energies of these molecules make a reaction with any H$_3$ molecules present in the vacuum chamber very likely [17,46–50]. This is corroborated by the detection of sizeable
amounts of H₂ in the vacuum system with a residual gas analyzer mounted near the trap. Furthermore, the molecules detected in a previous experiment using a linear rf trap also showed a response at \( m/q = 29 \) and not at 28 after some air had been leaked into the vacuum system.

**V. MOLECULAR ION TEMPERATURE**

Figure 6 shows the fluorescence of the Mg²⁺ ions directly after loading the trap. The laser frequency is repetitively scanned towards resonance and back with a period of 0.5 s. This produces the strong modulation in the photon count rate (note the logarithmic vertical scale). The high photon count rate in the first two seconds of Fig. 6 corresponds to detection of light coming from the glowing electron filament. In Fig. 6(b) we show a similar trace just after loading Mg²⁺ and HCO⁻ ions. All trapping and laser parameters were identical. Nevertheless Fig. 6(b) shows a greatly extended cooling time as compared to (a). Clearly the laser cooling of the Mg²⁺ takes much longer in the presence of HCO⁻. This confirms that the Mg²⁺ and HCO⁻ ions strongly interact, and therefore we expect the HCO⁻ molecules to be sympathetically cooled to cryogenic temperatures. We generally allow about one minute for the cloud to reach equilibrium.

It has been shown that the temperature of a single sympathetically cooled ion in the presence of a single laser cooled ion is equal to the limiting temperature of the single laser cooled ion [51]. This is not necessarily true for a cloud of ions. When the ions have reached equilibrium there is a balance between the heating and cooling rates. Heating in a Penning trap can be due to collisions with background gas neutral particles, trap potential imperfections (which are worse further away from trap center) or a misalignment of the trap electrodes with respect to the magnetic field direction. Also, trap imperfections allow for an energy transfer from the unstable magnetron motion to the cyclotron and/or axial motions. Since the heating and cooling rates may be different for different (spatially separated) ion species, the final temperature can also be different.

Larson et al. [1] have measured the temperature of sympathetically cooled \(^{198}\)Hg⁺ ions in a Penning trap with laser cooled \(^9\)Be⁺ ions. The \(^{198}\)Hg⁺ temperature was determined from a measurement of the Doppler broadened width of the \(^{198}\)Hg⁺ transition, using a separate probe beam. The \(^{198}\)Hg⁺
temperatures were found to range from 0.4 to 1.8 K, with Be$^+$ temperatures ranging from 0.05 to 0.2 K. The roughly 10 times higher temperature of the sympathetically cooled ions was ascribed to a weak coupling between the $^9$Be$^+$ and $^{198}$Hg$^+$ ions; the large difference in $m/q$ leads to a large centrifugal separation. Therefore the Coulomb interaction, which is essential for sympathetic cooling, will be very weak. The experiments reported by Imajo et al. [7] show that the temperature of sympathetically cooled $^{114}$Cd$^+$ ions was a factor of 1.7 higher than that of the laser cooled $^9$Be$^+$ ions. The lowest temperatures reached were 0.7 K for $^{114}$Cd$^+$ and 0.4 K for $^9$Be$^+$. Again, the temperature of the sympathetically cooled ions was deduced from laser induced fluorescence from the $^{114}$Cd$^+$ ions. The very first experiment on sympathetic cooling showed sympathetically cooled $^{20}$Mg$^+$ and $^{25}$Mg$^+$ ions through interaction with the most abundant and laser cooled isotope $^{24}$Mg$^+$ [5]. The temperature of the sympathetically cooled isotopes was found to be identical to that of the directly laser cooled ions. These results lead us to conclude that when the difference between the $m/q$ ratio of the sympathetically cooled ions and the laser cooled ions is small, the temperature difference between the two species will also be small. In addition, our numerical simulations show that the time necessary to sympathetically cool a particular ion species becomes very long when the ions have very different $m/q$ ratios, again indicating weak interaction for large $m/q$ difference. More importantly, the simulations indicate that the temperature difference between the sympathetically cooled and laser cooled ions is small when the $m/q$ difference is small [22]. We therefore expect a strong coupling between Mg$^+$ ($m/q=24$) and HCO$^+$ ions ($m/q=29$) and thus a small difference in final temperature.

Unfortunately the kinetic temperature of the HCO$^+$ molecules cannot be measured by laser induced fluorescence. There is no near two-level system that can be excited repeatedly to produce a measurable signal. This is due to two main reasons. Firstly, the repulsive Coulomb force between two ions acts over a very long range. Therefore the ion-ion collision responsible for the sympathetic cooling are unlikely to affect the internal states of the molecule, leaving the population thermally distributed over many rotational levels. Therefore the number of molecules in the desired initial state is very low. Secondly, after excitation of a particular transition in HCO$^+$, it is very likely that the molecule has been optically pumped into a rotational level that has no further interaction with the laser light. However, given the above arguments that the kinetic temperature of the HCO$^+$ molecules will be very close to the temperature of the Mg$^+$ ions on the basis of their similar $m/q$ ratio, we feel confident that the HCO$^+$ temperature can be estimated from a measurement of the Mg$^+$ temperature.

We deduce the temperature from the Doppler broadened width of the fluorescence curve as the cooling laser is tuned into resonance. We have not used an appropriately attenuated probe beam to measure the Doppler linewidth of the transition as was done in [1,5,52], but scan the frequency of the cooling laser itself. As a result, the ion temperature may change during the measurement. At large detuning the temperature can be slightly higher, and as the laser frequency is tuned towards resonance the ions are cooled. The ion temperature will be lowest near resonance. Therefore the resulting fluorescence curve will show deviations from the normal Doppler broaden end Gaussian line shape; the observed ion fluorescence will be somewhat higher in the wings as compared to a Gaussian. As a result we can only determine an upper limit for the Mg$^+$ (and HCO$^+$) temperatures. We also neglect the Lorentzian contribution from the natural linewidth of Mg$^+$, which has a half width at half maximum (HWHM) of 22 MHz. Note that because of the limited laser beam access mentioned in Sec. II it is the cyclotron temperature $T_\parallel$ that is measured [52]. A Gaussian curve was fitted to the linewidth measurement shown in Fig. 7. The Gaussian curve is a poor fit because of the above mentioned reasons related to scanning the frequency of the cooling laser frequency instead of an independent weak probe beam. From the Gaussian fit in Fig. 7 we find a width (HWHM) of 164 MHz which corresponds to a temperature of $4 \pm 1$ K.

After measuring the ion cloud temperature we drive the breathing mode frequency of HCO$^+$ to reconfirm its presence. By using the method reported in Sec. IV to selectively drive ions out of the trap we were able to reduce the number of HCO$^+$ ions, leaving the number of Mg$^+$ ions virtually unchanged. Successive reduction of the HCO$^+$ ions showed that lower temperatures could be obtained with less HCO$^+$ present. The observed temperatures range from 27 K at 30 seconds after loading the trap with a large cloud, to 4 K after careful optimization and cloud size reduction. By using a smaller cloud and lower $V_0$ a HWHM of 65 MHz could be obtained (neglecting the natural linewidth this corresponds to 0.5 K). However, for these small cloud sizes, the response to driving the breathing mode of HCO$^+$ was too small to reconfirm the presence of HCO$^+$.

**VI. CONCLUSIONS**

The molecular ions HCO$^+$ and N$_2$H$^+$ have been sympathetically cooled in a Penning trap through Coulomb interaction with laser cooled $^{24}$Mg$^+$ ions. We have explored two of the characteristic mass-dependent ion motions for use as a mass spectrometer. We find that axial center-of-mass motion is unsuited for mass spectrometry when more than one ion species is present in the trap. The radial breathing mode fre-
quencies, on the other hand, are shown to be ideally suited for this purpose. We determine the presence of $^{40}\text{Ar}^+$, $^{24,25,26}\text{Mg}^+$, $^{24}\text{Mg}^+$, and $^9\text{Be}^+$, and the molecular ions HCO$^+$, $\text{N}_2\text{H}^+$, and NH$^+$ through a measurement of their characteristic mass-dependent breathing mode frequencies. We estimate that the final temperature of the sympathetically cooled HCO$^+$ molecules is 4 K. Currently we are investigating the options for high-resolution spectroscopy of the cold HCO$^+$ molecules and driving the astrophysically interesting rotational transitions near 93 GHz.

**ACKNOWLEDGMENTS**

M.A. van Eijkelenborg would like to thank the Netherlands Organization for Scientific Research (NWO) for support during the initial stages of this project. This work was supported by the EPSRC.

[37] Through correspondence with H. Imajo we have come to believe that the numerical results presented in Ref. [8] were not calculated for the parameters quoted in the accompanying text.

[45] The creation of Mg$^{2+}$ seems to be assisted by the presence of N$_2$ molecules. At an electron filament bias voltage of 18 V Mg$^{2+}$ is only created in the presence of N$_2$ whereas it is not under ultra-high vacuum conditions.


