Opto-Electrical Cooling of Polar Molecules

M. Zeppenfeld, M. Motsch, P.W.H. Pinkse, and G. Rempe
Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Str. 1, D-85748 Garching, Germany
(Dated: October 7, 2009, PREPRINT v6)

We present an opto-electrical cooling scheme for polar molecules based on a Sisyphus-type cooling cycle in suitably tailored electric trapping fields. Dissipation is provided by spontaneous vibrational decay in a closed level scheme found in symmetric-top rotors comprising six low-field-seeking rovibrational states. A generic trap design is presented. Suitable molecules are identified with vibrational decay rates on the order of 100 Hz. A simulation of the cooling process shows that the molecular temperature can be reduced from 1 K to 1 mK in approximately 10 s. The molecules remain electrically trapped during this time, indicating that the ultracold regime can be reached in an experimentally feasible scheme.

PACS numbers: 37.10.Mn, 33.80.-b
Keywords: optical cooling, cold molecules, electrostatic trapping

The ability to prepare samples of ultracold molecules opens up exciting new possibilities in physics and chemistry, including ultrahigh-precision molecular spectroscopy and interferometry [1, 2], investigations of anisotropic collisions in quantum-degenerate gases [3], steering of chemical reactions [4], tests of fundamental physics such as the search for the electron dipole moment [5], and novel approaches to quantum computing and quantum simulations [6, 7, 8]. Reaching ultracold temperatures through laser cooling has the great advantage that it does not lead to particle loss and that it is a single-particle process which does not require suitable collision properties or high densities. However, laser cooling has so far only been demonstrated for atoms and ions with simple energy-level structures, whereas optical cooling of molecules has proven confoundingly difficult.

Optical cooling of molecules requires a change in paradigm: In contrast to ultracold atoms, for which efficient cooling was realized early on [9], but trapping proved to be a challenge due to the shallow optical and magnetic potentials available, electric trapping of polar molecules is relatively easy [10] and has, in fact, been demonstrated for molecules without any cooling [11]. Optical cooling of molecules could therefore start with trapped molecules and exploit the tremendous (∼ 1 K) energy-level shifts producible by laboratory electric fields, circumventing the usual requirements of standard laser cooling such as highly closed transitions, fast decay rates, and significant photon momentum transfer.

Making use of the aforementioned paradigm shift we here present a cooling scheme for molecules which is conceivable with present technology. Specifically, we replace photon recoil by an electric-field interaction energy as the means to remove energy from a molecular ensemble in a configuration reminiscent of Sisyphus cooling and single-photon cooling [12, 13, 14]. Spontaneous emission of photons serves only to remove entropy. As a result, the number of scattered photons required to achieve substantial cooling is dramatically reduced. Slowly decaying vibrationally excited states, generally offering stricter selection rules than electronic transitions, can therefore be used for the spontaneous decay.

Our cooling scheme is shown in Fig. 1. Two neighboring regions in space, each with a constant but different electric field, are realized by a suitable arrangement of electrodes. These electrodes also provide a high-electric-field enclosure around these regions to ensure trapping of molecules in low-field-seeking (lfs) states. Fig. 2 shows a possible design for the electrodes. Trapped molecules experience a potential step when moving from one region to the other. The magnitude of this potential step depends on the average orientation of the electric dipole moment of a molecule with respect to the electric field and may vary significantly for different molecular states. For one strong and one weak lfs molecular state we obtain a potential as a function of position as depicted by the curves |s⟩ and |w⟩ in Fig. 1.

Suppose a molecule possesses an excited state |e⟩ which decays into the states |w⟩ and |s⟩. We induce transitions...
between |w⟩ and |e⟩ in the low-field region of the trap and transitions between |s⟩ and |w⟩ in the high-field region. Doing so creates a unidirectional cycling process. During the cycle, the molecule loses a kinetic energy corresponding to the difference between the potential steps of the strong and the weak lfs state, leading to overall cooling.

The main advantage of this cooling scheme is the large amount of kinetic energy which can be removed from a molecule for each spontaneously emitted photon. For a representative dipole moment \( d_{el} \) of 1 Debye [D], oriented in an electric field \( E \) of 100 kV/cm, one obtains an interaction energy of \( E = \frac{1}{2}d_{el}E \times 1.61 \) K. Starting with an ensemble of molecules with a translational temperature below 1 K, this in principle allows the removal of all of a molecule’s kinetic energy in a single step. In practice, however, more than one spontaneous decay is necessary to cool a molecule: When the fields are kept constant, a molecule will generally end up in state |s⟩ in the low-field region with insufficient energy to move back to the high-field region but with at least the amount of energy obtained when moving from the high- to the low-field region in the state |w⟩. Further cooling to lower temperatures therefore requires the height of the electric-field step to be slowly ramped down, allowing the cooling cycle to repeat. Nonetheless, a few dozen spontaneous decays are more than enough to cool a molecule to below a mK.

Due to the small number of spontaneous photon emissions, the requirements imposed on the emission process are much less stringent than for standard laser cooling. Not only is the branching ratio for decay from the excited state to desired and undesired states much less critical, but the rate at which such transitions occur may also be much lower. As a result, the use of vibrational transitions for the spontaneous decay process is possible.

The advantage of vibrational compared to electronic excitations is that except in the case of strong resonances with other vibrational states, a molecule with one quantum of excitation in a single vibrational mode will decay primarily back to the vibrational ground state. Additionally, compared to the deep ultraviolet wavelengths required to excite electronic states of most simple chemically-stable molecules, many molecules have strong vibrational transitions in the wavelength range \( 3 - 10 \mu m \). The coverage of this wavelength range by tunable narrow-band light sources has been significantly improved in recent years by the commercial availability of quantum-cascade lasers and optical parametric oscillators, in addition to, e.g., lead-salt lasers.

Beyond the closed vibrational transition, the rotational transitions must be considered. The excited vibrational state must not only decay to a manageable number of rotational states, but each of these states must be lfs so that the molecule remains trapped. Disregarding linear molecules due to their generally weaker quadratic Stark interactions, symmetric-top molecules have the most stringent selection rules for dipole transitions. Describing the rotational states of a symmetric-top molecule by the quantum numbers for the total angular momentum \( J \), the angular momentum about the molecule’s symmetry axis \( K \) and the angular momentum about a lab-fixed axis \( M \), the selection rules for a parallel transition are \( \Delta J = 0, \pm 1, \Delta K = 0 \) and \( \Delta M = 0, \pm 1 \).[20] Furthermore, the lowest-order Stark interaction is \( E_{\text{Stark}} = -E \cdot d_{el} = -|E| |d_{el}| \frac{K M}{|J+1|} \). Observing that \( J \geq 0, |K| \leq J \) and \( |M| \leq J \)[20], we see that an excited state with \( |K| = J \geq 2 \) and \( M = -K \) best satisfies the conditions stated above. Such a state may decay into a total of only five rotational states, all of which are lfs. These can be repumped using additional lasers or microwave fields. Note that the condition of few decay channels to purely lfs states can also be satisfied for linear molecules, e.g., in a \( \Sigma \) electronic state using a vibrationally excited state with \( M = 0, J \geq 3 \).[20]

Use of vibrational excitations for opto-electrical cool-

| molecule | \( d_{el} \) [D] | \( f_{\text{vib}} \) [cm\(^{-1}\)] | \( \gamma \) [Hz] | molecule | \( d_{el} \) [D] | \( f_{\text{vib}} \) [cm\(^{-1}\)] | \( \gamma \) [Hz] |
|-----------|-------------|-------------|-------|-----------|-------------|-------------|-------|
| CF₃H     | 1.85        | 3036        | 0.65  | CF₅Cl     | 0.50        | 1105        | 79    |
| CF₃H     | 1.65        | 3036        | 0.65  | CF₃Br     | 0.65        | 1089        | 74    |
| CH₃CCH   | 0.78        | 3334        | 0.92  | CF₃I      | 0.92        | 1080        | 61    |
| CF₃CCH   | 2.36        | 3327        | 0.79  | BH₃CO     | 1.80        | 2217        | 274   |
| N(CH₃)₄  | 0.61        | 2933        | 0.61  | BH₃CO     | 1.80        | 2217        | 274   |

FIG. 2: Design of an electric trap for the cooling scheme. Regions of tunable homogeneous fields are achieved using parallel capacitor plates (a). Collisions with the plate surface are eliminated by alternatingly-charged microstructured surface electrodes (b). Transverse confinement is achieved by a high voltage electrode between the platea around the perimeter of the trap (a). By interrupting the perimeter electrode, an electric quadrupole guide can be connected to the trap for the injection and extraction of molecules (c).
The potential-energy step for each of the molecular states has no net effect, reducing the effective decay rate. | 3 | 3, 2, −2 | 3, 2, −3 |

The rate of the cooling process is influenced by three effects. Most significantly, the rate coefficients indicate the time in which 1−1/e of molecules perform some process, whereas the time in which 99% of molecules perform this process takes significantly longer. Ramping down the electric-field step too rapidly therefore causes the final energy of most molecules to substantially exceed the field-step energy so that efficient cooling is no longer possible. Secondly, the fraction of energy removed during each cooling cycle is below unity. Reducing the temperature by, e.g., a factor of ten requires several cooling cycles. Finally, spontaneous decay to the states | 2, 2, −1 |, | 3, 2, −1 |, and | 3, 2, −2 | in the low-field region of the trap has no net effect, reducing the effective decay rate.

The velocity distribution of the molecules in the low-field region of the trap for various times after cooling commences is shown in Fig. 2. As can be seen, significant cooling occurs in under a second. Note that the cooling rate decreases significantly as time progresses. For high temperatures, the cooling rate is limited by the decay rate of the vibrationally excited state, allowing the temperature to decrease exponentially with time. For low temperatures, the cooling rate is limited by the time it takes for the molecules to move between the two regions of the trap, with the cooling rate proportional to the velocity of the molecules. Therefore, at very low temperature the cooling process is no longer efficient, and the molecules must either be moved to a smaller trap or a
different cooling scheme must be applied.

The elementary description of opto-electrical cooling so far glosses over several issues which must be addressed to ensure the experimental viability of the method. In particular, achieving required trapping times, sufficient mixing of the individual velocity components, and validity of approximate selection rules are now discussed.

In addition to collisions with the background gas, Majorana flips and rovibrational heating by thermal black-body radiation are the identified loss channels for polar molecules stored in electric traps [21, 22]. Although rotational heating is a problem for extremely light molecules [22] and vibrational heating for heavy molecules, neither is the case for the molecules considered in Table I. For example, the heating rates to the lowest vibrational modes never exceed a few mHz at 300 K for CF$_3$CCH, the heaviest molecule in Table I.

Majorana flips are expected to have been a problem in past trap designs with a near-zero electric field in the central trap region [21]. However, the trap in Fig. 2 is specifically designed to allow a homogeneous offset field throughout the vast majority of the trap volume. Furthermore, field zeros near the edges of the trap can be reduced to singular points through clever electrode design, which essentially eliminates Majorana flips.

Opto-electrical cooling only removes energy from a single component of the velocity vector, making sufficient mixing of the velocity components a necessity. Electric-field inhomogeneities near the microstructured plate surface allow such mixing on a sufficiently short timescale. This is demonstrated by trajectory simulations discussed in the appendix.

The zero-field rigid-rotor harmonic-oscillator selection rules used so far imply a closed six-level system for opto-electrical cooling. These selection rules are modified in several ways for real molecules. Transitions with $\Delta K \neq 0$ and decay to other excited vibrational states are generally possible for symmetric top molecules via resonances between near-degenerate vibrationally excited states. Due to the few spontaneous emissions needed, such couplings will at most cause problems for individual molecule species.

For non-zero values of the electric field, $J$ ceases to be a good rotational quantum number and spontaneous decay with $|\Delta J| \geq 2$ becomes possible. The resulting sequences were checked by diagonalizing the rigid-rotor Hamiltonian for non-zero electric fields using molecular constants of CF$_3$H and calculating dipole transition matrix elements between the new eigenstates. Although the partitioning of spontaneous decay from the state $v=1$, $J=2, 2, -2$ to the five states $v=0$, $J=2$ and 3 is significantly changed already at electric fields of $\sim 50$ kV/cm, the spontaneous decay to states with $J \geq 4$ remains below 1% for fields up to 100 kV/cm. This effect on opto-electrical cooling is therefore negligible.

Achieving a temperature below 1 mK through opto-electrical cooling would allow other cooling schemes, requiring longer interaction times or higher phase-space density, to be implemented. Specifically, opto-electrical cooling can easily be extended to an accumulation scheme, for example to load molecules into a tightly confining optical dipole trap. The low temperatures and high densities thus achieved create extremely favorable starting conditions for a number of further cooling schemes such as evaporative cooling, cavity cooling, or sympathetic cooling with ultracold atoms.

Support by the Deutsche Forschungsgemeinschaft via the excellence cluster "Munich Centre for Advanced Photonics" and via EuroQUAM (Cavity-Mediated Molecular Cooling) is acknowledged.

* Electronic address: martin.zeppenfeld@mpq.mpg.de

[1] J. van Veldhoven et al., Eur. Phys. J. D 31, 337 (2004).
[2] S. Gerlich et al., Nature Phys. 3, 711 (2007).
[3] M. Baranov, L. Dobrek, K. Góral, L. Santos, and M. Lewenstein, Phys. Scr. T102, 74 (2002).
[4] R.V. Krems, Int. Rev. Phys. Chem. 24, 99 (2005).
[5] J.J. Hudson, B.E. Sauer, M.R. Tarbutt, and E.A. Hinds, Phys. Rev. Lett. 89, 023003 (2002).
[6] C.M. Tesch and R. de Vivie-Riedle, Phys. Rev. Lett. 89, 157901 (2002).
[7] D. DeMille, Phys. Rev. Lett. 88, 067901 (2002).
[8] A. Micheli, G.K. Brennen, and P. Zoller, Nat. Phys. 2, 341 (2006).
[9] H.J. Metcalf and P. van der Straten, Laser Cooling and Trapping, Springer, Berlin (1999).
[10] H.L. Bethlem et al., Nature 406, 491-494 (2000).
[11] T. Rieger, T. Junglen, S.A. Rangwala, P.W.H. Pinkse, and G. Rempe, Phys. Rev. Lett. 95, 173002 (2005).
[12] D.E. Pritchard, Phys. Rev. Lett. 51, 1336 (1983).
[13] J. Söding, R. Grimm, and Y.B. Ovchinnikov, Opt. Commun. 119, 652 (1995).
[14] G.N. Price, S.T. Bannerman, K. Viering, E. Narevicius, and M.G. Raizen, Phys. Rev. Lett. 100, 093004 (2008).
[15] S.J. Wark and G.I. Opat, J. Phys. B 25, 4229 (1992).
[16] D.R. Lide (Ed.), CRC Handbook of Chemistry and Physics, 71st Ed., CRC Press, Boca Raton (1990).
[17] M.E. Jacox, "Vibrational and Electronic Energy Levels of Polyatomic Transient Molecules" in NIST Chemistry WebBook, [http://webbook.nist.gov](http://webbook.nist.gov) (2003).
[18] Gaussian 03, Revision B.03, M.J. Frisch et al., Gaussian, Inc., Pittsburgh PA, (2003).
[19] S.A. Rangwala, T. Junglen, T. Rieger, P.W.H. Pinkse, and G. Rempe, Phys. Rev. A 67, 043406 (2003).
[20] W. Gordy and R.L. Cook, Microwave Molecular Spectra, John Wiley, (1984).
[21] M. Kirste, B.G. Sartakov, M. Schnell, and G. Meijer Phys. Rev. A 79, 051401(R) (2009).
[22] S. Hoekstra et al., Phys. Rev. Lett. 98, 133001 (2007).
DERIVATION OF THE RATE EQUATIONS

The rate equations used to simulate cooling of CF$_3$H can be derived as follows. The ensemble of molecules in the trap is represented by the number of molecules $p_{a}^{(i)}(v, t)dv$ with velocity between $v$ and $v + dv$ in the molecular state $a$ in part $i = 1, 2$ of the trap. Here, $i = 1$ denotes the low-field region and $i = 2$ denotes the high-field region of the trap.

In this description of the molecular ensemble, we ignore the position of the molecules within each trap region as well as the direction of the velocity vector $v$ with $v = |v|$, effectively assuming instantaneous spatial redistribution of the molecules within each trap region as well as instantaneous redistribution of the direction of $v$. Whereas the assumed instantaneous spatial redistribution should at most slightly affect the validity of the results of the simulation since the molecule’s thermal motion will rapidly redistribute the molecules through the trap, the assumed mixing of the components of $v$ is less obvious. In fact, in the case of a potential energy in the trap which is completely separable in Cartesian coordinates, no mixing of the velocity components would occur at all.

To address this question, molecule trajectory simulations in a trap based on the design in Fig. 2 of the paper were performed and the temporal correlation of the magnitude of the individual components of $v$ was calculated. The calculated correlation for a particle with a velocity of 10 m/s in the homogeneous-field region of the trap is shown in Fig. 5. Particularly for large $\tau$, the correlation function for $v_x$ and $v_y$ can be accurately reproduced by assuming a $\sim 20\%$ probability for the velocities to completely mix for each collision with the microstructured plate surface. This demonstrates that significant mixing of the velocity components occurs due to the field inhomogeneities near the plate surfaces. Due to the translational symmetry of the microstructures along the $z$-direction, this mixing does not include the $z$-component of the velocity, leading to significantly slower mixing for this velocity component. However, by arranging the microstructure plates such that the structure on the top and bottom plate is rotated by $90^\circ$ with respect to the other, all three velocity components mix on the shorter timescale. The resulting mixing is sufficiently strong that a major impact on the cooling rate does not occur.

To derive the rate equations for the molecule distributions $p_{a}^{(i)}(v, t)$, two processes must be taken into account. First, transitions between the various internal molecular states may occur in both regions of the trap. This is modeled by a fixed fraction of molecules in a given state switching to a different state per unit time interval,

$$\frac{d}{dt} |_{\text{trans}} p_{a}^{(i)}(v, t) = \sum_{a' = 1}^{6} (c_{a', a}^{(i)}p_{a'}^{(i)}(v, t) - c_{a, a'}^{(i)}p_{a}^{(i)}(v, t)).$$

with appropriate rate coefficients $c_{a, a'}^{(i)}$.

Second, molecules may diffuse between the two trap regions. For those molecules in region $i$ with a velocity component $v_x$ perpendicular to the interface between the trap regions, a fraction of $v_x, A/V_i$ of the molecules attempt to enter the other trap region per unit time. Here, $A$ is the surface area of the interface between the trap regions and $V_i$ is the volume of trap region $i$. For those molecules in region 2 of the trap, all molecules attempting to enter region 1 succeed, whereas for molecules in region 1, only those molecules with $v_x^2 > 2\Delta E_a/m$ succeed, where $\Delta E_a$ is the potential energy difference between the two trap regions for molecules in state $a$ and $m$ is the molecular mass. Finally we need to average over the possible values of $v_x$. For an isotropic velocity distribution in three dimensions, a single velocity component is evenly distributed so that the fraction of molecules leaving region 2 per unit time is

$$\frac{1}{2v} \int_0^v dv_x v_x A \frac{v}{V_2} = \frac{v A}{4V_2},$$

and the fraction of molecules leaving region 1 per unit time is

$$\frac{1}{2v} \int_0^v dv_x v_x A \frac{v}{V_1} = \frac{v_{a, 2}^2 A}{4v V_1}.$$  

Here, $v_{a, 2} = \sqrt{v^2 - 2\Delta E_a/m}$ is equal to the velocity a molecule in region 1 will have once it has reached region 2. Note that the integrals are normalized by dividing by $2v$ since $v_x$ can be both positive and negative but only molecules with (in this case) positive $v_x$ can enter the opposite trap region.
Every molecule which leaves one trap region must enter the opposite region. Nonetheless, a complication arises since the velocity of the molecules changes when they move between the regions. Molecules which enter region 1 in state $a$ with velocity in the range $v$ to $v + dv$ must have had a velocity in the range $v_{a,2}$ to $v_{a,2} + v dv/v_{a,2}$ in region 2.

As a result, the number of molecules in region 2 which could potentially increase the number of molecules $p_a^{(1)}(v, t)$ in region 1 with velocity in the range $v$ to $v + dv$ by switching regions is equal to $p_a^{(2)}(v_{a,2}, t) v dv/v_{a,2}$. Combining this with Eqs. (2) and (3) one obtains a diffusion rate

$$
\frac{d}{dt} p_a^{(1)}(v, t) = \begin{cases} 
\frac{v_{a,2}}{4} A V_2 \times \frac{v}{v_{a,2}} p_a^{(2)}(v_{a,2}, t) - \frac{A v_{a,2}^2}{4 v} p_a^{(1)}(v, t), & v \geq \sqrt{\frac{2 \Delta E_a}{m}} \\
0, & v < \sqrt{\frac{2 \Delta E_a}{m}}
\end{cases}
$$

(4)

Note that the $v$ in Eq. (2) is the velocity in region 2 and is therefore replaced by $v_{a,2}$ in Eq. (4). For $v^2 < 2 \Delta E_a/m$, the diffusion rate is zero due to the potential energy step.

For molecules entering region 2 we introduce $v_{a,1} = \sqrt{v^2 + 2 \Delta E_a/m}$ and the derivation of the diffusion rate is entirely analogous. One obtains as the final result,

$$
\frac{d}{dt} p_a^{(1)}(v, t) = \begin{cases} 
\frac{A v_{a,2}}{V_2} p_a^{(2)}(v_{a,2}, t) - \frac{A v_{a,2}^2}{V_1} p_a^{(1)}(v, t) + \sum_{a'=1}^{6} (c_{a',a}^{(1)} p_a^{(1)}(v, t) - c_{a,a'}^{(1)} p_a^{(1)}(v, t)), & v \geq \sqrt{2 \Delta E_a/m} \\
\sum_{a'=1}^{6} (c_{a',a}^{(1)} p_a^{(1)}(v, t) - c_{a,a'}^{(1)} p_a^{(1)}(v, t)), & v < \sqrt{2 \Delta E_a/m}
\end{cases}
$$

(5)

$$
\frac{d}{dt} p_a^{(2)}(v, t) = \frac{A V_1}{4 v_{a,1}^2} p_a^{(1)}(v_{a,1}, t) - \frac{A v}{V_2} p_a^{(2)}(v, t) + \sum_{a'=1}^{6} (c_{a',a}^{(2)} p_a^{(2)}(v, t) - c_{a,a'}^{(2)} p_a^{(2)}(v, t)).
$$

These rate equations are used for the cooling simulations in the main text.