The rotational temperature of polar molecular ions in Coulomb crystals

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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 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.

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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\[^\text{1}\], coherently controlled chemistry\[^\text{2}\], state-specific reaction studies\[^\text{3,4}\] and molecular internal state control experiments\[^\text{5}\].

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\[^\text{6,7}\]. 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 efficiently 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\[^\text{8}\], buffer gas cooling of molecules in magnetic traps\[^\text{9}\], and control of the motion of molecules by either static\[^\text{10}\] or optical electrical fields\[^\text{11}\].

Internal cold, but not spatially localized molecular ions have been produced either by photo-processes\[^\text{12,13}\], by buffer-gas cooling in RF multi-pole traps\[^\text{14,15}\] or by state selective recombination\[^\text{16}\]. Recently, by sympathetic cooling to translational temperatures in the mK-range in RF ion traps, spatially localized molecular ions in Coulomb crystals have been reported\[^\text{17,18}\].

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 ions. The strategy is to apply Resonance-Enhanced Multiphoton Photo-Dissociation (REMPD)\[^\text{19}\] as a tool to obtain knowledge of the populations in the various rotational states and hence determine the effective rotational temperature. One could most likely expect a measurable cooling of the internal degrees of freedom of the molecular ions due to 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–\(10^{13}\) Hz, no strong resonant coupling is expected Ref.\[^\text{20}\].

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\[^\text{17}\], at room temperature 99% will be in the vibrational ground state, precise spectroscopic data are available for \(^{24}\)MgH\(^+\)\[^\text{21}\], and finally in order to compare experimental results with theoretical simulations, the potential curves and permanent as well as transition dipole moments of \(^{24}\)MgH\(^+\) can be calculated with good precision\[^\text{22,23}\].

In Fig.\[^\text{1}\] the energy potential curves of the four lowest lying singlet electronic states of \(^{24}\)MgH\(^+\) are shown together with an indication of states and processes discussed in the text.

\[ \nu = 0, J \]
potential by a laser field $\varepsilon$. The letters in the ket-notation represent the vibrational and rotational quantum numbers, respectively. From the $|\nu'' = 0, J + 1\rangle_X$ state, the molecule can dissociate nearly exclusively into Mg and H$^+$ via the C potential curve by absorbing another photon from the $\varepsilon$ 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 $\Gamma_E \approx 3 \times 10^8$ 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 Fig. 1, these various mechanisms are in brief denoted by $\Gamma_{\nu J}$. Eventually, the molecule will reach the state $|\nu = 0, J\rangle_X$ from where it again can couple strongly to the laser field $\varepsilon$.

The experimental setup has previously been described in Refs. [24, 25]. In short, $^{24}\text{Mg}^+$ ions are produced by off-resonance photo-ionization by the pulsed laser field $\varepsilon$ indicated in Fig. 1 and trapped in a linear Paul RF trap [24] situated in a UHV chamber at background pressure of $\approx 1 \times 10^{-10}$ torr. The produced $^{24}\text{Mg}^+$ ions are laser-cooled on the $3s^2S_{1/2}$-$3p^2P_{3/2}$ transition by two cw laser beams counter-propagating along the center-axis of the trap to temperatures below 10 mK where they form a Coulomb crystal [24]. 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 $^{24}\text{Mg}^+$ crystal is shown in Fig. 2(a). The shape of the real crystal is spheroidal with rotational symmetry around the dotted line.

The $^{24}\text{MgH}^+$ molecular ions are formed through photochemical reactions between $^{24}\text{Mg}^+$ ions excited to the $3p^2P_{3/2}$ state and H$_2$ molecules leaked in the chamber at partial background pressure of $5 \times 10^{-10}$ torr for a few minutes [17]. The produced $^{24}\text{MgH}^+$ molecular ions are within tens of milliseconds translational sympathetically cooled by the remaining $^{24}\text{Mg}^+$ to a temperature below 100 mK, and a two-component Coulomb crystal is formed [17]. As seen in Fig. 2(b), due to dynamical radial confinement of the ions, the non-fluorescing $^{24}\text{MgH}^+$ molecular ions and the coolant $^{24}\text{Mg}^+$ ions segregate radially with the lighter mass ions, the $^{24}\text{Mg}^+$ ions, closest to the rotational symmetry axis [24]. 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 near spheroidal shape [24, 27, 28]. By determining the volume of the fluorescing region in Fig. 2(b), we can conclude that this particular crystal has a relative $^{24}\text{MgH}^+$ content of $\approx 65\%$.

The laser field $\varepsilon$ presented in Fig. 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 center is 500 $\mu$m, and the peak intensity was typically of the order of $I_{\text{peak}} \approx 10^7$ W/cm$^2$, corresponding to a peak power-broadening of the $|\nu = 0, J\rangle_X$–$|\nu'' = 0, J + 1\rangle_X$ transitions of $\approx 0.3$ cm$^{-1}$. The spectral width of each pulse was $\approx 0.25$ cm$^{-1}$, and the center frequency was calibrated to better than 0.1 cm$^{-1}$. During the experiments, the center frequency was scanned 0.95 cm$^{-1}$ at 1 Hz in order to obtain results which are independent of slow frequency drifts in the laser system. The resonance frequencies of the $X^1\Sigma(\nu = 0, J)\rightarrow A^1\Sigma(\nu'' = 0, J + 1)$ transitions, which are used in our REMPD scheme, are known with a precision of 0.05 cm$^{-1}$ from Ref. [21].

Before the REMPD lasers are applied, the produced $^{24}\text{MgH}^+$ 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 Fig. 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 $^{24}\text{Mg}^+$ is left in the trap as shown in Fig. 2(c). Before a new REMPD experiment is carried out, the trap is reloaded with $^{24}\text{Mg}^+$ ions and through reactions, Coulomb crystals with nearly the same number of $^{24}\text{Mg}^+$ and $^{24}\text{MgH}^+$ ions are created each time.

In Fig. 3 the normalized amount of $^{24}\text{MgH}^+$ 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): |ν = 0, J = 1⟩X−|ν′ = 0, J = 2⟩A and R(6): |ν = 0, J = 6⟩X−|ν″ = 0, J = 7⟩A, respectively.

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. This corresponds roughly to have an effective cooling rate Γ_c defined through d⟨E_{rot}/dt⟩ = −Γ_cE_{rot}, where E_{rot} is the average rotational energy. In Fig. 4, the simulated steady-state rotational temperature of the 24MgH^+ ions, defined as T_{rot} = T_{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 (see Fig. 4).

The steady-state rotational distributions are the starting points for all simulations.

When simulating the time evolution of the photo-dissociation process, the time scale is broken into two types of intervals defined by the presence or absence of the laser pulses. During a laser pulse, the effect of laser driven transitions between the various rovibrational states of the X^1Σ and A^1Σ potential curves is taken into account by at any time during the pulse assuming that the various populations are in steady-state with the instantaneous laser field strength and detunings. Based on the instantaneous populations in the A^1Σ potential curve, the dissociation rate via the C^3Σ potential curve is determined. During the laser pulse, spontaneous emission from the populated A^1Σ states to the various rovibrational states of the X^1Σ potential curve is included as well, while rovibrational transitions within the potential curves are neglected due to the short time scale of the pulses. Between consecutive pulses population redistribution processes among the rovibrational states in the electronic ground potential X^1Σ are simulated taking into account an effective sympathetic cooling, spontaneous emissions and interactions with the BBR field. Due to the complexity of the simulations, only the main ideas have been considered here, but the details will be presented elsewhere Ref. 20.

The ratios between the simulated dissociation rates for REMPD processes via the R(1) and R(6) resonances are presented in Fig. 4 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 20. The chosen dissociation ratio 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.

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 smaller 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 Fig. 3 is indicated in Fig. 5 as the hatched area. From Fig. 5 it is hence reasonable to conclude that the rotational temperature of the $^{24}$MgH$^+$ ions is higher than 120 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 $^{28}$. In terms of the rotational cooling rate $\Gamma_c$, we can correspondingly conclude that it must be smaller than $\sim 0.1$ 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.

When experimenting with polar molecular ions at room temperature, it hence seems necessary to implement a kind of active rotational cooling in order to achieve state specific molecular ion targets $^{24}$, $^{26}$, $^{30}$. Alternatively, one might choose to cool the trap environment to cryogenic temperatures $^{14}$, $^{15}$. 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 spatial localized state-specific targets.

In conclusion, with $^{24}$MgH$^+$ 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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FIG. 5: The ratios between the simulated dissociation rates for REMPD processes via the R(1) and R(6) resonances. The values of $T_{\text{rot}}$ are directly connected to a cooling rate $\Gamma_c$ included in the simulations (presented in Fig. 4). The curves represent three different peak-intensities of the laser pulses, whereas the hatched area represents a conservative estimated range derived from experimental data as those presented in Fig. 3.