Blackbody-Radiation–Assisted Laser Cooling of Molecular Ions

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The translational motion of molecular ions can be effectively cooled sympathetically to temperatures below 100 mK in ion traps through Coulomb interactions with laser-cooled atomic ions. The distribution of internal rovibrational states, however, gets in thermal equilibrium with the typically much higher temperature of the environment within tens of seconds. We consider a concept for rotational cooling of such internally hot, but translationally cold, heteronuclear diatomic molecular ions. The scheme relies on a combination of optical pumping from a few specific rotational levels into a "dark state" with redistribution of rotational populations mediated by blackbody radiation.

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Powerful techniques for manipulating, cooling, and trapping atoms have recently paved the way for extremely detailed investigations of atomic physics phenomena, as well as been essential ingredients in the development of research fields such as atom optics [1], physics of trapped condensed dilute gases [2], and quantum information [3]. Similar powerful techniques have not yet been established for molecules, but such developments are expected to be equally rewarding in the future.

Although molecules are routinely cooled internally and translationally in supersonic expanded beams [4], their high average translational velocities ($\sim$ 100–1000 m/s) limit this method to experiments requiring only short interaction times. The application of various laser cooling schemes, already developed for atoms, is unfortunately hampered by the radiative coupling of the many internal molecular energy levels which impedes multiple laser-induced excitations. Recently, three very different methods for trapping and cooling neutral molecules have, however, been demonstrated. One of the schemes relies on optical trapping of cold molecules produced by photoassociation of laser-cooled atoms [5–9]. This approach is expected to work for homo- or heteronuclear dimers of atoms amenable for laser cooling. Though the molecules are produced translationally very cold (down to $\sim 100\ \mu$K), the population of the internal rovibrational states are so far typically spread over many levels. Another scheme is based on buffer gas cooling of paramagnetic molecules held in a magnetic trap. In such experiments all the molecular degrees of freedom have been cooled to $\sim$400 mK by collisions with a He buffer gas maintained at cryogenic temperatures [10,11]. This method leaves the molecules essentially in the ground state internally. Finally, beams of neutral polar molecules have been decelerated by electrostatic fields [12], and confined in an electrostatic quadrupole trap [13] or in a tabletop "storage ring" [14] at translational temperatures down to $\sim$10 mK.

Molecular ions constitute another class of molecules that are equally interesting to cool and manipulate. For decades resonance-enhanced multiphoton ionization processes have been exploited to produce state-specific molecular ions in beam experiments [15]. The same procedure has also been applied in connection with traps [16], allowing for dramatically longer interaction times for succeeding experiments. A more general technique for cooling to the internal ground state of the molecular ions is buffer gas cooling by He atoms in a cryogenic environment, which has proven to cool trapped ionic molecules down to 10 K [17]. Most recently, it has been demonstrated that molecular ions can be very effectively translationally cooled ($T < 100$ mK) into ion Coulomb crystals in a linear Paul trap through Coulomb interaction with laser-cooled atomic ions [18]. In such experiments, the frequency of the ions' external vibrational motion is determined by the trap potential, and is typically $\sim$100–1000 kHz. Rotational and vibrational frequencies of the molecular ions, on the other hand, are many orders of magnitude larger ($\sim 10^{11}$–10^{14} Hz) and, as a consequence, exchange of energy quanta between internal and external degrees of freedom is forbidden by energy conservation. Accordingly, the internal degrees of freedom are not sympathetically cooled, and the rovibrational temperature of the heteronuclear molecules will reach equilibrium with the temperature of the surrounding trap setup within tens of seconds [19,20]. The long trapping times ($\sim$ hours) of these spatially localized ions, combined with long intervals between collisions ($\sim$ minutes, as estimated by the Langevin theory [21]), however, opens for internal cooling schemes which *rely on* and are not hampered by blackbody radiation, and which are efficient on the time scale of seconds.

In this Letter, we consider a cooling concept for the internal degrees of freedom of trapped and translationally cold heteronuclear diatomic molecular ions. Since at room temperature the vibrational degree of freedom is frozen out for all the lighter species, i.e., the vibrational quantum number is equal to $\nu = 0$, we focus on rotational cooling. Our concept involves the following processes: Pumping of population from "pump states" ($\nu = 0, N = 1$) and ($\nu = 0, N = 2$), where N denotes the rotational quantum number, into specific excited rovibrational states from which subsequent spontaneous emission brings population back into either one of the pump states, or into the ground state ($\nu = 0, N = 0$). The latter is referred to as being a dark state, since it is not affected by the pumping fields. Finally, blackbody radiation (BR) is responsible for the feeding of the pump states with populations from states with $N > 2$. In Fig. 1, a sketch of the cooling concept, realized by utilizing two resonant, dipole allowed Raman transitions ($\Delta N = 0, \pm 2$), is presented. In the absence of BR any initial population in rotational states with $N = 1$ and $N = 2$ would within a certain time be optically pumped into the dark state ($\nu = 0, N = 0$) due to the selection rules $\Delta N = \pm 1$ for spontaneous emission. In the presence of BR effective cooling into the internal ground state is possible from an initial thermal distribution with significant population in states with $N > 2$, as long as the rate of optical pumping and the rate of spontaneous emission from the vibrationally excited state are higher than the redistribution rate among the rotational states due to BR. The cooling time will in such cases be set by the inverse of the typical rotational redistribution rate.

In an experiment the Raman transitions will be driven by pulsed lasers. In that case, high population transfer is assured if each Raman pulse saturates its transition. This means the pulse time, τ, times the Raman coupling frequency, Ω_R, should fulfill (i) $\tau\Omega_R \gtrsim 10$, where $\Omega_R \simeq \Omega^2/\delta$ with Ω being the typical Rabi frequency of the dipole allowed electronic transitions and δ the corresponding detuning. Furthermore, a small incoherent scattering rate is required, leading to (ii) $\tau\Gamma_{\text{scat}} \lesssim 0.01$, with $\Gamma_{\text{scat}} \simeq \Omega_R A/\delta$, A being the pertaining Einstein coefficient.

We have modeled the dynamics of the BR-assisted cooling by rate equations including laser-induced and spontaneous transitions as described in the cooling concept. The calculations require the knowledge of Einstein A and B coefficients between all rovibrational levels in the cooling scheme, while laser-induced couplings out of the scheme can be neglected by choosing the laser detunings appropriately. The coefficients are calculated by first determining dipole moment functions and potential curves using standard quantum chemistry codes [22] (the energies of the levels of relevance are in agreement with published data within 1.5% [23]). Second, based on the dipole moment function and potential curves, the Numerov method [24] is used to calculate the nuclear wave functions and the A and B coefficients. Details of our calculations will be presented elsewhere [25]. The initial populations are taken to be Boltzmann distributed at room temperature ($T = 300$ K). In Fig. 2, we present the results of simulations in the case of MgH^+ which has been cooled translationally in the laboratory [18]. The unfilled columns represent the initial rotational populations, while the black columns show the populations after 100 s of cooling. In the simulation, Raman pulses couple the vibrational states of the $X^1\Sigma^+$ potential curve via the electronically excited $A^1\Sigma^+$ state, using lasers in the wavelength range ~279 nm [23]. Using a typical value $A \sim 10^8\ \text{s}^{-1}$ for the electronic transition and a detuning of $\delta = 10^{11}$ Hz to the red, we find that the saturation and scattering conditions (i) and (ii) above can be fulfilled for the pumped transitions from the rotational substate for 10 ns pulses with intensities ~100 kW/cm^2. The repetition rate of the Raman pulses was 100 Hz, which is much higher than the typical rate for rotational transitions due to BR. The figure shows that more than 70% of the population can be accumulated in the rovibrational ground state, equivalent to a thermal distribution at 8.5 K.

Figure 3 shows the evolution of the population in three representative rotational levels of MgH^+ for the Raman

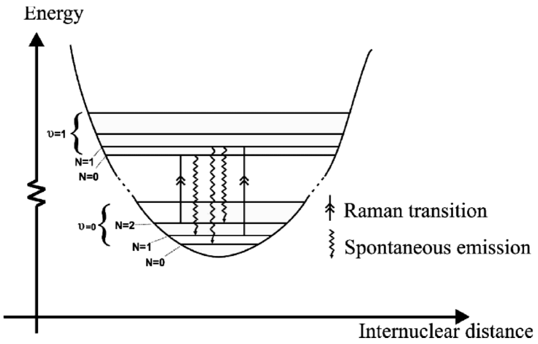

FIG. 1. Figure showing the intervibrational transitions needed for the Raman cooling scheme. A detailed explanation of the cooling principle is given in the text.

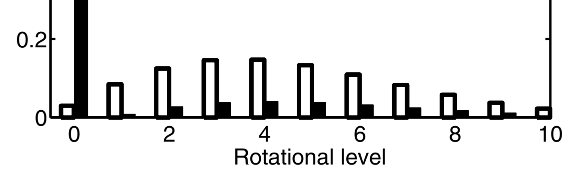

FIG. 2. Cooling of MgH^+ by the Raman scheme (see Fig. 1). The unfilled columns represent the initial rotational populations corresponding to a thermal distribution at $T = 300$ K. The filled columns represent the population distribution after 100 s of cooling. See the text for details on the cooling parameters.

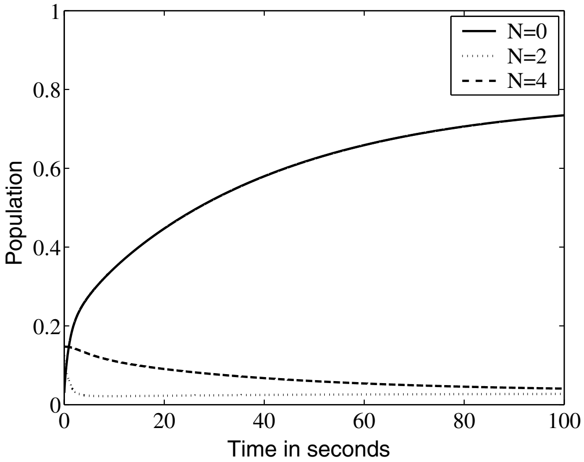

FIG. 3. Evolution of the populations of the rotational levels with quantum numbers $N = 0, 2, 4$ as a function of cooling time for MgH$^+$.

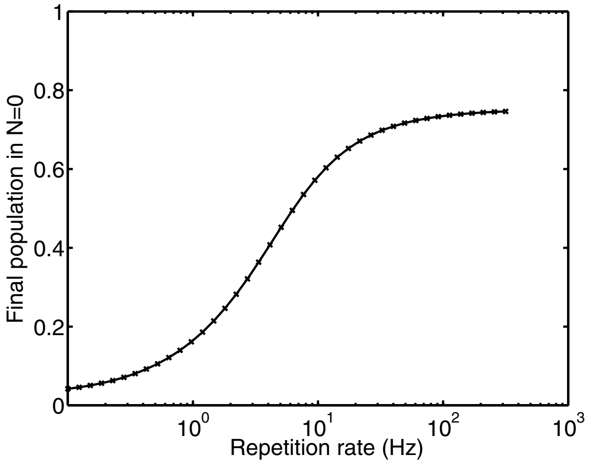

FIG. 4. Population in the rovibrational ground state of MgH$^+$ after 100 s of cooling as a function of the repetition rate of the pumping lasers. Each laser pulse saturates the transition it pumps.

scheme discussed above. After 100 s of cooling the system has practically reached steady state.

Figure 4 explores the sensitivity of the cooling efficiency for MgH$^+$ on the repetition rate of the Raman pulses for a fixed cooling time of 100 s. Already for modest repetition rates, say, 20–30 Hz, we observe a significant cooling efficiency, and repetition rates larger than 100 Hz do not significantly increase the cooling efficiency. This is experimentally very encouraging since laser systems with nanosecond pulses typically have repetition rates in the interval 10–100 Hz.

The Raman scheme discussed above is effective for molecular ions which have an excited electronic state that can be addressed by laser light in the visual or near-visual range. If such excited states are absent, a scheme based on continuous-wave near infrared (IR) sources introducing direct couplings *within* the ground electronic potential curve can be applied. This direct scheme works as follows: One IR source couples $(\nu = 0, N = 1)$–$(\nu = 2, N = 0)$ which, although dipole forbidden, for typical molecules is easily saturated due to the anharmonicity of the potential curve. The excited $(\nu = 2, N = 0)$ cascades down by dipole allowed transitions, first to the $(\nu = 1, N = 1)$ excited state and then to the $(\nu = 0, N = 0)$ dark state or the $(\nu = 0, N = 2)$ state. The latter state is pumped by another laser into the $(\nu = 1, N = 1)$ state, from which decay into the dark state or back into the $(\nu = 0, N = 2)$ state will take place.

As an example of the application of this direct scheme we consider ArH$^+$ which is supposed to have no stable excited electronic states [26]. Figure 5 shows the initial thermal ($T = 300$ K) distribution over rotational states for ArH$^+$ and the final steady-state distribution after 50 s of cooling. In the cooled distribution, more than 95% of the population is in the $X^1\Sigma^+$ rovibrational ground state, equivalent to a temperature of 7 K. ArH$^+$ is a strong vibrational infrared emitter [27,28], and the rotational transition rates are of the same order of magnitude as in MgH$^+$ [29] and, consequently, the cooling is very effective. The IR stimulated processes, which drives the $(\nu = 0, N = 1)$–$(\nu = 2, N = 0)$ and $(\nu = 0, N = 0)$–$(\nu = 1, N = 1)$ transitions, require lasers with wavelengths around 1.9 and 3.8 μm, respectively [30]. These wavelengths are conveniently covered by near-IR continuous-wave optical parametric oscillators (OPO's) [31]. To ensure that the scheme remains insensitive to the intrinsic linewidth and drifts in the OPO, one should require an effective rate for the pumped transitions of $\sim$90% of the A coefficients, at a detuning of $\sim$10 MHz. This is fulfilled at an intensity of a few hundreds of W/cm^2, which is realistic using a laser beam with a few tens of mW power focused to a beam waist of $\sim$100 μm.

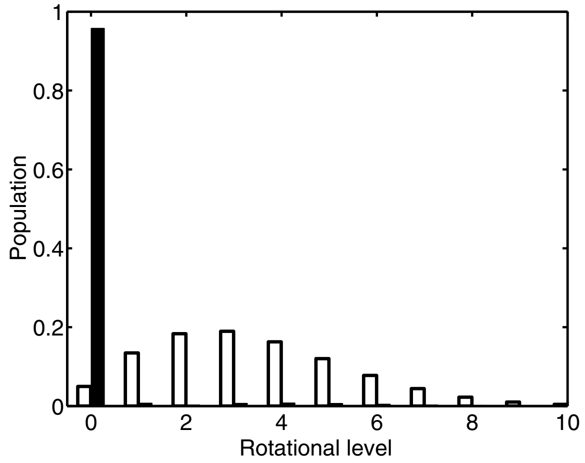

FIG. 5. Cooling of ArH$^+$ by the direct scheme. The unfilled columns represent the initial rotational populations corresponding to a thermal distribution at $T = 300$ K. The filled columns represent the population distribution after 50 s of cooling. See the text for details on the scheme, and the cooling parameters.

Note that such a waist is much larger than the localization of translationally cold ions [18].

To make sure that all magnetic sublevels of the rotational states are addressed by the pump laser fields, the polarization of the pumping radiation must be varied within each optical pulse in the case of the Raman scheme and at a rate faster than rotational transition by BR in the case of the direct scheme. In both cases this can be done by using a modulated Pockels cell eventually combined with splitting the pulses to enter the trap region from different directions.

Here we have focused on the description of schemes for cooling the rotational degree of freedom of molecular ions with the ground state symmetry, $^1\Sigma^+$, and without hyperfine splittings. Such splittings, when present, are typically much smaller than the bandwidth ~1–30 GHz of typical pulsed laser systems applicable in the Raman scheme (e.g., ~1 MHz in BeH$^+$ [32]), and, hence, all hyperfine levels will be addressed by the pump fields. Also, the schemes can be extended to molecular ions with more complicated ground state configurations at the cost of more detailed considerations of the laser systems used [25].

If one considers an implementation of the schemes in connection with cooling in storage rings [19,20] a larger focal spot of the laser would be required in order to obtain overlap with the ion beam. This significantly increases the laser power requirements, and leads us to conclude that the pulsed Raman scheme could be considered while the direct scheme would be impossible, due to the limited power of present day OPO systems.

Since the schemes for cooling of the internal degrees of freedom are independent of the charge of the molecular system, the schemes will be equally applicable to neutrals if the requirements on trapping time and spatial localization can be met.

The state-selected and strongly localized molecular ions produced by the above presented cooling schemes have many potential applications and will be interesting for a large variety of studies including controlled chemical reactions, dissociative recombination with unprecedented rotational resolution [19,20], implementations of quantum logics, and mimicking of conditions in the interstellar medium where many small and cold molecular ions play an important role [33].

In conclusion, we have shown how initially translationally cold, trapped molecular ions can be internally cooled by simple optical pumping schemes when assisted by the blackbody radiation. The schemes are simple and robust, and the light source requirements are modest compared to state-of-the-art laser systems.

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[1] See, e.g., C. S. Adams, M. Sigel, and J. Mlynek, Phys. Rep. **240**, 143 (1994).

[2] See, e.g., F. Dalfolo *et al.*, Rev. Mod. Phys. **71**, 463 (1999).

[3] See, e.g., M. A. Nielsen and I. L. Chuang, *Quantum Computation and Quantum Information* (Cambridge University Press, Cambridge, 2000).

[4] D. R. Miller, in *Atomic and Molecular Beam Methods*, edited by G. Scoles (Oxford University Press, Oxford, 1988).

[5] T. Takekoshi, B. M. Patterson, and R. J. Knize, Phys. Rev. Lett. **81**, 5105 (1998).

[6] A. Fioretti *et al.*, Phys. Rev. Lett. **80**, 4402 (1998).

[7] A. N. Nikilov *et al.*, Phys. Rev. Lett. **82**, 703 (1999).

[8] A. N. Nikilov *et al.*, Phys. Rev. Lett. **84**, 246 (2000).

[9] B. L. Tolra, C. Drag, and P. Pillet, Phys. Rev. A **64**, 061401(R) (2001).

[10] J. D. Weinstein *et al.*, Nature (London) **395**, 148 (1998).

[11] D. Egorov *et al.*, Phys. Rev. A **63**, 030501(R) (2001).

[12] H. L. Bethlem, G. Berden, and G. Meijer, Phys. Rev. Lett. **83**, 1558 (1999).

[13] H. L. Bethlem *et al.*, Nature (London) **406**, 491 (2000).

[14] F. M. H. Crompvoets *et al.*, Nature (London) **411**, 174 (2001).

[15] K. Bergman, in *Atomic and Molecular Beam Methods* (Ref. [4]).

[16] D. E. Goeringer, W. B. Witten, and J. M. Ramsey, Int. J. Mass Spectrom. Ion Process. **106**, 175 (1991).

[17] See, e.g., D. Gerlich, Phys. Scr. **T59**, 256 (1995), and references therein.

[18] K. Mølhave and M. Drewsen, Phys. Rev. A **62**, 011401(R) (2000).

[19] U. Hechtfischer *et al.*, Phys. Rev. Lett. **80**, 2809 (1998).

[20] Z. Amitay *et al.*, Science **281**, 75 (1998).

[21] D. J. Wineland *et al.*, J. Res. Natl. Inst. Stand. Technol. **103**, 259 (1998).

[22] M. J. Frisch *et al.*, GAUSSIAN 94, Revision E.1, Gaussian, Inc., Pittsburgh, PA, 1995.

[23] K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure, IV Constants of Diatomic Molecules* (Van Nostrand Reinhold Company, New York, 1979).

[24] R. J. Le Roy, LEVEL 7.4: A Computer Program for Solving the Radial Schrodinger Equation for Bound and Quasibound Levels, University of Waterloo Chemical Physics Report No. CP-642 R3, 2001. The source code and manual for this program are available on the WWW site http://leroy.uwaterloo.ca.

[25] I. S. Vogelius *et al.* (to be published).

[26] C. J. H. Schutte, Chem. Phys. Lett. **350**, 181 (2001).

[27] N. Picqué, G. Guelacvili, and S. Civis, J. Chem. Phys. **113**, 2134 (2000).

[28] P. Rosmus, Theor. Chim. Acta **51**, 359 (1979).

[29] K. B. Laughlin *et al.*, Phys. Rev. Lett. **58**, 996 (1987).

[30] C. J. H. Schutte, Chem. Phys. Lett. **345**, 525 (2001).

[31] See, e.g., E. V. Kovalchuk *et al.*, Opt. Lett. **26**, 1430 (2001), and references therein.

[32] J. Fišer and J. Vojtík, Chem. Phys. **205**, 351 (1996).

[33] T. W. Hartquist and D. A. Williams, *The Chemically Controlled Cosmos—Astronomical Molecules from the Big Bang to Exploding Stars* (Cambridge University Press, Cambridge, 1995).