Nondestructive Identification of Cold and Extremely Localized Single Molecular Ions

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We demonstrate a simple and nondestructive method for identification of a single molecular ion sympathetically cooled by a single laser cooled atomic ion in a linear Paul trap. The technique is based on a precise nondestructive determination of the molecular ion mass through a measurement of the eigenfrequency of a common motional mode of the two ions. The demonstrated mass resolution is sufficiently high that molecular ion mass doublets can potentially be distinguished from each other. The obtained results represent an important step towards single molecule gas phase chemical physics.

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In recent years, many techniques for controlling molecules in the gas phase have been developed for gas phase chemical physics. For neutral molecules, these new techniques range from internal state control by optical means (see Refs. [1,2], and references therein) to trapping of molecules by static electric fields or other means at temperatures down to ~10 mK (See Ref. [3] and references therein). In ion traps, molecular ions have likewise been cooled both internally and externally to temperatures of ~10 K by buffer gasses [4] or externally to ~10 mK through the Coulomb interaction with laser cooled atomic ions [5,6].

Although larger cold ensembles of ions already have proven useful in reaction studies [4–6], a single molecular ion sympathetically cooled [7] through the Coulomb interaction with a single laser cooled atomic ion in a linear Paul trap is in many ways an ideal system for studies of internal state control and selective chemistry based hereupon. First, the molecular ion can easily be translationally cooled to temperatures below 10 mK, where its kinetic energy and the Doppler broadening of optical transitions are negligible. Second, at these low temperatures the ions become spatially extremely well-localized targets occupying a volume of only $\sim 10\ \mu\mathrm{m}^3$ or smaller. This degree of localization is generally important when manipulations with focused laser beams are desired and hence it opens up the possibility of bringing laser based quantum control of molecular dynamics [8,9] to the single molecule level. Third, since the ions can stay trapped and unperturbed for minutes or longer, interaction time regimes not accessible in beam experiments can be explored. This might, e.g., be exploited in studies of metastable states of doubly charged cations [10,11]. Combined with internal state control, for instance by laser cooling of the internal degrees of freedom of the molecule [12] or by having the molecular ion produced in various specific rovibrational states by resonance enhanced multiphoton ionization [13], one will, e.g., have an ultimate target for studying resonances in reactions [14,15] and for doing adaptive learning experiments [9] with more straight forward analyzable results.

A prerequisite for doing single molecular ion studies is a technique which allows for identification of the molecular ion species with a relatively high efficiency before and after the process under study. Unfortunately, techniques such as fluorescence detection on specific molecular lines will generally not be applicable when single molecular ions are studied due to the lack of closed transitions.

In this Letter, we demonstrate a simple general technique allowing for unique identification of a single trapped molecular ion essentially with an efficiency of unity. The technique relies on a nondestructive mass measurement through resonant excitation of an oscillation mode of the two-ion system. In the past, the simple relation between masses and oscillation frequencies has been exploited in a large variety of measurements, including the most precise mass measurement of molecular ions today [16]. In contrast to such high-precision experiments, a strong Coulomb coupling between ions (the molecular ion of interest and an additional atomic ion) is essential in our identification scheme. For the harmonic potential of our trap, one can readily show that for two equally charged ions close to their equilibrium positions, the two eigenfrequencies for their motion along the axis of alignment are given by [17]

$$\nu_{+/-}^2 = [(1+\mu) \pm \sqrt{1-\mu+\mu^2}]\nu_1^2, \tag{1}$$

with $\mu = M_1/M_2$, where M_1 and M_2 are the masses of the two ions, and ν_1 is the oscillation frequency of a single ion with mass M_1. In the following, the corresponding motional modes will be referred to as the center-of-mass mode (ν_-) and the breathing mode (ν_+). By determining ν_1 for an ion with a known mass M_1, the mass M_2 of the other ion can be deduced from a measurement of one of the frequencies ν_+ and ν_-. For two identical ions with mass M_1, the center-of-mass mode frequency is equal to ν_1. Since two equally charged ions have identical equilibrium positions independent of their masses, it is hence possible to measure ν_1 and ν_- with ions located at the same positions in the trap, which minimizes systematic errors arising from slight anharmonicities in the trap potential.

The essential parts of our experiment are sketched in Fig. 1. The Ca^+ ions used in the experiments to sympathetically cool the molecular ions were produced by an isotope selective photoionization process [18,19], while the molecular ions used for illustrating the technique were produced in reactions between the Ca^+ ions and a thermal gas of O_2 [6]. In the experiments, we apply laser cooling to at least one $^{40}Ca^+$ ion, such that the ions are directly or sympathetically cooled down to temperatures of a few mK. At such low temperatures, the ions are localized to within a small fraction of their equilibrium distance [6,20]. The ions are forced to line up along the trap axis by making the radial trap frequencies higher than the axial one. The positions of the $^{40}Ca^+$ ions are directly observed by a charge-coupled device (CCD) camera through detection of fluorescence light emitted during the laser cooling process. An image of two $^{40}Ca^+$ ions is shown in Fig. 2(a). The two-ion eigenfrequencies are measured by applying a harmonically oscillating perturbing force along the alignment axis. When the drive frequency of the force is near one of the eigenfrequencies, the amplitude of the ions' motion along this axis is enhanced. For exposure times longer than the oscillation period this leads to a spatial smearing of the fluorescence signal in the CCD images as shown in Fig. 2(b). In the experiments we have applied a perturbing force in two different ways. The simplest method consists of applying an oscillating electric field along the trap axis by adding an oscillating voltage to two diagonally positioned end-electrodes as shown in Fig. 1. The other method is based on modulating the radiation pressure force on the laser cooled ion(s) by a modulation of the laser intensity of one of the beams propagating along the trap axis using an electro-optical chopper (EOC, see Fig. 1).

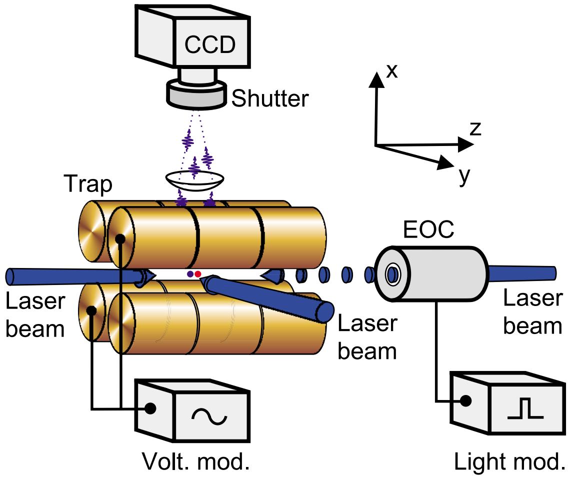

FIG. 1 (color online). Sketch of the experimental setup. Cooling of the $^{40}Ca^+$ ion [left (blue) dot] is provided by three laser beams as shown, while the molecular ion [right (red) dot] will be cooled sympathetically. See text for details.

The images presented in Fig. 2 show snapshots from a series of measurements where ν_1 was measured for two $^{40}Ca^+$ ions and ν_- for one $^{40}Ca^+$ ion and one unknown ion, which presumably is a $^{40}Ca^{16}O^+$ ion formed in a reaction between one of the ions shown in Fig. 2(a) and an O_2 molecule. Figures 2(a) and 2(c) show the fluorescence from the laser cooled $^{40}Ca^+$ ions before any perturbing force was applied. Since the single $^{40}Ca^+$ ion in Fig. 2(c) is located exactly at the same position as one of the ions in Fig. 2(a), we can be confident that there is only one nonvisible singly charged ion present. When tuning the frequency of a perturbing electric field to maximize the amplitude of the ions' forced motion for the two cases presented in Fig. 2, we found the resonance frequencies $\nu_1 = 98.7(1)$ kHz and $\nu_- = 89.4(1)$ kHz, respectively. The mass M_1 of the $^{40}Ca^+$ ion is known to be 39.97 a.m.u., and by combining this with the found frequencies via Eq. (1) one gets $M_2 = 56.1(4)$ a.m.u. Although not impressive, this precision is already sufficient to conclude that the nonvisible molecular ion is indeed a $^{40}Ca^{16}O^+$ ion and not a CaO^+ ion with another isotopic composition.

To discriminate between equally charged atomic or molecular ions with the same total number of nucleons, a relative mass resolution of $\sim 10^{-4}$ is typically needed. This level of accuracy cannot be reached using the simple technique discussed above, since the measured resonance frequency is subject to a systematic shift of up to $\sim 1\%$, depending on the damping effect of the laser cooling force and the trap frequency. However, by detecting only the in-phase component of the motion of the ions with respect to the periodic perturbing force, a dispersive shaped signature of the trap resonance is found. The zero crossing of this curve yields the trap resonance frequency

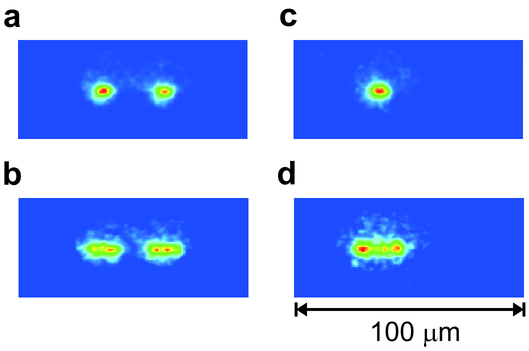

FIG. 2 (color online). Images of fluorescence from $^{40}Ca^+$ ions. (a) Two $^{40}Ca^+$ ions at thermal equilibrium in the trap. (b) The same two $^{40}Ca^+$ ions as in (a), but with a modulated voltage applied to the trap electrodes at a frequency near the resonance frequency $\nu_1 = 98.7$ kHz. (c) The same situation as in (a), but with one of the $^{40}Ca^+$ ions and presumably a nonfluorescing $^{40}Ca^{16}O^+$ ion. (d) Image of the $^{40}Ca^+$ ion in (c), but when a modulated force at a frequency close to the resonance frequency $\nu_- = 89.4$ kHz is present. In all the experiments the radial trap frequencies were 380 kHz and the exposure time of the CCD chip was 100 ms.

free of lowest order damping dependent shifts. In this manner a relative mass resolution better than $\sim 10^{-4}$ is indeed feasible [21]. In a first experiment to demonstrate such a mass resolution, we have chosen to work with ions of different isotopes of calcium as test masses instead of molecular ions. This is done since in our setup it is relatively easy to create ions of the various isotopes either by isotope selective photoionization [18,19] or charge exchange processes [19,22], furthermore, in the first experiments we want to have complete knowledge of our test masses. However, since the internal degrees of freedom of molecular ions do not couple to the external motion in the trap, there is no reason to believe the results should be different with molecular ions. In Fig. 3, the position resolved fluorescence of two $^{40}\mathrm{Ca}^+$ ions [Fig. 3(a)] and one $^{40}\mathrm{Ca}^+$ ion and one $^{42}\mathrm{Ca}^+$ ion [Fig. 3(b)] is shown as a function of the intensity modulation frequency of a single cooling laser beam. For these data the laser intensity was modulated with the laser field only present for 1.3 μs in each period, and with the camera gated to only record light emitted within a time span of 1.1 μs during the presence of the modulated light. In both the cases presented in Fig. 3, the phase of the ions' motion changes rapidly around specific modulation frequencies. With M_1 being the mass of the $^{40}\mathrm{Ca}^+$ ion, according to the discussion above these frequencies equal the resonance frequencies ν_1 and ν_-. The resonance frequencies are derived from fits to data series like those shown in Fig. 3, where the spatial fluorescence intensity distribution of one ion is modeled by the function

$$I(z, \nu_{\mathrm{drive}}) = I_0 \exp\left\{-\frac{[z - z_0(\nu_{\mathrm{drive}})]^2}{\Gamma_z(\nu_{\mathrm{drive}})^2}\right\} + I_B, \qquad (2)$$

where ν_{drive} is the drive frequency, I_0 is the ion signal, I_B is the background level, $z_0(\nu_{\mathrm{drive}})$ is the mean in-phase position of the ion and

$$\Gamma_z(\nu_{\mathrm{drive}}) = \frac{\alpha_\nu}{(\nu_{\mathrm{drive}} - \nu_-)^2 + \gamma_\nu^2} + \Gamma_{\mathrm{res}} \qquad (3)$$

is the spatial width of the fluorescence signal with Γ_{res} being the spatial resolution of the imaging system, γ_ν being the width of the resonance and α_ν being a constant related to the amplitude of the forced motion. Finally,

$$z_0(\nu_{\mathrm{drive}}) = \frac{\alpha_z(\nu_{\mathrm{drive}} - \nu_-)}{(\nu_{\mathrm{drive}} - \nu_-)^2 + \gamma_\nu^2} + z_{\mathrm{off}}, \qquad (4)$$

where z_{off} is the ion position in the absence of modulation forces and α_z is a constant related to the amplitude of the forced motion. In Fig. 4, the results of such fits are presented for three combinations of calcium isotopes. From a statistical analysis of these data, we find $\mu_{40/42,\mathrm{mean}} = 0.9526(3)$ and $\mu_{40/44,\mathrm{mean}} = 0.9095(3)$, respectively, as the mean values. From the best tabulated values of atomic masses [23], the expected values are $\mu_{40/42,\mathrm{table}} = 0.952441$ and $\mu_{40/44,\mathrm{table}} = 0.909174$, respectively. These coincide with our observations at a level of 1.4×10^{-4} and 3.4×10^{-4}, respectively. The deviations reflect the size of the systematic errors in the experiments due to the asymmetry, which arises when applying laser cooling to only one ion, as well as the timing resolution of the camera system [21]. The accuracy in these measurements is already sufficient to discriminate between some singly charged atoms or molecules with an identical number of nucleons, such as $^{13}\mathrm{C}_2\mathrm{H}_2^+$ and $^{14}\mathrm{N}_2^+$ which have a relative mass difference of 5.8×10^{-4} [16]. Without significant changes in our setup, we should in the future be able to reach the level of 10^{-5} or lower [21]. This level of accuracy can of course not compete with the precision of the best dedicated mass measurements scheme [16], but it will certainly be sufficient for most chemical physics experiments.

In the near future, we plan to test the above proven accuracy on various molecular ions. An obvious test of the resolution would be to measure the relative mass difference of the mass doublet $^{40}\mathrm{Ca}^{18}\mathrm{O}^+$ and $^{42}\mathrm{Ca}^{16}\mathrm{O}^+$, which is expected to be 1.4×10^{-4} [23].

It should be noted that, in contrast to the electrical perturbation scheme [24], the laser force modulating technique allows easy excitation of both the center-of-mass mode and the breathing mode, such that both the frequencies ν_- and ν_+ can be determined. With the knowledge of these two frequencies, no reference measurement of ν_1 is needed in order to determine M_2.

Since the presented identification technique does not rely on spectroscopic sideband resolution, it can be applicable in a large variety of experiments. The range of

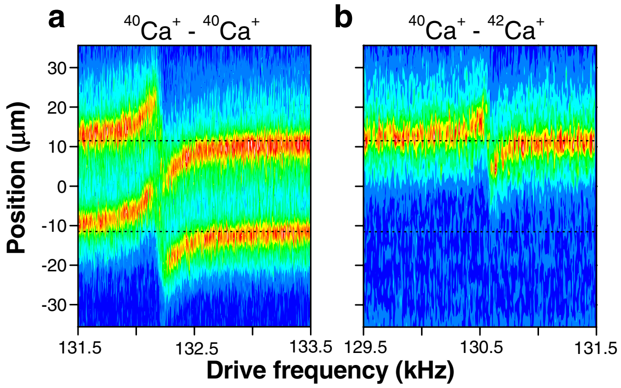

FIG. 3 (color online). The position resolved fluorescence along the trap axis as a function of the drive frequency of the intensity modulated laser beam. (a) Two $^{40}\mathrm{Ca}^+$ ions. (b) One $^{40}\mathrm{Ca}^+$ ion and one $^{42}\mathrm{Ca}^+$ ion, where only the $^{40}\mathrm{Ca}^+$ ion is fluorescing. Each gray scale (false-colored) contour plot is composed of axial projections of the fluorescence intensities in gated images recorded during the frequency scans [scan rates: (a) 2 Hz/image, (b) 8 Hz/image]. Dashed lines indicate equilibrium positions of the ions in the absence of modulation. The dark gray (red) areas near the dashed lines corresponds to high intensity, while the dark (blue) areas are low intensity regions. The radial trap frequencies were 400 kHz in all experiments.

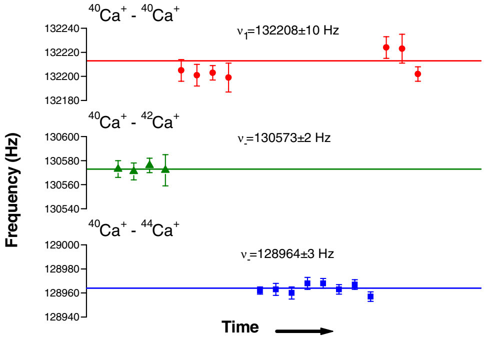

FIG. 4 (color online). Resonance frequencies obtained for three combinations of calcium isotopes. Each data point represents the resonance frequency found from fits to data series as those shown in Fig. 3. The stated resonance frequencies are the statistical average values of the data points. The horizontal position of the data points reflects the time order of the experiments.

molecular mass-to-charge ratios, where the technique can be used, spans at least from 2 to ~500, depending on the choice of the laser cooled ion [25]. As already indicated by the results in Fig. 2, the identification technique is an excellent tool in single ion reaction experiments, and its nondestructive nature as well as the short measurement time needed (~1 min) makes it particularly useful when consecutive reactions [6] or other successive manipulations like building up more complex molecular ions from step-by-step reactions are pursued. Since processes leading to a change in the mass or charge of the target molecule can be detected with essentially 100% efficiency, the technique is very attractive for, e.g., single molecule photoionization and dissociation studies, including coherent-control experiments [8,9].

In conclusion, we have presented a simple single molecule identification technique which potentially allows for a nondestructive discrimination between equally charged atomic and molecular ions with an identical number of nucleons. Through the sympathetic cooling procedure a localized and cold single molecule target is available for further studies in an environment with very weak perturbations.

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