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LETTER TO THE EDITOR

The rotational temperature of polar molecular ions in Coulomb crystals

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Abstract

With MgH⁺ ions as a test case, we investigate to what extent the rotational motion of smaller polar molecular ions sympathetically cooled into Coulomb crystals in linear Paul traps couples to the translational motions of the ion ensemble. By comparing the results obtained from rotational resonance-enhanced multiphoton photo-dissociation experiments with data from theoretical simulations, we conclude that the effective rotational temperature exceeds the translational temperature (<100 mK) by more than two orders of magnitude, indicating a very weak coupling.

Molecules which are translationally cold, spatially localized and internally prepared in specific states constitute ideal targets for a large variety of investigations, including high resolution spectroscopy [1], coherently controlled chemistry [2, 3], state-specific reaction studies [4, 5], and molecular internal state control experiments [6].

For atoms such targets have for years been available by combining laser cooling techniques with trapping and, perhaps most spectacularly, been exploited in quantum logics experiments [7, 8]. It is, however, extremely difficult to adopt the same techniques for molecules due to the general lack of closed optical transitions. For polar molecules a further complication arises since the rovibrational degrees of freedom couple rather efficient to the black body radiation (BBR) of the surroundings. Recently, various methods that at least partially approach the ideal situation have, however, been demonstrated for neutral molecules. These include photo-association of cold atoms [9], buffer gas cooling of molecules in magnetic traps [10], and control of the motion of molecules by either static [11] or optical electrical fields [12]. Internally cold, but not spatially localized molecular ions have been produced either by photoprocesses [13, 14], by buffer-gas cooling in RF multi-pole traps [15, 16] or by state selective recombination [17]. Recently, by sympathetical cooling to translational temperatures in the mK-range in RF ion traps, spatially localized molecular ions in Coulomb crystals have been reported [18, 19].

In this letter, we investigate whether there is a sufficient coupling between the internal degrees of freedom of polar molecular ions and the external motion of the ions in a Coulomb crystal to achieve a significant sympathetic cooling of the internal states of the molecular



Figure 1. The four lowest spin singlet potential energy curves for ²⁴MgH⁺ including various symbols and processes discussed in the text. The potential curves are found using the state average multi-reference self consistent field (MCSCF) method, the computational details are given in [23].

ions. The strategy is to apply resonance-enhanced multiphoton photo-dissociation (REMPD) [20] as a tool to obtain knowledge of the populations in the various rotational states and hence determine the effective rotational temperature. Most likely, a measurable cooling of the internal degrees of freedom of the molecular ions will be due to the coupling of the dipole moment of the molecules to the motion of the charges of the ions in the Coulomb crystal. However, since the typical frequencies of the normal modes of the Coulomb crystal will be $\sim 10^6$ Hz while the rovibrational frequencies will be $\sim 10^{11}$ Hz– $\sim 10^{13}$ Hz, no strong resonant coupling is expected [21].

An ensemble of ${}^{24}MgH^+$ molecules, which is translational, sympathetically cooled by laser cooled ${}^{24}Mg^+$ atomic ions in a linear Paul trap, has been chosen as a test case for many reasons. The ${}^{24}MgH^+$ ions are easy to produce and sympathetically cool [18], at room temperature, 99% will be in the vibrational ground state, precise spectroscopic data are available for ${}^{24}MgH^+$ [22], and finally in order to compare experimental results with theoretical simulations, the potential energy curves and permanent as well as transition electronic dipole moments of ${}^{24}MgH^+$ can be calculated with good precision [23, 24].

In figure 1, the potential energy curves of the four lowest lying spin singlet electronic states of ²⁴MgH⁺ are shown together with an indication of states and processes of relevance to the investigations. The resonant part of the two-photon REMPD process consists of a rotational state-selective excitation from the electronic ground potential $X^1\Sigma(\nu = 0, J)$ to a state in the electronic excited potential $A^1\Sigma(\nu'' = 0, J + 1)$ by a laser field ε . The letters ν and *J* represent the vibrational and rotational quantum numbers, respectively. From the state $A^1\Sigma(\nu'' = 0, J + 1)$, the molecule can dissociate nearly exclusively into Mg and H⁺ via the C potential curve by absorbing another photon from the ε field. However, with the field strengths applied in our experiments, the excited molecule primarily spontaneously decays back to a vibrational excited state in the electronic ground state potential $X^1\Sigma$ with a rate $\Gamma_E \approx 3 \times 10^8 \text{ s}^{-1}$. Subsequently, further spontaneous emissions, stimulated processes due to the coupling to the BBR field, and transitions induced by an effective coupling to the external motion of the ions take place. In figure 1, these various mechanisms are in brief denoted by $\Gamma_{\nu J}$. Eventually, the molecule will reach the state $X^1\Sigma(\nu = 0, J)$ from where it again can couple strongly to the laser field ε .



Figure 2. (a) 2D projection-image of a pure Coulomb crystal of approximately 3000 fluorescing $^{24}Mg^+$ ions. The length of the crystal is 1070 μ m. (b) A two-component crystal, consisting of \sim 35% $^{24}Mg^+$ and \sim 65% $^{24}MgH^+$ ions (non-fluorescing), obtained by letting $^{24}Mg^+$ ions in the crystal in (a) react with a gas of H₂. (c) A nearly pure $^{24}Mg^+$ crystal obtained after ns-laser pulses have been applied for 60 s to dissociate the $^{24}MgH^+$ molecules in the crystal shown in (b). The dashed ellipse indicates the position of the outer surface of the initial crystal in (a). The dotted line in (a) indicates the axis of rotational symmetry.

The experimental set-up has previously been described in [25, 26]. In short, ²⁴Mg⁺ ions are produced by off-resonance photo-ionization by the pulsed laser field ε indicated in figure 1 and trapped in a linear Paul RF trap [25] situated in a UHV chamber at background pressure of $\sim 1 \times 10^{-10}$ Torr. The produced ²⁴Mg⁺ ions are laser-cooled on the 3s² S_{1/2}–3p² P_{3/2} transition by two cw laser beams counter-propagating along the centre-axis of the trap to temperatures below 10 mK where they form a Coulomb crystal [25]. The two-dimensional projection images of such crystals are obtained by monitoring the fluorescence by a CCD camera. A typical projection image of a pure ²⁴Mg⁺ crystal is shown in figure 2(a). The shape of the real crystal is spheroidal with rotational symmetry around the dotted line.

The ²⁴MgH⁺ molecular ions are formed through photochemical reactions between ²⁴Mg⁺ ions excited to the $3p^2 P_{3/2}$ state and H₂ molecules leaked in the chamber at partial background pressure of 5×10^{-10} Torr. for a few minutes [18]. The produced ²⁴MgH⁺ molecular ions are within tens of milliseconds translational sympathetically cooled by the remaining ²⁴Mg⁺ to a temperature below 100 mK, and a two-component Coulomb crystal is formed [18]. As seen in figure 2(b), due to dynamical radial confinement of the ions, the non-fluorescing ²⁴MgH⁺ molecular ions and the coolant ²⁴Mg⁺ ions segregate radially with the lighter mass ions, the ²⁴Mg⁺ ions, closest to the rotational symmetry axis [25]. The amount of each ion species in the crystal can be deduced from the fact that each species in the trap will have a uniform density inversely proportional to its mass and that for crystals containing two species with a small difference in mass, the outer boundary will have a nearly spheroidal shape [26–28]. By determining the volume of the fluorescing region in figure 2(b), we can conclude that this particular crystal has a relative ²⁴MgH⁺ content of ~65%.

The laser field ε presented in figure 1 originates from a frequency doubled dye laser pumped by a Nd:YAG laser. The pulse repetition rate is 20 Hz, and the duration of each pulse is approximately 5 ns. The waist of the field at the trap centre is 500 μ m, and the peak intensity was typically of the order of I_{peak} ~ 10⁷ W cm⁻², corresponding to a peak power-broadening of the A¹ Σ ($\nu'' = 0, J + 1$) \leftarrow X¹ Σ ($\nu = 0, J$) transitions of ~0.3 cm⁻¹. The spectral width of each pulse was ~0.25 cm⁻¹, and the centre frequency was calibrated to better than 0.1 cm⁻¹. During each experiment, the centre frequency was continuously scanned 0.95 cm⁻¹ at the rate



Figure 3. The amount of ²⁴MgH⁺ ions relative to the initial content of ²⁴MgH⁺ in the crystal as a function of the time in which the ²⁴MgH⁺ ions are exposed to the dissociation laser pulses. The triangles and circles represent data for the R(1) and R(6) resonances, respectively (see text). In this case $I_{peak} = 1.9 \times 10^7$ W cm⁻².

of 1 Hz in order to obtain results which are independent of slow frequency drifts in the laser system. The resonance frequencies of the $A^1\Sigma(\nu''=0, J+1) \leftarrow X^1\Sigma(\nu=0, J)$ transitions, which are used in our REMPD scheme, are known with a precision of 0.05 cm⁻¹ from [22].

Before the REMPD lasers are applied, the produced ${}^{24}MgH^+$ ions are allowed to internally equilibrate for about one minute, a time long enough to ensure that the produced molecular ions are in the vibrational ground state and that any effective cooling of the rotational degrees of freedom will be revealed in the experiments. In the experiments, crystals like the one shown in figure 2(b) are exposed to the laser pulses while CCD images are being recorded at a rate of 6 Hz. After a typical exposure time of tens of seconds, all molecules have been dissociated, and a nearly pure crystal of ${}^{24}Mg^+$ is left in the trap as shown in figure 2(c). Before a new REMPD experiment is carried out, the trap is reloaded with ${}^{24}Mg^+$ ions, and through reactions, Coulomb crystals with nearly the same number of ${}^{24}Mg^+$ and ${}^{24}MgH^+$ ions are created each time.

In figure 3, the normalized amount of ²⁴MgH⁺ molecular ions are shown for two out of about ten REMPD experiments where the ε field has been tuned to the resonance of the R-branch transitions R(1): A¹ $\Sigma(\nu'' = 0, J = 2) \leftarrow X^1\Sigma(\nu = 0, J = 1)$ and R(6): A¹ $\Sigma(\nu'' = 0, J = 7) \leftarrow X^1\Sigma(\nu = 0, J = 6)$.

In order to derive an estimate for the rotational temperature from the outcome of the REMPD experiments, simulations including various strengths of an effective sympathetic rotational cooling have been performed. In the model, this cooling has been accounted for by introducing an artificial decay rate from the rotational states J to J - 1 proportional to J + 1. This corresponds to have an effective cooling rate Γ_c defined through $d\overline{E}_{rot}/dt = -\Gamma_c \overline{E}_{rot}$, where \overline{E}_{rot} is the average rotational energy. In figure 4, the simulated steady-state rotational temperature of the ²⁴MgH⁺ ions, defined as $T_{rot} = \overline{E}_{rot}/k_B$, is presented as a function of the cooling rate Γ_c . In the absence of sympathetic cooling, the rotational distribution is observed to equilibrate to the temperature of the BBR field in the trap region (~300 K). It is, however, clear that only a very modest cooling rate Γ_c (~0.1 s⁻¹) will change this situation dramatically. The steady-state rotational distributions are the starting points for all simulations.



Figure 4. (a) The steady-state rotational temperature of ²⁴MgH⁺ as a function of the effective cooling rate Γ_c (see text for detailed definitions). (b) The population distributions for three different rotational temperatures: white: $T_{\rm rot} = 300$ K; grey: $T_{\rm rot} = 100$ K; and black: $T_{\rm rot} = 3$ K. The colours of the bars correlate to the colour of the three squares in (a).

When simulating the time evolution of the photo-dissociation process, the time line is divided in two types of intervals: intervals where the laser pulses are present and intervals defined by the time between consecutive laser pulses. The intensity of the pulses is assumed to be Gaussian in time and in the simulations, the length of the pulses is set to be 6τ with τ being the FWHM of a single pulse ($\tau = 5$ ns). During a laser pulse, the laser field ε drives transitions between the various rovibrational states of the $X^1\Sigma$ and $A^1\Sigma$ potential curves (see figure 1). In order to reduce the computational time, we assume that, at any instant during the pulse, the various internal state populations are in steady-state with the instantaneous laser field strength and detunings. At each time step, the probability p_{Diss} for dissociation via the $C^{1}\Sigma$ potential curve due to the field ε is determined from the instantaneous populations in the $A^1\Sigma$ potential curve (see figure 1), and the norm p_{Norm} of the remaining molecular wavefunction is renormalized to $p_{Norm} - p_{Diss}$. During the laser pulse, spontaneous emission from the populated $A^{1}\Sigma$ states to the various rovibrational states of the $X^{1}\Sigma$ potential curve is included as well while rovibrational transitions within each potential curve are neglected due to the shortness of the pulses. Between consecutive pulses population redistribution processes among the rovibrational states in the electronic ground potential $X^{1}\Sigma$ are simulated taking into account an effective sympathetic cooling, spontaneous decay, and interactions with the BBR field. For short these processes are presented by the symbol $\Gamma_{\nu J}$ in figure 1. Due to the complexity of the simulations, only the main ideas have been considered here, but the details will be presented elsewhere [21].

The ratios between the simulated dissociation rates for REMPD processes via the R(1) and R(6) resonances are presented in figure 5 as a function of the effective rotational temperature obtained by including a certain cooling rate Γ_c in the calculations. The dissociation rates have been extracted 10 s after initiation of the photo-dissociation process where the various populations and the dissociation rate are simulated to be in steady state [21]. The ratio of dissociation via the R(1) and R(6) resonances provides a simple experimental way of distinguishing between low (≤ 1 K) and high (≥ 100 K) rotational temperatures T_{rot} as the ratio changes drastically for temperatures below ~ 50 K.



Figure 5. The ratios between the simulated dissociation rates for REMPD processes via the R(1) and R(6) resonances. The ratio (*y*-axis) is on a logarithmic scale. The values of T_{rot} are directly connected to a cooling rate Γ_c included in the simulations. The connection between T_{rot} and Γ_c is presented in figure 4. The curves represent three different peak-intensities of the laser pulses, whereas the two grey horizontal lines represent a conservatively estimated range based on a series of experimental data set, including the one presented in figure 3.

The ratio of dissociation rates is fortunately nearly insensitive to intensity variations. Even a factor of four in the actual peak intensity does not significantly change the ratio. This indicates that a small error in calibration of the power meter used in the experiments or smaller uncertainties in the laser beam positioning should not affect the measured ratio. A conservative estimated interval of this ratio that is in agreement with a series of experimental data as those presented in figure 3 is indicated in figure 5 by the two grey horizontal lines. From figure 5 it is hence reasonable to conclude that the rotational temperature of the ²⁴MgH⁺ ions is higher than 100 K, and likely as high as room temperature, which is the same rotational temperature found in storage ring experiments with very weak coupling between the individual ions [29]. In terms of the rotational cooling rate Γ_c , we can correspondingly conclude that it must be smaller than ~ 0.1 s⁻¹.

Since the permanent dipole moment of ${}^{24}MgH^+$ (3.6 Debye) is not particularly small, and its rotational frequencies are not extraordinary, we expect that molecular ions in Coulomb crystals do not generally become rotationally cold. Also since the typical trapping potentials of Penning traps are typically similar to those of RF traps, no gain with respect to rotational cooling in such traps is expected.

At present we cannot rule out rotational state changing collisions in the initial phase of the sympathetic cooling process where the temperature is typical of the order of 1000 K and consequently rather close collisions appear. Hence, when experimenting with polar molecular ions at room temperature, it hence might be necessary to implement a kind of active rotational cooling in order to achieve state specific molecular ion targets. [24, 30, 31]. Alternatively, one might choose to cool the trap environment to cryogenic temperatures [15, 16]. For non-polar molecular ions, the coupling between the internal degrees of freedom and the modes of the Coulomb crystal as well as the BBR field is smaller than for polar molecules. Hence, such ions produced by, e.g., a state-selective REMPI-process would possibly be able to reside in

this state through sympathetic cooling, and could lead to spatially localized state-specific targets.

In conclusion, with ²⁴MgH⁺ ions as the test case, we have proven that the rotational motion of smaller polar molecular ions sympathetically cooled into a Coulomb crystal does not become significantly cooled, but very likely stays in nearly thermal equilibrium with the surrounding environment.

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