Blackbody-radiation–assisted molecular laser cooling

I. S. Vogelius and L. B. Madsen
Department of Physics and Astronomy, University of Aarhus, 8000 Århus C, Denmark

M. Drewsen
QUANTOP - Danish National Research Foundation Centre for Quantum Optics, University of Aarhus, 8000 Århus C, Denmark

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.

PACS numbers: 33.80.Ps

Powerful techniques for manipulating, cooling and trapping atoms have recently paved the way for extremely detailed investigations of atomic physics phenomena, as well as being essential ingredients in the development of research fields such as atom optics, physics of trapped condensed dilute gases, and quantum information. 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, their high average translational velocities (~ 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 and quantum information. 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 ~ 100μK), 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 ~ 400 mK by collisions with a He buffer gas maintained at cryogenic temperatures. This method leaves the molecules essentially in the ground state internally. Finally, beams of neutral polar molecules have been decelerated by electrostatic fields and confined in an electrostatic quadrupole trap or a tabletop “storage ring” at translational temperatures down to ~ 10 mK.

Molecular ions constitute another class of molecules that are equally interesting to cool and manipulate. For decades resonance-enhanced multiphoton ionization (REMPI) processes have been exploited to produce state-specific molecular ions in beam experiments. The same procedure has also been applied in connection with traps, 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. Most recently, it has been demonstrated that molecular ions can be very effectively translationally cooled (~ 100 mK) into ion Coulomb crystals in a linear Paul trap through Coulomb interaction with laser cooled atomic ions. In such experiments, the frequency of the ions external vibrational motion is determined by the trap potential, and is typically ~ 100 – 1000 kHz. Rotational and vibrational frequencies of the molecular ions, on the other hand, are many orders of magnitude larger (~ 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. The long trapping times (~ hours) of these spatially localized ions, combined with long intervals between collisions (~ minutes, as estimated by Langevin theory), however, opens for internal cooling schemes which rely on and are not hampered by blackbody radiation, and which are efficient on the timescale 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 ν = 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 effected 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 states 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, \(\tau\), times the Raman coupling frequency, \(\Omega_R\), should fulfill (i) \(\tau \Omega_R \gtrsim 10\), where \(\Omega_R \simeq \Omega^2/\delta\) with \(\Omega\) being the typical Rabi frequency of the dipole allowed electronic transitions and \(\delta\) 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 modelled the dynamics of the BR-assisted cooling by rate equations including change in population of the involved rovibrational states due to both spontaneous and stimulated processes. In practice this means that the calculations require the knowledge of Einstein \(A\) and \(B\) coefficients for a selection of rovibrational transitions. In short, the dipole moment functions and potential curves are obtained \(ab\ initio\) using Gaussian94 [22]. The energies of the levels of relevance are in agreement with published data within 1.5\% [23]. Einstein coefficients are subsequently calculated from the dipole moment function and potential energy curve using the Numerov method [24]. Details of the calculations will be presented elsewhere [25]. The initial populations are taken to be Boltzmann distributed at room temperature \((T = 300\, \text{K})\). In Fig. 2, we present the results of such 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 seconds 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 \(~ 279\, \text{nm}\) [26]. We find that the saturation and scattering conditions (i) and (ii) above can be fulfilled for the pumped transitions from any rotational sub-state for 10 ns pulses with intensities \(\sim 100\, \text{kw/cm}^2\). 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 1](image1.png)

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

![Figure 2](image2.png)

**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 \(T = 300\, \text{K}\). The filled columns represent the population distribution after 100 s of cooling. See the text for details on the cooling parameters.

Figure 3 shows the evolution of the population in three representative rotational levels of MgH\(^+\) for the Raman scheme discussed above. After 100 s of cooling the system has practically reached steady–state.
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$^+$. 

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 infra-red (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]. Fig. 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, requires lasers with wavelengths around 1.9$\mu$m and 3.8$\mu$m, 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 $\sim 100\mu$m. 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 on the time scale of the optical pulses in the case of the Raman scheme and at a rate faster than rotational transition by BR is 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, however, are typically much smaller, e.g. $\sim 1$ MHz in BeH$^+$ [25], than the bandwidth $\sim 1 - 30$ GHz of typical pulsed laser systems applicable in the Raman scheme, 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 [14,20] 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.

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, implementations of quantum logics, and for the 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.

L.B.M. is supported by the Danish Natural Science Research Council (Grant No. 51-00-0569). M.D. is supported by the Danish National Research Foundation through the Quantum Optics Centre QUANTOP as well as by the Carlsberg Foundation.

[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.E. Goeringer, W.B. Witten, and J.M. Ramsey, Int. J. Mass Spectrom. Ion Processes, 106, 175 (1991).

[12] See, e.g., G. Gerlich, Physica Scripta T59, 156 (1995), and references therein.

[13] K. Bergman, in Atomic and Molecular Beam Methods, edited by G. Scoles (Oxford University Press, Oxford, 1988).

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

[15] See, e.g., G. Gerlich, Physica Scripta T59, 156 (1995), and references therein.

[16] K. Molhave and M. Drewsen, Phys. Rev. A 62, 011401(R) (2000).

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

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

[19] D.J. Wineland et al., J. Res. NIST, 103, 259 (1998).

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

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

[22] R.J. Le Roy, LEVEL 7.4: A Computer Program for Solving the Radial Schrodinger Equation for Bound and Quasisbound Levels, University of Waterloo Chemical Physics Report CP-642 R3 (2001). The source code and manual for this program is available on the WWW site http://leroy.uwaterloo.ca

[23] T.S. Vogelius et al. in preparation.

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

[25] N. Picqué, G. Guelachvili, and S. Civis, J. Chem. Phys. 113, 2134 (2000).

[26] P. Rosmus, Theoret. Chim. Acta (Berl.) 51, 359 (1979).

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

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

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

[30] J. Fisser and J. Vojtk, Chem. Phys. 205, 351 (1996).

[31] 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).