We present a mass spectrometric technique for identifying the masses and relative abundances of Coulomb-crystallized ions held in a linear Paul trap. A digital radio-frequency wave form is employed to generate the trapping potential, as this can be cleanly switched off, and static dipolar fields are subsequently applied to the trap electrodes for ion ejection. Close to 100% detection efficiency is demonstrated for Ca\(^+\) and CaF\(^+\) ions from bicomponent Ca\(^+\)-CaF\(^+\). Coulomb crystals prepared by the reaction of Ca\(^+\) with CH\(_2\)F. A quantitative linear relationship is observed between ion number and the corresponding integrated time-of-flight (TOF) peak, independent of the ionic species. The technique is applicable to a diverse range of multicomponent Coulomb crystals—demonstrated here for Ca\(^+\)-NH\(_3\)^+ and Ca\(^+\)-CaOH\(^+\)-CaOD\(^+\)—and will facilitate the measurement of ion-molecule reaction rates and branching ratios in complicated reaction systems.

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I. INTRODUCTION

Recent improvements in cold molecular beam methods and their combination with ion traps are facilitating exciting new developments in the observation of cold, controlled ion-molecule reactions [1,2]. It is not sufficient, however, to simply conduct experiments in the cold regime; the resulting products must be quantitatively detected to extract information about the reaction process, such as the rate, the product branching ratio, and energy dependence.

Trapped, laser-cooled ions can undergo a phase transition to adopt a highly ordered “Coulomb crystal” structure. Cotrapped ions of a different species may be sympathetically cooled through elastic collisions with the laser-cooled ions, forming multicomponent Coulomb crystals. In this way, cold molecular ion targets of species that cannot be laser cooled can be prepared. Imaging the fluorescence continuously emitted by the laser-cooled ions enables real-time observation of the crystal framework, as depicted in Fig. 1(b). Due to the dependence of the trapping field on the charge-to-mass ratio of the ions, different ionic species are located in separate regions of the Coulomb crystal. In chemical reactions, this separation can be exploited and reaction rates can be measured through monitoring the changing shape of the crystal. For instance, the reaction of laser-cooled ions with neutral reactants—and the disappearance of fluorescing ions—is accompanied by changes in the crystal framework as product ions heavier (lighter) than the laser-cooled species migrate to the outer (inner) region of the crystal [1,3]. Hence, even though the nonfluorescing sympathetically cooled ions cannot be observed directly, comparison of molecular dynamics (MD) simulations with observed fluorescence images enables quantitative determination of ion numbers (see Fig. 1).

In complicated chemical systems with multiple product channels, however, MD simulations alone are insufficient for establishing accurate reaction rates. For example, in the reaction between C\(_2\)H\(_2\)^+ (sympathetically cooled into a Ca\(^+\) Coulomb crystal) and NH\(_3\), there are numerous exothermic pathways: proton transfer, charge transfer, two H-elimination pathways, and two H\(_2\)-elimination pathways [4]. In this case, both the reactant ions and numerous “dark” (nonfluorescing) product ions are lighter than the laser-cooled species, and thus would be indistinguishable in the dark inner core. A change in the ratio of the numbers of light ions of different mass would have little effect on the crystal framework. In some instances, resonant-excitation mass spectrometry (MS) methods can be utilized. The scanning of an additional radio-frequency (rf) field resonantly excites the secular motional frequencies of trapped ions, allowing the ion masses to be determined [5–7]. In the limiting case of a single molecular ion sympathetically cooled by a single laser-cooled ion, the mass of the molecular ion can be precisely measured, with for example \(^{26}\)Mg\(_2\)\(^+\) and \(^{28}\)MgD\(_2\)\(^+\) experimentally distinguishable [8]. While several variants of this nondestructive technique have been developed [9,10], resonant-excitation MS remains limited in application to small crystals with only a few different ion types; when motional frequency spectra are recorded for large multicomponent crystals, the features are poorly resolved and difficult to unambiguously assign, and the relative abundances cannot be ascertained quantitatively [3]. An alternative approach, termed ion crystal weighing, employs a pulsed electric field to excite the center-of-mass mode of the ions [11]. The frequency of the mode, and hence the mass of the crystal, can be deduced from the Fourier-transformed autocorrelation of the ion fluorescence signal. While ion crystal weighing is applicable to larger crystals, interpretation of the results is challenging when more than two ionic species are present or when the identities of the dark ions are unknown.

Adopting the principles of Wiley-McLaren time-of-flight MS (TOF-MS) [12], Hudson and co-workers recently demonstrated the ejection of ions from a linear Paul trap into a TOF tube and onto an external detector [13]. Ion ejection was achieved by switching off the rf voltages and converting the trap electrodes into a repeller-extractor pair by applying static voltages. However, when using resonantly driven cosine rf
FIG. 1. The number of ions in a given Ca\(^+\) Coulomb crystal can be established to within ±5 ions by fitting the experimental image to MD simulations. A simulated crystal image with 50 Ca\(^+\) ions is shown in panel (a), alongside an experimental Ca\(^+\) crystal image in panel (b). The simulated crystal is overlaid on the experimental image in panel (c), illustrating the excellent agreement between the positions of the ions in the simulated and experimental crystals. This approach is also adopted for multicomponent crystals; in panel (d), a bicomponent Ca\(^+\)-CaF\(^+\) experimental crystal (in which only the Ca\(^+\) ions are fluorescing) is overlaid with a simulated Ca\(^+\)-CaF\(^+\) crystal comprising 30 Ca\(^+\) ions and 35 CaF\(^+\) ions. Only the Ca\(^+\) ions are made visible in the simulation, for ease of comparison between the images.

II. EXPERIMENTAL METHODS

The experiments presented in this paper utilize a linear Paul trap operated under UHV conditions, illustrated in Fig. 2. The cylindrical trap electrodes, 4 mm in radius, have a diagonal electrode-surface separation of 2\(z_0\) = 7.0 mm and are each composed of three segments (endcap separation 2\(z_0\) = 5.5 mm), to which a combination of rf and static voltages are applied. The conventional time-dependent trapping potential in a linear Paul trap is of the form \(\phi_{rf}(x,y,z) = \frac{V_{rf}}{r} \cos(\omega_{rf} t)\), with \(V_{rf}\) being the peak-to-peak voltage amplitude and \(\omega_{rf}\) the rf drive frequency. However, as first demonstrated in the 1970s [16,17], a cosine wave function is not essential for the generation of a trapping potential. A DIT, as we utilize in this work, employs a rectangular wave form of period \(T\) and a fractional pulse width \(\tau\), yielding a time-dependent trapping potential [18,19]:

\[
\phi_{rf}(x,y,t) = \frac{V_{rf}}{2} \left( \frac{x^2 - y^2}{r_0^2} \right) P_\tau(t),
\]

where

\[
P_\tau(t) = \begin{cases} 
1 & \text{if } |t| \leq \tau T/2, \\
0 & \text{if } \tau T/2 < |t| \leq (1 - \tau)T/2, \\
-1 & \text{if } (1 - \tau)T/2 < |t| \leq (1 + \tau)T/2, \\
0 & \text{if } (1 + \tau)T/2 < |t| \leq (2 - \tau)T/2, \\
1 & \text{if } (2 - \tau)T/2 < |t| \leq T,
\end{cases}
\]

and

\[
P_\tau(t + T) = P_\tau(t).
\]
where we can represent the pulsed wave form as the sum of its cosine Fourier components, 

$$ P_n(t) = \sum_{n=1}^{\infty} a_n \cos(n \omega t \tau). $$

Axial confinement of ions in the trap is obtained through the application of static voltages ($U_{dc}$) to the endpieces of the segmented electrodes, 

$$ \phi_{tot}(x,y,z) = \frac{u \phi_0}{\xi^2} (z^2 - \frac{r^2}{2}), $$

with $\eta = 0.244$ being a geometrical factor for this trap. The total electric potential is thus $\phi = \phi_0(x,y,z) + \phi_{tot}(x,y,z)$. The equations of motion for a single trapped ion can be expressed as a Hill differential equation (commonly known as a Mathieu equation for harmonic potentials), 

$$ (d^2u/d\xi^2 + u|a_u + 2q_u f(\xi)|) = 0, $$

where $f(\xi) = \cos(2\xi)$ for a cosine rf field and $f(\xi) = P_d(\xi)$ for a digital rf field, $\mu \in [x,y]$, and $\xi = \frac{u}{\eta U_d}$. The stability of an ion trajectory is dependent on the dimensionless trapping parameters $a_u$ and $q_u$. The $(q_u,a_u)$ plane is divided into stable and unstable regions; for stable values of $a_u$ and $q_u$, the solutions to the equations of motion are bound and the ion will be confined in the trap. In a DIT, the Hill differential equations are dependent on the fractional pulse width ($\tau$), which can be varied to yield a stability diagram comparable to that of a cosine trap. (See Ref. [18] for a derivation of the stability criterion in a DIT.) Bandelow et al. have recently experimentally confirmed the applicability of the $a_u$ and $q_u$ parameters in mapping the stability regions of a hyperbolic Paul DIT [20,21].

We can define dimensionless stability parameters that are dependent on the mass ($m$) and charge ($Q$) of the species [2,18],

$$ a_x = a_y = -\frac{\eta Q U_{dc} \mu}{m r_0^2 \omega^2}, \quad (4) $$

$$ q_x = -q_y = -\frac{2Q V_{dc}}{m r_0^2 \omega^2}, \quad (5) $$

which enable one to construct a DIT stability diagram in terms of $U_{dc}$ and $V_{dc}$ (see Fig. 3). From the secular potential, defined as the sum of the pseudopotential (the harmonic time-averaged potential arising from the oscillating rf fields) and the static endpiece potential, one can derive the digital trap depth,

$$ \phi_{sec}(r_0) = \frac{Q^2}{2m \omega^2} r_0^2 - \frac{Q U_{dc} r_0^2}{2z_0}, \quad (6) $$

FIG. 3. (Color online) (a) The regions of stability for several ionic species in the DIT operating at $\tau = 0.25$ and $\omega t_\text{rf} = 2\pi \times 1.33$ MHz. For clarity, only the stability region of Ca$^+$ is shaded black; for all other species, the stability region is enclosed by the relevant colored (shaded) curves. Regions of overlapping stability indicate the operating parameters ($V_{dc}, U_{dc}$) where species can be coretrapped. (b) A closer view of the experimentally accessible region of the stability diagram.

FIG. 4. Experimental digital rf trapping wave form ($\sim$4 to 0 $\mu$s) and ejection pulse ($0 \mu$s onwards).

with $c = \frac{1}{2} \sum_{n=1}^{\infty} a_n^2 n^2$ being a sum over the Fourier-component amplitudes $a_n$. In a DIT, $a_n = \frac{1}{n} \sin(n \pi \tau)$ (where $n \in \mathbb{N}$) and thus the trap depth depends on the fractional pulse width $\tau$; in a cosine trap, $c = 0.5$. The digital rf voltage is applied at a frequency of $\omega t_\text{rf} = 2\pi \times 1.33$ MHz, with typical trap parameters $V_{dc} = 50$ V, $U_{dc} = 1.0$ V, and $\tau = 0.25$ yielding $a_u$ and $q_u$ values that fall within the regions of stability for all ionic species considered in this work.

The experimental digital wave form (Fig. 4) exhibits a nonzero pulse decay time and thus deviates from the ideal digital wave form. MD simulations—in which the measured digital wave form can be directly utilized—indicate that this deviation from the ideal wave form has a very minor impact on the trap depth and does not adversely affect crystal formation, crystal stability, or the ejection properties of the system. This is in agreement with Sudakov and Nikolaev, who found nonideal wave forms to have an insignificant effect on the calculated regions of stability in a DIT [22]. Hence assuming the real digital wave form is well represented by an ideal digital wave form, a trap depth of $\sim 1.21$ eV is calculated—shallower than the cosine trap depth of $\sim 1.36$ eV as previously utilized in our research group [23], but entirely sufficient for most applications.

To form Coulomb crystals, calcium atoms in an effusive skinned beam are nonresonantly ionized (at 355 nm) in the trap center. The resulting Ca$^+$ ions are laser cooled on the 4s $^3S_1/2 \rightarrow 4p^2P_{1/2}$ transition at 397 nm, with a 866-nm repump beam addressing population lost to the 3d $^3D_{3/2}$ state. The cooling lasers are reflected back along the trap axis to achieve bidirectional cooling. An additional 397-nm beam at 45° to the trap axis provides radial cooling. Fluorescence continuously emitted by laser-cooled Ca$^+$ ions is imaged by a lens into an intensified charge-coupled device camera system, yielding a twodimensional image of the Coulomb crystal. High-precision leak valves facilitate the controlled introduction of neutral reactants into the ion trap chamber, typically held at pressures of $\sim 1 \times 10^{-9}$ mbar. In this way, we generate molecular ions through chemical reactions between
the neutral reactant gas and trapped Ca$^+$ ions, or with trapped sympathetically cooled ions.

After the quadrupole trapping voltages are switched off, ions are radially ejected into the TOF tube by dipolar repeller and extractor fields of $+220$ and $+97$ V, respectively, applied with a rise time of 70 ns, and are accelerated towards a grounded mesh of 88% transparency mounted across the entrance of the TOF tube [see Fig. 5(b)]. The ions are detected by a MCP detector at the end of the flight tube. The repeller and extractor voltages employed were found empirically to give the best TOF mass resolution for Ca$^+$, and this two-stage acceleration arrangement is equivalent to a Wiley-McLaren TOF scheme [12]. In the experiments reported here there was (nominally) zero delay in the switching from the trapping voltages to the ejection voltages (see Fig. 4); although the delay can be varied easily in the digital trap, minimizing the delay was found to optimize the mass resolution.

III. SIMULATIONS

Coulomb crystals are simulated using a custom-written MD crystal simulation program, which takes the experimental digital wave form as the input rf trapping voltage. Simulated crystal images can thus be directly compared to those observed experimentally, as demonstrated in Fig. 1. A MATLAB program is used to model the ion trajectories upon ejection by calculating the electric fields in the ion trap and the TOF tube, using SIMION to solve the Laplace equation numerically and including ion-ion repulsion. Taking the identity, position, and velocity of each ion within a Coulomb crystal (as output by the MD code) and the experimental ejection voltages as input parameters, ion trajectories are calculated using a velocity Verlet algorithm [24,25]. For Coulomb crystals composed of $\leq 200$ ions, simulations indicate that the detection efficiency is limited only by the transmittance of the grounded mesh; detection efficiency is independent of the particular species, for all species considered in this work.

IV. RESULTS AND DISCUSSION

To verify the predicted detection efficiency experimentally, the number of Ca$^+$ ions in a given crystal is determined for several hundred Coulomb crystals of various sizes by comparing the experimental image immediately prior to ejection to a set of simulated crystal images (see Fig. 1). Following crystal ejection, the area under the relevant mass peak is calculated by integration of the (background-subtracted) TOF trace. Figure 5(a) illustrates the linear correlation between the number of ions in a Ca$^+$ Coulomb crystal and the integrated TOF peak recorded upon crystal ejection, for up to 200-ion crystals. The measurement error is governed by the uncertainty in the comparison between an experimental crystal and its MD simulation ($\pm$5 ions). The mass resolving power of the technique, defined as $m/\Delta m$ where $\Delta m$ is the full width at half maximum of the mass spectrum peak, is 90 for a typical 100-ion Ca$^+$ crystal and $>70$ for all Ca$^+$ crystals containing up to 200 ions: The slightly lower resolving power for larger crystals is due to the greater spread of initial positions and velocities in those cases. Crystals with more than 200 ions were not considered experimentally due to imaging limitations; the objective lens and camera restrict the field of view.

To establish the applicability of this DIT MS technique to multicomponent Coulomb crystals, mixed crystals of Ca$^+$ and CaF$^+$ are prepared by admitting a low pressure of CH$_3$F gas to the ion trap chamber, leading to the reaction Ca$^+$ +...
V. CONCLUSIONS

In summary, we have established DIT MS to be a robust technique for the quantitative characterization of multicomponent Coulomb crystals produced, in this work, by chemical reactions of the trapped ions. The ejection process is efficient, with a linear correlation between the number of ions ejected and the corresponding integrated TOF peak, and a detection efficiency that is independent of the crystal size or the ions involved. The DIT MS technique is applicable to a diverse range of multicomponent Coulomb crystals and hence to a diverse range of chemical reactions—not only reactions of laser-cooled ions but also of sympathetically cooled ions. While the ejection process is destructive, repeating the process with reloaded crystals at a range of reaction times allows the determination of accurate reaction rates and branching ratios in complicated ion-molecule reactions. With the ability to unambiguously detect both the masses and the relative numbers of reactions of the trapped ions, DIT MS has the potential to be a powerful detection technique in the study of sympathetically cooled molecular ion reactions—utilized as a stand-alone method or in combination with existing techniques such as MD simulations.

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CH$_3$F $\rightarrow$ CaF$^+$ + CH$_3$. The resulting CaF$^+$ product ions sympathetically cool into the Ca$^+$ Coulomb crystal, forming a dark outer shell—indicated by the flattening of the fluorescing Ca$^+$ core in the crystal images [see Figs. 1(d) and 6(a)]. Repeating simulations for variable numbers of laser-cooled ions and dark ions enables a determination of the number of each species in the crystal, assuming there is only one “dark” component. The mass-to-charge ratio of CaF$^+$/Ca$^+$ is 1.475, well within the desired range for optimal sympathetic cooling [1,2], and this work demonstrates that multicomponent Coulomb crystals can be formed in a DIT.

As Fig. 7 illustrates, a linear relationship is observed between the integrated TOF mass peaks and ion numbers—for both the fluorescing Ca$^+$ and the nonfluorescing CaF$^+$ ions. The gradients of the lines-of-best-fit, $(4.0 \pm 0.2) \times 10^{-10}$ Vs ion$^{-1}$ for Ca$^+$ and $(3.9 \pm 0.4) \times 10^{-10}$ Vs ion$^{-1}$ for CaF$^+$ (for up to 60 CaF$^+$ ions), established using a linear least-squares fitting procedure with uncertainties considered in both coordinates, are in quantitative agreement. These results are also in quantitative agreement with the Ca$^+$-only crystal results shown in Fig. 5(a), demonstrating the utility of the technique: equal detection efficiency is observed regardless of ion mass. There are too few crystals in the data set with $>60$ CaF$^+$ ions to extend the trend further, and the precision with which CaF$^+$ ion numbers can be estimated from simulations decreases at higher CaF$^+$/Ca$^+$ ratios. Trajectory simulations indicate that the observed linear trend will hold for larger numbers of ions (up to 400-ion crystals), and for a diverse range of ionic species, provided the mass-to-charge ratios of cotrapped species are similar and there are sufficient number of laser-cooled ions for efficient sympathetic cooling.

The mass resolution is investigated by the ejection of crystals containing species differing in mass by 1 u. Tricomponent Ca$^+$-CaOH$^+$-CaOD$^+$ crystals are formed in a two-step process. H$_2$O vapor is admitted to the chamber through a leak valve, where reaction with Ca$^+$ (in the 3$d^2$D excited states populated by the laser-cooling process) [26] yields CaOH$^+$ molecular ions. D$_2$O is then admitted through a second leak valve, forming CaOD$^+$ ions. As Fig. 6(b) illustrates, peaks arising from CaOH$^+$ and CaOD$^+$ are resolved in the spectrum, indicating a resolution better than 1 mass unit at 58 u.

The applicability of this DIT MS technique for species lighter than Ca$^+$ is confirmed with tricomponent Ca$^+$-NH$_3^+$-NH$_2^+$ Coulomb crystals. NH$_3$ is resonantly ionized at 312.5 nm, with some of the sympathetically cooled NH$_3^+$ ions subsequently reacting with neutral NH$_3$ to form NH$_2^+$, yielding tricomponent crystals. Following the same imaging and ejection process detailed above, the TOF spectra again exhibit well-resolved peaks, as shown in Fig. 6(c). In this system, both the dark species are lighter than Ca$^+$. Accordingly, conventional comparisons of the experimental crystals with simulated images do not reveal the relative numbers of NH$_3^+$ and NH$_2^+$ ions, as both species are located in the dark inner core. The same applies to multicomponent Ca$^+$-CaOH$^+$-CaOD$^+$ crystals, where the CaOH$^+$ and CaOD$^+$ species are both heavier than Ca$^+$ and therefore are both located in the dark outer shell. DIT MS enables us to ascertain the relative numbers of dark ions which are otherwise indistinguishable in the experimental and simulated images.


