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Rotational state resolved photodissociation spectroscopy of translationally and vibrationally cold MgH⁺ ions: toward rotational cooling of molecular ions

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Abstract. The first steps toward the implementation of a simple scheme for rotational cooling of MgH^+ ions based on rotational state optical pumping is considered. The various aspects of such an experiment are described in detail, and the rotational state-selective dissociation spectra of translationally and vibrationally cold MgH^+ ions are presented, with and without the optical pumping laser being present. While rotational cooling is as yet not evident, first results showed evidence of a change in the rotational distribution in the presence of the optical pumping laser.

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Contents

1.	Introduction		2
2.	Rota	Rotational cooling of molecular ions	
	2.1.	Simplified scheme for cooling of MgH ⁺	4
	2.2.	Infrared diode laser system for cooling of MgH ⁺	5
3.	Photodissociation spectroscopy of cold molecular ions		
	3.1.	Trapping and laser cooling of Mg^+ ions	8
	3.2.	Production of translationally cold MgH ⁺ ions	9
	3.3.	Equilibration and manipulation of the rotational state distribution	10
	3.4.	Rotational state selective photodissociation of MgH ⁺ molecular ions	10
	3.5.	The MgH ⁺ dissociation spectrum	13
	3.6.	Numerical simulation of the spectrum	14
4.	Effe	ct of the lead salt diode laser	18
5.	Con	clusion and outlook	18
Ac	Acknowledgments		19
Re	References		

1. Introduction

Detailed control and active manipulation of the internal as well as external degrees of freedom of molecules are of great value for the advancement of several research fields. Most fundamentally, with such tools at hand, unprecedented high-precision spectroscopic data can be obtained for comparison with quantum chemistry models, for accurate measurements of natural constants and for metrology purposes [1]–[5]. Advances in the control and manipulation of molecules may well open new quantum information processing implementations [6]. State-prepared molecular targets can also lead to refined reaction studies, which includes unimolecular reactions with coherent light fields [7, 8] or bimolecular reactions between two reaction partners in well-characterized quantum states [9]. Finally, the option of having a dense ensemble of identically prepared molecules enables the realization of new collective phenomena, such as the Bose–Einstein condensation of molecules [10, 11].

During the past decade, research on cold molecules, whether neutral or ionic species, has developed rapidly. For neutrals, the advances have, in particular, been relying on developments within the following approaches to the formation of cold molecules: photoassociation of laser-cooled atoms [12]–[16], buffer-gas cooling of molecules held in magnetic traps [17], deceleration [18], filtering [19] and trapping [20]–[23] of molecules by electrostatic fields, Feshbach resonance-generated molecules in degenerate quantum gases [10, 11] and deceleration of molecules by intense laser pulses [24]. Most recently, molecules produced by Feshbach resonances have been brought to the vibrational ground state of electronic molecular potentials by the additional use of stimulated Raman adiabatic passage schemes [25]–[28]. Also recently, photoassociated molecules have been formed directly in the rovibrational ground state [29] or transferred to the vibrational ground through shaped fs-laser pulses [16]. Cooling techniques for molecular ions have been developed in parallel. It has now become a standard to work with molecular ions that are sympathetically cooled into Coulomb crystallization through the Coulomb interaction with laser-cooled atomic ions [30]–[36]. In the past few years, the

2

technique of He buffer-gas ion cooling [37] has furthermore been extended to molecular anions [38]. More recently, even the combination of cold neutral and ionic molecular techniques has made appreciable progress [39, 40].

In the present paper, the focus is on the recent development in our group toward the preparation of trapped and sympathetically cooled molecular ions in specific rovibrational states through a simple optical pumping scheme [41, 42]. In the following, a detailed description of the scientific approach and our first experimental results on characterization and manipulation of the rotational distribution of translationally cold MgH⁺ ions in the vibrational ground state are presented. In section 2, the basics of the rotational cooling scheme will be presented including a description of the light source to be applied for the cooling of MgH⁺. Next, in section 3, the formation of translationally cold MgH⁺ ions is described, and the rotational state-selective dissociation scheme for rotational state distribution measurements is discussed. This section presents, furthermore, the photodissociation spectrum of translationally cooled ion ensembles as well as numerical simulations of the measured spectrum. In section 4, a first result indicating that the rotational distribution in the ground vibrational state can in fact be altered by the application of a single continuous wave (cw) laser, which resonantly drives only a single rovibrational transition, is shown. Finally, in section 5, the results presented are summed up, and an outlook for near-future experiments is given.

2. Rotational cooling of molecular ions

Due to the possibility of a long storage time of molecular ions (typically hours), internal equilibrium with the blackbody radiation (BBR) field can in general easily be reached for polar molecules. For light diatomic molecular ions almost all of the population will be in the vibrational ground state at room temperature (e.g. more than 99.9% for MgH⁺). However, for such ions, a 300 K BBR field will give rise to population of a significant number of rotational states. Even for a light diatomic molecular ion such as MgH⁺, with a large rotational constant of B = 9 K for low-lying vibrational levels in the electronic ground state, more than ten rotational levels reach populations of more than a few per cent. In order to perform experiments of the type mentioned in the first part of the introduction, it is hence of great interest to narrow the rotational distribution, and in particular to cool the rotational motion as close as possible to the rotational ground state.

It is well known that the rotational temperature can be significantly reduced by buffer gas cooling with helium [37]. While this is a widely applicable tool, it leads, for trapped laser-cooled molecular ions, where the translational temperature is of the order of 10 mK, to an undesired heating of the translational motion due to collisions with the buffer gas. This problem could in principle be circumvented by employing laser-cooled atoms as buffer gas; however, charge-exchange processes will likely neutralize the molecular ions as was found in the case of MgH⁺–Rb [43]. If the research objective with the cold molecules relies on long-term internal state coherences, any buffer gas cooling has to be avoided.

Another well-known and general way of reducing the rotational temperature is to alter the BBR field by cryogenic cooling as well as efficient shielding of the entire ion trap. In this way, temperatures below 10 K can be reached [37, 44]; however, optical access to the trapped ions is limited by the shielding, and furthermore for heavier molecular ions like CaO^+ or BaO^+ [32, 45], a significant part of the population would still remain in higher rotational states.

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Figure 1. Simplified scheme for rotational cooling of MgH⁺. A laser drives the $|v = 0, J = 2\rangle - |v = 1, J = 1\rangle$ transition, which leads to optical pumping toward the $|v = 0, J = 0\rangle$ state. In combination with BBR-driven transitions, rotational cooling is obtained.

Cooling by optical techniques seems less straightforward due to the many, unevenly spaced rotational states. Nevertheless, rotational cooling by optical pumping can be obtained, as first proposed by Bahns *et al* [46], by chirping the frequency of a laser through specific P-branch transition frequencies. More recently, vibrational cooling by a spectrally shaped fs-laser pulse was demonstrated [16]. The same method can in principle be applied for rotational cooling if the ground rotational state can be spectrally resolved by the spectral shaping device and vibrational heating avoided.

In the present work, some decisive steps toward a realization of the scheme proposed by Vogelius *et al* [41, 42, 47] are described. Using this scheme optical pumping to the rotational ground state can be obtained by driving only a single or two dipole allowed transitions while *taking advantage* of the BBR field to redistribute population among the rotational levels. Numerical simulations show that starting from an initial thermal distribution at 300 K more than 70% of the population can be cooled to the ground state for MgH⁺ ions (using the so-called Raman scheme), and for ArH⁺, even about 90% can be obtained (using the so-called direct scheme based on dipole allowed transitions within the X¹ Σ ⁺ ground state potential). The generality of this optical pumping technique was demonstrated in [42] by extending the scheme from ¹ Σ electronic ground states, as for MgH⁺ and ArH⁺, to molecules having a ² Σ , ³ Σ or ² Π ground state. From an experimental point of view the proposed scheme is attractive since it requires only a few commercially available laser sources. In the following, a particularly simple scheme that requires just a single infrared cw laser source is discussed.

2.1. Simplified scheme for cooling of MgH^+

More specifically, we will focus on the experimentally simple case illustrated in figure 1 where a single laser source optically pumps population from $|v = 0, J = 2\rangle$ to $|v = 0, J = 0\rangle$ via the $|v = 1, J = 1\rangle$ state. As in the originally proposed scheme [41], the BBR field redistributes the population between rotational levels (according to the selection rule $\Delta J = \pm 1$), which in combination with the optical pumping leads to rotational cooling. The temporal evolution and the steady state of the distribution over rotational states can be found by propagating a set of coupled rate equations as described in [42]. For the cooling scheme illustrated in figure 1, the



Figure 2. (a) Steady state population and (b) temporal evolution of the lowest rotational states for the cooling scheme illustrated in figure 1.

steady state population and the temporal evolution of selected rotational states are shown in figure 2 for a cw laser intensity that saturates the $|v = 0, J = 2\rangle - |v = 1, J = 1\rangle$ transition (the induced Rabi frequency is eight times larger than the Einstein A coefficient for the transition). The steady state population of the ground state is 64%, not much lower than the ~70% that can be obtained by applying an additional laser source [41] or an incoherent radiation source [42]. The steady state is reached in about 1 min, a period much shorter than the storage time of cold molecular ions (several hours) and a few times shorter than the average time between collisions with residual gas, which we estimate to be 200 s ion⁻¹.

2.2. Infrared diode laser system for cooling of MgH⁺

For the implementation of the rotational cooling scheme illustrated in figure 1, a tunable laser source that is sufficiently powerful to saturate the $|v = 0, J = 2\rangle - |v = 1, J = 1\rangle$ transition in MgH⁺ at 1608.96 \pm 0.05 cm⁻¹ (corresponding to 6.2 μ m wavelength) [48] is required. We have chosen to use a PbSe-based lead salt diode laser (Laser Components GmbH) for this purpose. Alternatively, an optical parametric oscillator system or a quantum cascade laser could fulfill the criteria; however, these systems are either more expensive or lack continuous coverage of the part of the infrared spectrum relevant for rotational cooling of other molecular ions than MgH⁺ [42]. The lead salt diode laser set-up is shown in figure 3. The diode laser is housed in a liquid nitrogen dewar with a heating element for control of the diode temperature. The laser light passes through a BaF₂ window in the dewar and is collimated by an off-axis parabolic mirror. A further telescope and a cylindrical lens (not shown in figure 3) shape the beam such that in the center of the ion trap described below, the horizontal full-width at half-maximum (FWHM) of the diode laser beam profile is about 3.2 mm and the vertical FWHM is about 0.9 mm. With a total power of 200 μ W available in the ion trapping region and assuming a laser linewidth of 20 MHz [49], the intensity is sufficient to saturate the $|v = 0, J = 2\rangle - |v = 1, J = 1\rangle$ transition for all orientations of the molecule when the polarization of the laser is scrambled on a timescale faster than the lifetime of the $|v = 1, J = 1\rangle$ level. Other transition frequencies within the 0–1 band are sufficiently far away that they are unaffected by the diode laser [48]. The HeNe laser beam shown in figure 3 overlaps with the lead salt laser beam and serves as a guiding tool for the



Figure 3. Set-up of the lead salt diode laser system. Details of the various components are given in the text. The diode laser and the HeNe laser beam overlap but are displaced here for clarity. The gas cell and the etalon (not transmitting for the HeNe laser) are removable. OAP, off-axis parabolic mirror; CM, concave spherical mirror; SL, spherical lens. Planar mirrors are indicated by the rectangles and the dashed lines indicate flip mounted mirrors.

infrared lead salt laser beam as well as calibration of the monochromator. The monochromator enables coarse wavelength measurement with about 2 cm^{-1} accuracy. In order to obtain a more accurate absolute frequency reference, an ammonia-filled cell (6 cm long, filled with \sim 25 mbar NH₃ and equipped with CaF₂ windows) is employed for absorption spectroscopy. For precise relative frequency measurements, a solid germanium etalon is applied. Its free spectral range is $0.048632(10) \text{ cm}^{-1}$ for a laser frequency within 20 cm^{-1} of 1609 cm^{-1} and temperature in the range 18-22 °C. In all experiments, an ac-coupled mercury-cadmium-telluride detector (Judson J15D with PA-101 pre-amplifier) is utilized. The spectra in figure 4 demonstrate that the $|v = 0, J = 2\rangle - |v = 1, J = 1\rangle$ transition frequency of 1608.96 cm⁻¹ can be reached by the diode laser. In (a) the transmission spectrum of the Ge etalon is shown when the diode laser frequency is scanned by modulation of the injection current. Figure 4(b) shows the detector signal for the same scan range when the ammonia cell is inserted in the beam path (lower trace) and when it is removed (upper trace). The broad line (about 0.2 cm^{-1} wide) present in both spectra near 1609.45 cm^{-1} is due to absorption in water present in the air along the 1.9 m long beam path from the laser to the detector. By subtracting the upper trace from the lower one, the water line as well as the background slope due to current-dependent output power of the laser approximately cancel out as shown in (c). Here, only three approximately 0.02 cm^{-1} wide ammonia lines remain. The observed linewidths in (b) and (c) are dominated by collision broadening for water as well as ammonia (the Doppler width is only 5×10^{-3} cm⁻¹ and the laser linewidth is expected to be even smaller, about 6×10^{-4} cm⁻¹ [49]). From a coarse frequency



Figure 4. Spectra obtained with the lead salt diode laser set-up shown in figure 3. (a) Transmission spectrum of the Ge etalon. (b) Transmission spectrum of the ammonia cell (lower trace) and detector signal with the cell removed from the beam path (upper trace) showing a water absorption line near 1609.45 cm⁻¹. The latter trace is displaced by 1 V for clarity. (c) Difference between the lower and upper traces in (b). The three lines marked by A, B and C are ammonia absorption lines. The vertical dashed line indicates the frequency of interest for rotational cooling of MgH⁺.

measurement with the monochromator combined with an evaluation of the frequency spacing between the lines marked A, B and C in (c) and the presence of the nearby water line, the lines in figure 4(c) can be identified. The lines are due to transitions at 1609.06116 cm⁻¹ (A), 1609.46570 cm⁻¹ (B) and 1609.50671 cm⁻¹ (C), respectively [50]. In figure 4, the absolute frequency scale is constructed by first fixing the scale to 1609.06116 cm⁻¹ at the center of line A and then scaling the frequency axis according to the etalon spectrum in (a). From these spectra it is a simple matter to scan the laser around the desired frequency of 1608.96 ± 0.05 cm⁻¹ [48] in order to search for an effect of the laser on the rotational state distribution.

3. Photodissociation spectroscopy of cold molecular ions

In order to determine the rotational state distribution for the vibrational ground state of the $X^1\Sigma^+$ electronic ground state of MgH⁺, a signal that reflects the population in a given rotational state is obtained by rotational state-selective photodissociation spectroscopy [51]. In short, such measurements consist of four steps. Firstly, Mg⁺ ions are loaded into the trap and laser-cooled. Secondly, H₂ is introduced to form MgH⁺ molecular ions through reactions between Mg⁺ and H₂. Thirdly, the MgH⁺ ions are left to equilibrate with the BBR field and any additionally applied radiation fields (e.g. the laser field of the lead salt laser described above) for at least 120 s. Finally, by applying a pulsed laser the MgH⁺ ions are dissociated in a rotational state selective two-photon dissociation process. Since the dissociation products, Mg and H⁺, are both lost from

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Figure 5. Ion trap set-up. The arrows indicate the applied laser beams: the cooling beams (solid dark blue parallel to the *z*-axis), the photoionization beam (solid green arrow at a 45° angle with respect to the *z*-axis), the pulsed laser (dashed light blue) and the lead salt diode laser beam (solid red arrow at a 45° angle with respect to the *z*-axis). Further details of the set-up are given in the text.

the trap, the loss rate of molecular ions equals the dissociation rate. Details of the experimental procedure are discussed in the following.

3.1. Trapping and laser cooling of Mg^+ ions

The experimental set-up is sketched in figure 5. The linear Paul trap consists of four cylindrical rods, each sectioned into three parts. By applying an rf voltage to diagonally opposite rods and a dc voltage to the eight end electrodes, a cylindrically symmetric harmonic confining potential characterized by angular oscillation frequencies ω_z and ω_r is created (see [31] for further details). The axial trap frequency ω_z is for a single ion given by

$$\omega_z = \frac{\sqrt{2}\kappa \, Q U_{\rm dc}}{M},\tag{1}$$

where *M* and *Q* are the mass and the charge of the ion, and κ is a constant related to the trap geometry. The effective radial oscillation frequency is given by $\sqrt{\omega_r^2 - \omega_z^2/2}$, where ω_r is given by

$$\omega_{\rm r} = \frac{QU_{\rm rf}}{\sqrt{2}Mr_0^2\Omega_{\rm rf}},\tag{2}$$

where $U_{\rm rf}$ and $\Omega_{\rm rf}$ are the amplitude and frequency of the applied rf voltage and r_0 is the distance from the trap center to the surface of the electrodes. ²⁴Mg⁺ ions are loaded into the trap by crossing an effusive beam of Mg atoms originating from an oven at 540 K, with a laser beam at 285 nm (intensity ~100 W cm⁻²) in the trap center for resonance-enhanced isotope selective two-photon ionization of ²⁴Mg [52]. The ²⁴Mg⁺ ions are Doppler laser cooled on the 3s ${}^{2}S_{1/2}$ -3p ${}^{2}P_{3/2}$ transition near 280 nm by two laser beams counter-propagating parallel to the



Figure 6. Numbers of Mg^+ and MgH^+ ions during the experimental procedure. The regions 1-4 correspond to the processes loading, molecule formation, equilibration and dissociation as described in sections 3.1-3.4, respectively. The images I, II and III are snapshots of the Coulomb crystals at the times indicated on the graph. The horizontal direction corresponds to the z-axis of figure 5.

z-axis (total intensity $\sim 1 \text{ W cm}^{-2}$). The ions are observed in real time by imaging light, emitted spontaneously during the laser cooling process, onto a charge-coupled device (CCD) camera with a magnification of 4.0. At the temperature of $\sim 10 \,\text{mK}$ obtained by Doppler laser cooling the ions form an ordered structure, a so-called Coulomb crystal. In figure 6 (image I) a projection image of a cylindrically symmetric Coulomb crystal is shown. Since the ions are observed in real time the loading process can easily be terminated by blocking the photoionization laser beam, once the Coulomb crystal has reached the desired size. The sudden termination of the loading process can be seen in region 1 on the graph in figure 6. Subsequently, a rotatable mechanical shutter (denoted as oven shutter on figure 5) is turned to block the atomic beam in order to avoid impact with the trapped ions.

3.2. Production of translationally cold MgH⁺ ions

MgH⁺ ions are formed by leaking H₂ gas into the trap chamber (base pressure 3.0×10^{-10} Torr) through a leak-valve such that a steady-state pressure of 1.5×10^{-9} Torr is maintained. Reactions exclusively take place with $^{24}Mg^+$ ions excited to the $3p^2P_{3/2}$ state in the laser cooling process, since reactions between ²⁴Mg⁺ in the ground state and thermally excited hydrogen molecules are not energetically allowed [30]. The formed molecular ions stay trapped since the kinetic energy acquired in the reaction only amounts to a small fraction of the trap depth. The molecular ions are sympathetically cooled to a temperature below 100 mK through the Coulomb interaction with the remaining laser-cooled ²⁴Mg⁺ ions and a two-component Coulomb crystal is formed (see image II in figure 6). Due to the mass dependence of the trapping potential (see equation (2)), the heavier molecular ions separate radially outside the lighter atomic ions. When the desired number of ²⁴MgH⁺ ions has been formed after 1–2 min, the cooling laser is red detuned by about 200 MHz, which effectively terminates reactions, as seen on the graph in figure 6 at the transition between regions 2 and 3, and the leak valve is closed.

3.3. Equilibration and manipulation of the rotational state distribution

Since the molecular ions are formed in a range of rovibrational states in the $X^1\Sigma^+$ or other electronic potentials, a waiting time of 1–2 min is introduced for the molecular ions to equilibrate internally with the BBR field. The vibrational decay within the electronic ground state toward v = 0 is fast with rates of about 20 s^{-1} , while the rotational equilibrium of the v = 0 level is subsequently reached within 1 min [53] as also observed in the cases of OH and OD [23] as well as CH⁺ [54]. During the waiting time, and an additional 1 min period, any radiation fields for rotational cooling are also applied. The numbers of Mg⁺ and MgH⁺ ions remain constant as can be seen in region 3 on the graph in figure 6. In the same period H₂ is pumped by an ion pump such that in the last minute of the period, the total pressure is less than 3.5×10^{-10} Torr. This means that the total rate for collisions with residual gas (including H₂) is not much higher than at the base pressure of the vacuum chamber.

3.4. Rotational state selective photodissociation of MgH⁺ molecular ions

Finally, in order to determine the rotational distribution, the MgH⁺ ions are dissociated by resonance-enhanced two-photon dissociation by applying a pulsed laser near 281 nm (10 Hz repetition rate, 9 ns FWHM pulse length, peak intensity of $2 \times 10^6 \,\mathrm{W \, cm^{-2}}$ in a beam with horizontal FWHM of 0.7 mm and vertical FWHM of 1.5 mm). The pulsed UV laser beam is generated by frequency doubling of the output from an Nd:YAG pumped Sirah Cobra Stretch dye laser (rhodamine 6G laser dye) by using the built-in frequency doubling unit. The UV beam is split into two such that one beam passes to the trap, whereas the other is used for power monitoring. The built-in horizontal walk-off compensation of the dye laser ensures that in the trap center the beam is displaced by less than 50 μ m in the horizontal plane when the fundamental wavelength is scanned over the relevant range of 560-562 nm. The drift of the beam position is limited to 100 μ m over several hours. The dye laser is calibrated to lines in Ne by optogalvanic spectroscopy using a hollow cathode lamp. The linewidth of the fundamental dye laser output is less than 0.08 cm⁻¹. When all MgH⁺ ions have been dissociated, an Mg⁺ Coulomb crystal much smaller than the original one is left behind (see image III in figure 6). A small number of non-fluorescing ions heavier than ²⁴Mg⁺ remains. These ions are either ²⁵Mg⁺ or ²⁶Mg⁺ ions formed by charge-exchange reactions² between Mg atoms and ²⁴Mg⁺, or unknown molecular ions, most likely N₂⁺, formed by ionization of residual gas molecules by the pulsed laser.

3.4.1. Photodissociation scheme. The rotational state-selective scheme for photodissociation of MgH⁺ ions in the X¹ $\Sigma^+(v = 0, J)$ state is illustrated in figure 7. In a first resonant step the molecular ion is excited by the pulsed ns laser to the A¹ Σ^+ state on a P- or R-line of the 0–0 band near 281 nm [48]. In a second step, the molecular ion is excited within the same pulse to a continuum state of the C¹ Σ^+ potential, from where it rapidly dissociates to a neutral Mg atom and a proton. As mentioned above, these are both unbound in the trap. Since the rate for the A–C excitation step cannot be expected to be much higher than the spontaneous decay rate from the A to the X state, the spontaneous decay back to rovibrational states in the electronic ground state must be considered even during the presence of the ns-laser pulse. The electronic

² Similar reactions have previously been exploited with calcium ions [55].



Figure 7. Scheme for resonance-enhanced two-photon dissociation of MgH⁺. The two dashed arrows in the figure represent UV photons near 281 nm originating from the pulsed ns-laser system.

A-X decay as well as subsequent spontaneous rovibrational decay within the electronic ground state potential leads to a distribution of the population in rotational states, which generally differs from the equilibrium distribution in the absence of the pulsed laser. Additionally, once a specific rovibrational level is emptied by the pulsed laser, transitions driven by BBR and applied radiation fields will tend to fill up that level again, which in turn gives another contribution to the redistribution of the population. Due to these redistribution processes, the dissociation rate measured when the ns laser is tuned to be in resonance with a specific P- or R-line is not directly proportional to the steady state population of the initial $X^1 \Sigma^+ (v = 0, J)$ state. In order to fully account for the many processes, numerical modeling is required as done in [51, 56]. It turns out that the decay of the number of MgH⁺ ions is well described by a biexponential decay. The rapidly decaying component corresponds to dissociation of MgH⁺ found in the $X^{1}\Sigma^{+}(v=0, J)$ state at the beginning of the dissociation process. The slowly decaying component arises from dissociation of MgH⁺ ions initially populating other rotational states or from MgH⁺ ions transferred to other rotational states through excitation to the A state followed by spontaneous decays. In both cases, the rate for transfer back to the $X^1 \Sigma^+ (v = 0, J)$ state is effectively limited by the rotational transition rates within the $X^{1}\Sigma^{+}(v=0)$ vibrational level. This leads typically to periods of a few minutes for the dissociation of all MgH⁺ ions in a crystal as seen in figure 6, region 4.

The temporal evolution of the number of non-fluorescing ions in the Coulomb crystals, $N_{\rm nf}$, can be modeled by

$$N_{\rm nf}(t) = N_{\rm r} \,\mathrm{e}^{-\Gamma_{\rm r}t} + N_{\rm s} \,\mathrm{e}^{-\Gamma_{\rm s}t} + \Gamma_{\rm i}t,\tag{3}$$

where Γ_r and Γ_s are the rapid and slow dissociation rates, respectively, N_r and N_s are constants and Γ_i is the rate at which impurity molecular ions are produced by photoionization of the residual gas in the vacuum chamber.

In the present experiments, the intensity of the pulsed ns laser is so low that the rapidly decaying component is hardly distinguishable; hence only Γ_s is considered below. The number

of non-fluorescing ions needed for evaluation of the dissociation rate is found as described in the following section.

3.4.2. Determination of the dissociation rate of MgH^+ molecules. In figure 6, the numbers of Mg^+ and MgH^+ ions are found by determining the volumes occupied by each species and using the fact that in a Coulomb crystal the ion density of

$$n = \frac{2\varepsilon_0 M \omega_{\rm r}^2}{Q^2} \tag{4}$$

is constant for each species. In the present work, the density of Mg⁺ and MgH⁺ ions is 10.2×10^4 and 9.8×10^4 mm⁻³, respectively.

For a two-component crystal composed of singly charged ions of different mass, the mass dependence of the radial trap frequency (see equation (2)) leads to a radial separation between the outer (heavier) species and the inner (lighter) species. The inner component has a cylindrical structure, whereas the edge of the outer component maintains its spheroidal shape [57]. The volume of the outer component of non-fluorescing ions, V_{nf} , can be found as $V_{nf} = V - V_f$, where V is the total volume of the two-component crystal and V_f is the volume of the inner core of fluorescing ions. In this expression for V_{nf} the radial separation between the two components has been neglected, which is a good approximation for ions of similar mass [57]. V_f is found (in units of cubic-pixel) by considering a bounded region of a digital projection image of a two-component crystal (as in figure 6, image II) with pixel values above a certain threshold. This region is divided into slices one pixel wide, the radius and hence the volume of each slice is determined and finally all volumes are summed. The total crystal volume V is determined as follows. First, note that since the outer boundary of a one-component Coulomb crystal is very well approximated by a spheroid of half-length L and radius R, its volume V can be calculated as

$$V = 4\pi R^2 L/3 = 4\pi \alpha^2 L^3/3,$$
(5)

where $\alpha = R/L$ is the aspect ratio. From digital projection images as shown in figure 6 (image I), the crystal volume can then be found by determining 2*R* and 2*L* as the longest uninterrupted column and row, respectively, of pixels with a value above a chosen threshold. For a prolate two-component crystal as shown in figure 6, image II, the spheroidal shape of the outer component is essentially identical to that of a one-component crystal of the heavier ion species [57]. Hence the total crystal volume can be found from equation (5) by approximating *L* with the half-length of the inner core and using the aspect ratio for a one-component crystal of MgH⁺ is well approximated by that of an Mg⁺ crystal, which can be deduced from images such as image I in figure 6. In the case of ions with a larger relative mass difference, the aspect ratio for a heavy (non-fluorescing) species should be calculated from the aspect ratio of a one-component crystal of the lighter fluorescing species using equation (5) in [58].

The volume measurements can be converted from units of a cubic-pixel to a physical volume by taking the magnification of 4.0 and the pixel size of $9.9 \,\mu m \times 9.9 \,\mu m$ into account. With this conversion and the ion density calculated according to equation (4), the number of ions as given in figure 6 is determined. By fitting equation (3) to the number of non-fluorescing ions in region 4 of figure 6, the dissociation rates can be determined.



Figure 8. (a) Fortrat parabola for the $X(v = 0, J) - A(v = 0, J + \Delta J)$ transitions [48] in the resonant first step of ²⁴MgH⁺ dissociation. (b) Dissociation spectrum for ²⁴MgH⁺ ions in equilibrium with room temperature BBR showing Γ_s versus the wavenumber of the frequency doubled pulsed dye laser. A small variation of the dye laser power across the wavenumber range is taken into account by a linear normalization to the dissociation rate at the R(4) line. The wavenumber is determined from the fundamental wavelength of the dye laser. A slight deviation between the observed and the predicted resonance frequencies due to the limited wavelength reproducibility of the ns-laser and the calibration precision was corrected for by shifting the axis by 1.6 cm⁻¹. The solid line represents a numerical simulation based on the procedure described in section 3.6. The corresponding rotational temperature is found to be 230 K.

We note that any uncertainty in converting from cubic-pixels to ion numbers does not influence the dissociation rates.

3.5. The MgH⁺ dissociation spectrum

Following the experimental procedure described in sections 3.1–3.4, the dissociation rate Γ_s can now be determined while varying various parameters, such as the ns-laser pulse energy and frequency as well as the frequency and intensity of the lead salt diode laser. In order to determine whether the lead salt diode laser can cause any change in the rotational distribution, it is of interest to evaluate the dissociation rate from low-lying rotational levels in the vibrational ground state of the X state. The Fortrat parabola of the relevant transitions in the 0–0 band of the X–A electronic transition is indicated in figure 8(a). In figure 8(b) the recorded spectrum of Γ_s (without the lead salt diode laser applied) is shown together with the results of simulations discussed in detail in the following section. The R(4) and R(5) lines are clearly seen with a slight asymmetry of the R(5) line revealing the presence of the P(1) line. The R(0), R(1), R(2) and R(3) lines are unresolved due to power broadening.

3.6. Numerical simulation of the spectrum

In order to understand the spectrum presented in figure 8, numerical simulations including the photoexcitation via the X–A transition, photodissociation via the A–C transition induced by the pulsed laser, spontaneous decay A–X, rovibrational redistribution in the ground state potential due to the BBR field, as well as a possible coupling between rovibrational levels due to sympathetic cooling through long-distance collisions with the laser-cooled ions have been carried out.

A full quantum mechanical treatment of the system, taking into account a basis set consisting of all rotational sub-states and laser light-induced coherences, would give the best description, but would require impractically long computing times. As a consequence, we have chosen to simulate the dynamics of the molecules internal states by propagating a set of coupled rate equations that describe the temporal evolution of the population vector $\vec{p} = [p_X(v = 0-5, J = 0-19), p_A(v = 0, J = 0-19), p_C]$, which contains the populations of rovibrational levels $|v, J\rangle$ of the corresponding states X, A and dissociative continuum states in C. Its temporal evolution is governed by the coupling matrix $\mathbf{K}(t)$ through the matrix equation $d\vec{p}/dt = \mathbf{K}(t)\vec{p}(t)$. To avoid numerical integration of this system of equations, which is computationally expensive, the time line is split into intervals small enough that the rates in the entries of $\mathbf{K}(t)$ can be considered constant in each interval. As indicated in figure 9, the coupling matrix changes only during the ns-laser pulse, and the long period between pulses can be treated as a single time step. Consequently, the temporal evolution of the system can be found through the solutions of the linear ordinary differential equations for each interval:

$$\frac{\mathrm{d}p}{\mathrm{d}t} = \mathbf{K}_i \vec{p}(t) \quad \Rightarrow \quad \vec{p}(t_{i+1}) = \exp(\mathbf{K}_i(t_{i+1} - t_i))\vec{p}(t_i), \tag{6}$$

with the total solution being

$$\vec{p}(M) = \left[\prod_{i=0}^{N-1} \exp(\mathbf{K}_i(t_{i+1} - t_i))\right]^M \vec{p}(0),$$
(7)

where N is the number of intervals and M is the number of pulses. The various coupling rates in **K** are determined in the following subsections. Since the dissociation rate from C is much faster than spontaneous decay back to A or X, $p_{\rm C}$ represents the number of dissociated MgH⁺ ions.

3.6.1. Photoexcitation X–A. As the starting point for our approximation of the photoexcitation rate, we first consider the Rabi oscillations induced between two levels $|v = 0, J\rangle_X$ and $|v' = 0, J' = J \pm 1\rangle_A$ by the pulsed laser in the dipole approximation. The Rabi frequency is given by

$$\chi_{J,J\pm 1}(t) = \frac{\mu_{XA}\sqrt{f_{\nu=0,\nu'=0}S_{J,J\pm 1}}}{\hbar}E(t),$$
(8)

where μ_{XA} is the transition dipole moment between X and A, $f_{v=0,v'=0}$ is the Franck–Condon factor, $S_{J,J+1} = J + 1$ and $S_{J,J-1} = J$ are the Hönl–London factors for R(J) and P(J) transitions, respectively, and E(t) is the electric field amplitude of the pulsed laser at time *t*. Likewise, the generalized Rabi frequency describing the two-level population oscillation period is written as

$$\Omega_{J,J\pm 1}(t) = \sqrt{\chi_{J,J\pm 1}(t)^2 + \Delta_{J,J\pm 1}^2},$$
(9)



Figure 9. (a) Reduced level diagram of MgH⁺ showing transitions and typical timescales. Full arrows: transitions induced by the pulsed laser, i.e. photoexcitation from the electronic ground state X to the excited level A and photodissociation from the excited state A to the dissociative state C. Dashed arrows: spontaneous decay from A to rovibrational levels in X. Dotted arrows: rovibrational redistribution within the electronic ground state X due to interactions with a 300 K BBR field. (b) In the simulation, the timeline is split into *N* intervals, each one small enough that the coupling rates can be considered constant in each interval.

where $\Delta_{J,J\pm1}$ is the detuning of the pulsed laser frequency with respect to the transition frequency between the two levels. Since the population oscillation period is typically much shorter than the pulse length, we can without larger errors approximate the population in the two levels by the time averaged values of one generalized Rabi oscillation. Consequently, it is natural to assume coupling rates of the order of $\Omega_{J,J\pm1}/\pi$ times the peak-to-peak population amplitude of the Rabi oscillation, $\chi^2_{J,J\pm1}/\Omega^2_{J,J\pm1}$. However, to reach the desired steady-state population, the absorption rate is scaled by the coefficient

$$H_{J,J\pm 1} = \frac{\Omega_{J,J\pm 1}^2}{2(\Omega_{J,J\pm 1}^2 + \Delta_{J,J\pm 1}^2)},$$
(10)

and the emission rate by $1 - H_{J,J\pm 1}$, leading to the following entries in the coupling matrix **K**:

$$\Gamma_{v,J;v',J\pm 1}^{\text{abs}} = \frac{\chi_{J,J\pm 1}^2 \Omega_{J,J\pm 1}^2}{2\pi (\Omega_{J,J\pm 1}^2 + \Delta_{J,J\pm 1}^2)}$$
(11)

and

$$\Gamma_{v,J;v',J\pm 1}^{\text{em}} = \frac{\chi_{J,J\pm 1}^2(\Omega_{J,J\pm 1}^2 + 2\Delta_{J,J\pm 1}^2)}{2\pi(\Omega_{J,J\pm 1}^2 + \Delta_{J,J\pm 1}^2)},$$
(12)

for absorption and emission, respectively.

Since the laser light is linearly polarized, the selection rule $\Delta m_J = 0$ prevents the probing of the sublevels $m_J = J$ and $m_J = -J$ on P(J) transitions. To account for this in the simulations without explicit use of rotational sub-states, the dissociation rate of P(J) transitions is scaled by the factor $\frac{2J-1}{2J+1}$.

3.6.2. Photodissociation A-C. Since the final state of the A–C transition is a continuum state, the rate for excitation to the C state is expected to be largely independent of the rovibrational state in A as well as of the laser wavelength over the relatively narrow range of 280.5–280.8 nm applied in the present work. Furthermore, at the applied intensity, the dissociation process proceeds on a timescale much faster than higher-order light-induced processes as well as spontaneous decay from the C state. As a consequence, the dissociation rate is modeled by

$$\Gamma_{\rm diss}(t) = \alpha I(t),\tag{13}$$

where I(t) is the intensity at time t of the laser pulse and α is a constant to be determined from the measured dissociation spectrum.

3.6.3. Spontaneous decay A–X. From the mean lifetime, τ_A , of the excited state, the rate of spontaneous decay from $|v, J\rangle_A$ to $|v', J \pm 1\rangle_X$ is approximated by

$$\Gamma_{v,J;v',J\pm 1} = \frac{f_{v,v'}}{\tau_{\rm A}} \frac{S_{J,J\pm 1}}{S_{J,J+1} + S_{J,J-1}},\tag{14}$$

where $f_{v,v'}$ is the Franck–Condon factor between the two vibrational levels and $S_{J,J\pm1}$ is the Hönl–London factor. The lifetime has been calculated to be $\tau_A = 4.4 \text{ ns}$ [56], whereas the Franck–Condon factors derived from molecular spectroscopy data are tabulated in [48]. Since more than 99.9% of the population decays back into the v = 0-5 levels of the X state, in the simulations the vibrational distribution has been truncated to v = 0-5.

3.6.4. Rovibrational redistribution in X due to BBR. The rovibrational redistribution in the electronic ground state due to BBR is modeled in the same way as the previous cooling simulations described [41]. In short, the electronic ground-state potential and the permanent

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17

dipole moment function are evaluated using the program packet Gaussian [59] with a coupled cluster single, double and triple excitation (CCSDT) approach based on a 6-311++G basis set. Next, rovibrational wavefunctions are found by solving the Schrödinger equation using the Numerov method via the program Level 7.5 [60]. Finally, Einstein A coefficients, $A_{v,J;v',J\pm 1}$, are found from these wavefunctions and the permanent dipole moment. The corresponding Einstein B coefficients are given by

$$B_{v,J;v',J\pm 1} = \frac{c^3}{4hv_{v,J;v',J\pm 1}^3} A_{v,J;v',J\pm 1},$$
(15)

$$B_{v',J\pm1;v,J} = \frac{g_{v,J}}{g_{v',J\pm1}} B_{v,J;v',J\pm1},$$
(16)

where $v_{v,J;v',J\pm 1}$ is the frequency difference between level $|v, J\rangle$ and level $|v', J\pm 1\rangle$ and $g_{v,J} = 2J+1$ is the degeneracy of level $|v, J\rangle$.

From the Einstein coefficients, coupling rates are found by assuming a 300 K BBR background, $W(v_{v,J;v',J\pm 1})$, using

$$\Gamma_{v,J;v',J\pm 1} = A_{v,J;v',J\pm 1} + B_{v,J;v',J\pm 1} W(v_{v,J;v',J\pm 1})$$
(17)

3.6.5. Sympathetic rotational cooling. The possibility of a weak sympathetic rotational cooling of the molecular ions in their long-distance collisions with the laser-cooled ions is accounted for by introducing a heuristic decay rate from rotational levels J to J - 1 with a strength proportional to J + 1 [51]. This corresponds to an effective rotational state-independent cooling rate Γ_c defined by $d\bar{E}_{rot}/dt = -\Gamma_c \bar{E}_{rot}$, where \bar{E}_{rot} is the average rotational energy.

3.6.6. Interpretation of the spectrum. Three parameters are varied to match the simulated spectrum to the experimentally recorded spectrum shown in figure 8. Firstly, the pulsed laser intensity is adjusted to match the observed widths of the various transitions. Secondly, the dissociation proportionality constant, α , is adjusted to match the observed dissociation rate. Finally, the cooling rate constant Γ_c , which influences the ratio between the dissociation rates on different lines, is fitted.

The observed spectrum can be modeled quite well as indicated by the solid line in figure 8 for which the fitting parameters are $I_{\text{peak}} = 0.3 \times 10^6 \text{ W cm}^{-2}$, $\alpha = 120 \text{ s}^{-1} \text{ W}^{-1} \text{ cm}^2$ and $\Gamma_c = 0.02 \text{ s}^{-1}$. The fitted value of I_{peak} is in order of magnitude agreement with the value of $2 \times 10^6 \text{ W cm}^{-2}$, estimated by assuming a Gaussian laser beam profile. Though the fitted value of Γ_c is nonzero, it is so small that in combination with BBR alone, it would lead to a distribution with mean rotational energy as high as $\bar{E}_{\text{rot}} = k_B \times 230 \text{ K}$. To validate that this result is not critically dependent on model parameters, in the modeling of the Rabi oscillations on the X–A transitions, the parameter H has been multiplied and divided by 2 in other fits to the observed spectrum. The best fits give rise to values of Γ_c in the range $0.01-0.03 \text{ s}^{-1}$, which corresponds to rotational temperatures in the range 200-260 K. This result, together with the approximations made in the modelling, makes us conclude that the rotational temperature is within the range of 150-300 K in agreement with previous work on MgH⁺ [51] as well as on HD⁺ [61]. In order to obtain a better temperature determination, it would be desirable to reduce the role of redistribution processes. This could in principle be obtained by applying laser pulses with higher intensities. This would, however, compromise the spectral resolution due to power broadening of the X–A transitions. A future better solution is



Figure 10. Dissociation spectrum showing Γ_s versus the wavenumber of the frequency doubled pulsed dye laser. The filled circles (red) show the dissociation rate measured with the lead salt diode laser turned off. The open triangles (blue) show the dissociation rate measured when the lead salt diode laser at 1608.96 cm⁻¹ is applied during the equilibration period as well as during the dissociation process.

to introduce a second strong laser pulse that drives the dissociative A–C transition while being far-off resonant with all X–A transitions. An interesting feature of the simulated spectrum is a drop in the dissociation rate when the pulsed laser is on resonance with a transition, as also experimentally observed on the R(4) line. This phenomenon occurs on resonance, since in this case the leading edge of the laser pulse is sufficiently intense to deplete the addressed level in the X-potential through excitation to the A-potential and subsequent spontaneous emission, before dissociation from the A state becomes appreciable.

4. Effect of the lead salt diode laser

When the lead salt diode laser at 1608.96 cm⁻¹ is applied during the equilibration time (region 3 in figure 6), the distribution of population in the rotational levels is expected to change. In figure 10, a first result showing a reduction of the dissociation rate Γ_s for the R(5) line, when the $|v = 0, J = 2\rangle - |v = 1, J = 1\rangle$ transition is addressed by the lead salt laser, is presented. While this result is consistent with rotational cooling, a larger part of the spectrum will have to be recorded and modeled before a firm conclusion can be drawn.

5. Conclusion and outlook

The results presented here clearly show evidence of changes in the dissociation rate of MgH⁺ ions in a specific rotational state of the vibrational and electronic ground states when a single optical pumping field is applied. The next step is to search for parameters to optimize rotational cooling.

Provided that the experimentally simple scheme for rotational cooling discussed above can be demonstrated, it should be straightforward to extend the cooling scheme by applying additional laser sources and incoherent radiation fields [47]. Rotational cooling schemes may furthermore be sought applied to single molecular ions [32, 36] and possibly even to appropriately chosen complex molecular ions [34, 35]. In the latter case, since the rovibrational modes are typically coupled, relatively efficient rovibrational cooling schemes may be feasible by addressing only a single or a few rovibrational transitions.

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