

A proposal for laser cooling of OH molecules

F Robicieux

Department of Physics, Auburn University, AL 36849-5311, USA

Received 1 May 2009, in final form 19 August 2009

Published 22 September 2009

Online at stacks.iop.org/JPhysB/42/195301

Abstract

We describe a possible method for laser cooling OH molecules. The method is based on exciting the $\Delta J = 2$ stimulated Raman transition in the ground electronic and vibronic state. The molecules are assumed to already be trapped with a temperature of ~ 10 mK or less in a spatially varying magnetic field. By exciting the molecule in a region of high magnetic field, the subsequent spontaneous photon emission at lower magnetic field removes centre-of-mass energy from the molecule. The vacuum decay rate from the $J = 7/2, F = 4, M_F = 4$ to $J = 5/2, F = 3, M_F = 3$ is roughly 0.31 Hz and the next cascade to $J = 3/2, F = 2, M_F = 2$ is roughly 0.15 Hz. A cavity tuned to stimulate both transitions in a small region of space can enhance the decay. Simulations of the radiative transitions indicate that up to 20% of a population of OH molecules with an average energy of 10 mK will finish with energies less than 200 μ K.

1. Introduction

Research into methods for achieving ultracold molecular gases has become a recent focus for several groups. By cooling molecules, one can achieve new standards in precision measurements, reach new regimes for chemical reactions and perhaps generate new kinds of highly correlated systems. Recent successes in producing cold molecules have been achieved through Stark deceleration [1], the atom coil gun [2], photoassociation of ultracold atoms [3, 4], buffer gas cooling [5], Stark filter [6], spinning nozzle [7], pulsed optical field [8] and collision with an atomic beam [9]. Direct laser cooling of molecules is notably absent from this list. There are a few proposals for using lasers to cool molecules but these methods lack the simplicity that can be achieved in the laser cooling of atoms. For example, a recent paper has indicated that one of the proposed methods for laser cooling using cavities is more problematic than original estimates indicated [10]. By a careful choice of molecules with good Franck–Condon overlaps, Stuhl *et al* [11] have proposed TiO as a candidate for laser cooling in a MOT using pulsed electric fields to help remix the states.

For atoms, cooling by lasers has been a very important experimental development. This has allowed the formation and study of highly correlated gases, improvements in spectroscopy and advances in many other systems too numerous to mention. Loosely speaking, laser cooling is achieved by stimulated absorption of a photon followed by

a spontaneous emission that provides the damping needed for cooling. However, this technique has not been applied to molecules. While specific excited states can be populated by a laser-driven transition, there are usually a very large number of final states that are populated after the spontaneous emission. This quickly leads to most of the molecule population becoming trapped in states not driven by the laser unless a large number of repumping lasers are included. The basic reason for this is that the Born–Oppenheimer potential curve for the electronic excited state is usually not parallel to that for the ground state leading to non-zero Franck–Condon overlaps for several rotational–vibrational levels. Also, many electronically excited molecules have enough energy to dissociate; thus, each electronic excitation often leads to a fraction of the molecules being destroyed with the fraction depending on the branching ratio for dissociation compared to radiation. Even pure vibrational transitions often have roughly ten possible final states.

In the context of attempts to trap antihydrogen, it was noted [12, 13] that antihydrogen Rydberg atoms can substantially cool in a magnetic trap due to emission of microwave photons from Rydberg states; in some cases, emission of ~ 10 photons leads to approximately a factor of 10 decrease in kinetic energy. It might be surprising that microwave photons can provide substantial cooling since their associated momentum is negligible. The reason why they are effective is that the magnetic dipole moment can change substantially during a spontaneous emission and this

change leads to a change in the centre-of-mass potential for the antihydrogen. A similar effect was noted in [14] where blackbody photons could lead to rapid thermalization of electrons in a spatially varying magnetic field. Thus, one does not need the photon momentum to provide cooling; one can use the change in properties of internal states, coupled to spatially varying external fields, to provide the necessary damping forces. As a more familiar example from laser cooling, Sisyphus cooling also works because the region of photon absorption is different from where the photon is emitted so that the emitted photon has more energy than the absorbed photon. To summarize, if an internal property of the atom/molecule changes, then the momentum kick can come from external fields and relatively few photons are needed to achieve substantial cooling. In this scenario, even slow decay paths become viable options for cooling.

This type of process is available for molecules and could be a route for laser cooling. In fact, two different methods that exploit general properties of molecules are available. In both methods, a large change in the characteristics of the molecule lead to substantial cooling with few photon absorptions and emissions. In the appendix, we sketch possible methods using vibrational transitions that requires $\sim 5\text{--}10$ repumping lasers. Below we describe a method that does not require *any* repumping lasers but does require high- Q cavities for two transitions in the terahertz regime.

The method we will mainly address in this paper uses a *rotational* transition in the molecule assisted by a high- Q cavity. The OH molecule is assumed to already be trapped in a spatially varying magnetic field and have a centre-of-mass kinetic energy less than ~ 10 mK. To be specific, this paper will treat the rotational transitions of OH in detail using the effective Hamiltonian parameterization of the ${}^2\Pi_{1/2,3/2}$ states given in [15]. Suppose the OH molecule is in the ${}^2\Pi_{3/2} J = 7/2, F = 4, M_F = 4$ state. There is only one path for radiative decay: first to the $J = 5/2, F = 3, M_F = 3$ state (0.31 Hz) and then to the $J = 3/2, F = 2, M_F = 2$ state (0.15 Hz). If a two-photon stimulated Raman transition connects the $J = 3/2, F = 2, M_F = 2$ state and $J = 7/2, F = 4, M_F = 4$ states¹, then the system is closed, without any repumping necessary. (In principle, direct two photon excitation could give the same transition with one photon nearly resonant with the 3/2 to 5/2 transition and the other nearly resonant with the 5/2 to 7/2 transition, but the frequencies are difficult to achieve, i.e. roughly 2.5 and 3.5 THz.)

Unfortunately, the decay cascade takes ~ 10 s in vacuum. However, if the atoms are in a high- Q cavity, the density of photon states at the transition frequencies can be greatly increased which will lead to much shorter decay times.

To shorten the notation, we will use $|2\rangle$ for the $F = 2$ state, $|3\rangle$ for $F = 3$ and $|4\rangle$ for $F = 4$. The frequency

¹ In the simulations below, we will assume the on-resonance transition rate from 3/2 to 7/2 is 70 Hz. If two visible photons are used for the stimulated Raman transition, then the power needed can be estimated from $\hbar\Omega \sim (dE)^2/\Delta\epsilon$ where d is the dipole moment, E is the electric field and $\Delta\epsilon$ is the detuning of the visible photon from the nearest resonance transition. Taking $d \sim ea_0$ (i.e. one atomic unit of dipole moment), $\Omega = 70$ Hz and $\Delta\epsilon = 10^{-18}$ J (i.e. 6 eV), gives a laser electric field of $\sim 10^2$ V cm⁻¹ which is an irradiance ($I = c\epsilon_0 E^2/2$) of roughly 10 W cm⁻².

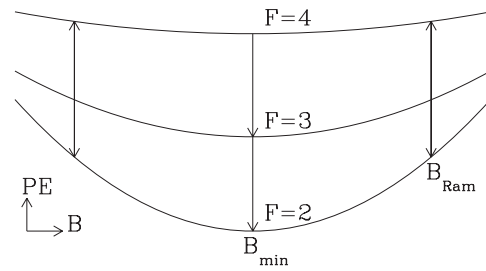


Figure 1. A schematic energy level diagram with the relevant transitions. A two-photon transition couples the $F = 2, M = 2$ state with the $F = 4, M = 4$ state with the electronic and vibrational quanta in the ground state. The two photon could be from stimulated Raman transition where the difference frequency of the two photons is the energy splitting of the $F = 2, M = 2$ and $F = 4, M = 4$ states. When the molecule moves to the region of small $|\vec{B}|$ it is stimulated to make two sequential photon transitions back to the ground state by high- Q cavities. Because the magnetic moment decreases with increasing F , the emitted photons carry away more energy than that absorbed in the original transition. This energy difference gives a net cooling to the centre of mass motion of the molecule.

for the $|2\rangle \leftrightarrow |3\rangle$ transition is ~ 2.51 THz and the $|3\rangle \leftrightarrow |4\rangle$ transition is ~ 3.54 THz. The magnetic moments for states 2, 3 and 4 are² 1.96, 1.70 and 1.60 MHz G⁻¹.

The general idea for the cooling mechanism is sketched in figure 1. An OH molecule is in a magnetic trap with energy less than ~ 10 mK. A laser is tuned to make a stimulated Raman transition from state 2 to 4 but detuned so that the transition occurs where the magnetic field is (for example) $B_{\text{Ram}} = B_{\text{min}} + 40$ G, not at $B = B_{\text{min}}$. If a cavity (or cavities) is tuned so that each of the decay transitions are stimulated near $B = B_{\text{min}}$, then the molecule will lose

$$\frac{\Delta E}{h} = (1.96 - 1.60)\text{MHz G}^{-1} \times 40 \text{ G} = 14.4 \text{ MHz} \quad (1)$$

which corresponds to 690 μK . Thus, ten stimulated Raman transitions followed by cascades could remove ~ 7 mK of energy. There are many ways for thinking about how the molecule loses energy in the cycle. One way is that after the stimulated Raman transition the molecule does not have as large a magnetic moment and is, thus, not accelerated as strongly to the $B \sim B_{\text{min}}$ region. When it reaches $B \sim B_{\text{min}}$, it will have a smaller speed compared to what it would have had if it were still in the ground state; thus, when it radiates back to the ground state, it will have a lower total energy given by the difference in magnetic moment times the difference in magnetic field.

To maximize the cooling, the laser detuning needs to be changed with time. The laser should start with a detuning where the transition takes place at large $|\vec{B}|$ and chirped so that at later time the transition takes place at smaller $|\vec{B}|$. If the laser

² To obtain these moments, we generated the effective Hamiltonian including fine structure, hyperfine structure, rotation, vibration, lambda doubling and the magnetic field. We diagonalized this effective Hamiltonian as a function of the B -field strength. Since these states are the highest within their manifold, there are no crossings over the range of B proposed here. We obtained the moment by fitting the energy to a straight line; however, the fit was excellent so that taking the moment to be constant is an excellent approximation.

were not chirped, the cooling would stop once the molecule cooled below the energy needed to reach the resonance B -field.

The cavity (or cavities) plays a crucial role in two respects. The first is that the radiative decays will occur on a shorter timescale than in vacuum. This brings the timescale to a more reasonable, although still long, value. The other is that the radiative decay mainly occurs where the largest possible energy change can occur. Thus, fewer photons are needed to remove energy from the molecule.

In the following section, we describe calculations of energy loss by OH molecules. Following that, we describe some of the difficulties with using this method. In the appendices, we describe a couple of other methods for laser cooling that would be difficult to implement although there does not appear to be physics reasons why they will not work.

2. Laser cooling OH

In this section, we describe the features of our calculations and some of the results. A schematic of the experimental arrangement is shown in figure 2. The grey oval indicates the centre of the trapping region. For the simulations below, the properties of the trap arise from a few simple elements. The cavity that separately stimulates the two spontaneous decays is indicated by the mirrors and gives a small enhancement region along the z -axis. There is a uniform B -field in the z -direction. The spatially varying part of the magnetic field arises from six ‘wires/bars’ carrying current. The four straight bars have the direction of the current indicated by arrows; these give an increasing B -field as the molecule moves away from the z -axis. The two mirror coils have current in the same direction and are separated by more than their radius. Thus, the B -field along the z -axis has a local minimum halfway between the mirror coils. By an appropriate choice of the strength of the various currents, the local minimum of the magnitude of \vec{B} is a single point at the centre of the trap. The two lasers that cause the stimulated Raman transition are not shown but must be nearly parallel with the z -axis to give the appropriate change of M .

2.1. Cavity properties

We used [10] extensively to try to make the properties of the cavity and the enhancement of the modes as self-consistent and reasonable as possible.

The decay rate in a cavity, Γ_c , compared to the free space decay rate, Γ_a , is given by

$$\Gamma_c = C\Gamma_a, \quad (2)$$

where C is the cooperativity. The cooperativity of a single mode confocal cavity is given by

$$C = \frac{6F}{\pi kL} \quad (3)$$

and the cavity waist is

$$w_0 = \sqrt{\frac{R}{k}}, \quad (4)$$

where $k = \omega/c = 2\pi/\lambda$ with λ being the wavelength of the light, the cavity length L and the mirror radius of curvature R

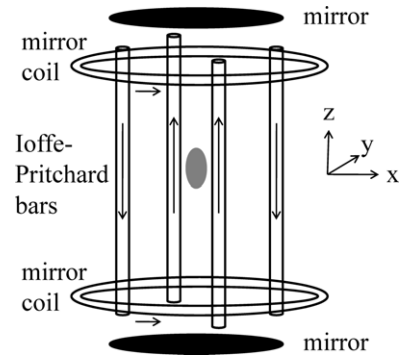


Figure 2. A schematic of the proposed experimental arrangement. The grey oval indicates the centre of the trap where the OH molecules experience the smallest B -field. There is a uniform B -field in the z -direction. The four rods with the directions of the currents shown as arrows give a magnetic field that increases from the centre of the trap outwards in the x, y -directions. The two mirror coils have currents in the same direction but are separated by a distance greater than their radius so that the magnetic field increases from the centre of the trap in the $\pm z$ -direction. The two mirrors indicate the orientation of the cavity that stimulates each of the spontaneous decays.

are the same, and F is the finesse. The cavity line width is given by

$$\kappa = \frac{\pi c}{2RF} \quad (5)$$

with c being the speed of light.

We are proposing to use transitions of roughly 2.5 and 3.5 THz. Clearly, the finesse of a cavity at this wavelength is important. Unfortunately, we could not find a source for a reasonable expectation for this frequency range. However, we note that there has been work involving cavities with resonances in the range of 10–100 of GHz. In [16], they quote a cavity using superconducting mirrors with $Q = 7 \times 10^7$ for a 51 GHz resonance. In this study, the mirror separation was ~ 2.75 cm and the finesse of this cavity was $F = Q\lambda/2L \sim 7 \times 10^6$. The cavity finesse in this experiment was more than an order of magnitude larger than what will be used in the simulations below.

As an example with round numbers, supposing $F = 10^5$ and $L = R = 1$ cm. In this case the waist and cooperativity are $w_0 = 0.44$ mm and $C = 1100$ for the $|2\rangle \leftrightarrow |3\rangle$ transition, and are 0.37 mm and 770 for the $|3\rangle \leftrightarrow |4\rangle$ transition. For both transitions, the width is $\kappa = 160$ kHz. Using these cooperativities, the decay rates are ~ 240 Hz for the $4 \rightarrow 3$ transition and ~ 170 Hz for the $3 \rightarrow 2$ transition for OH at the centre of the cavity. Note that the size of the waist is much smaller than the size of the region that the molecule initially moves through; because the molecule is within the enhancement region only a part of the time, the effective spontaneous decay rate is initially substantially less than the ~ 200 Hz at the centre of the trap. However, the spontaneous decay tends to occur at the minimum magnitude of the magnetic field which enhances the amount of energy removed by each photon.

The cavity could be the most difficult aspect of the experiment. The reason is that the cavity (or cavities) has

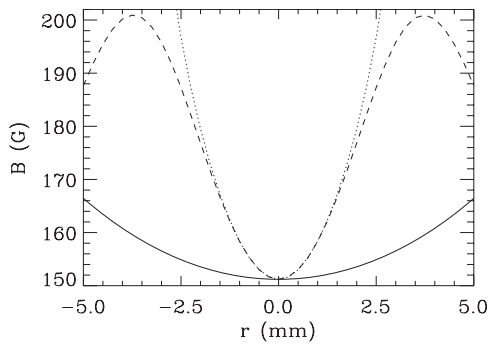


Figure 3. The magnitude of the magnetic field along three different lines. The solid curve is for a line along the z -axis, the dotted curve is for a line along the x -axis and the dashed curve is for a line in the xy -plane at 45° from the x -axis.

to be tuned to two different frequencies and each frequency depends on the magnetic field with a different slope. A detuning for even one transition would cause the cooling rate to substantially drop.

2.2. Magnetic field

In order to perform calculations, a particular form for the magnetic field needed to be chosen. Since we are proposing to use a cavity to enhance the radiative decay rate, the results will be enhanced if the magnetic field does not shift the transition out of resonance over the cavity waist. This suggests using a magnetic field with a higher multipole moment so the field does not change rapidly near $B = B_{\min}$. In the experiments attempting to trap the antimatter version of the hydrogen atom [17], fairly high multipole fields are used. For higher multipole moments, the windings become progressively more complicated. For the simulations, we chose the simplest geometry and obtained good results; relatively straightforward modifications of the B -fields could produce better results.

We chose the B -field to result from the sum of three contributions: a uniform field, two mirror coils and four parallel wires (see figure 2). The uniform field was in the z -direction with a strength of 100 G. The two mirror coils were aligned with their axis in the z -direction and positioned at $z = \pm 1.5$ cm with a radius of 1.0 cm with a current such that the B -field at the centre of a single coil is 150 G. The four ‘wires’ gave alternately currents along z or in the $-z$ direction; the wires were parallel to the z -axis and position at $x = \pm 0.5$ cm, $y = 0$ (current along z) and at $x = 0$, $y = \pm 0.5$ cm (current along $-z$). Each ‘wire’ could consist of many actual wires; the total current through a ‘wire’ was taken to be 150 A. Figure 3 shows the magnitude of the magnetic field in three different directions. Note that the magnetic field has a larger curvature in the xy -direction in order to confine the molecules in a region where the cavity can enhance the decay.

Many forms for the magnetic field should allow cooling. One of the reasons for choosing this form for \vec{B} is so there is only one minimum and the minimum is where B is flat. In this situation, the region of space where the cavity enhances decay is maximized due to two effects. (1) The cavity only enhances decay at the resonance frequency of the cavity which

means the magnitude of \vec{B} should not change much over the cavity waist; this is best accomplished when the magnitude of B is a minimum, saddle point or maximum because then B (and hence the molecular resonance frequency) changes quadratically. (2) If the extremum is a minimum, the bottom of the potential well, which is where the cold molecules will finish, coincides with the cavity enhancement and, thus, cooling can progress down to very low temperatures. There are choices of the currents that give a saddle point at the centre of the trap (proportional to $az^2 - c(x^2 + y^2)$ with a and c positive constants near the trap centre) which will only provide cooling up to the point where the molecules have enough centre-of-mass kinetic energy to reach the trap centre.

Another important point is that the kicks from the photons are weak so the form for the magnetic field must not have cylindrical symmetry. If the field has a symmetry that gives a conserved quantity, then that could strongly decrease the effect from cooling. For example, if $|\vec{B}|$ were cylindrically symmetric, then the centre-of-mass L_z of the molecule would be conserved; as the molecule cooled, the $L_z^2/(2Mr^2)$ barrier would push the molecule to large radius where it would no longer overlap the lasers. If necessary the rotational asymmetry around the z -axis could be enhanced by not having the four parallel wires be symmetrically placed; for example, having them at $x = \pm 0.45$ cm, $y = 0$ (current along z) and at $x = 0$, $y = \pm 0.55$ cm (current along $-z$) would give a more rapid variation of L_z with time.

2.3. Calculation of OH properties

For the arguments in this paper, it is not necessary that the energy levels and magnetic moments be calculated to spectroscopic accuracy. However, it is necessary to get the rough sizes correct.

The calculations were carried out using the formulation of [15, section 8.5.4] for the structure of the different rotational, vibrational and hyperfine states. We used the information in section 9.4.3 for the magnetic moments and splittings in the $2^2\Pi$ ground state.

For the states used in this paper, there are no curve crossings over the range of magnetic fields used in the simulations. Also, the magnetic moments hardly vary with the range of B in our simulation because each of the states is the highest total angular momentum, F , and highest M_F within each rotational manifold (see footnote 2). The magnetic moments used in the simulation were obtained by fitting the B -dependent energies from numerical diagonalization of the effective Hamiltonian.

The radiative decay rates from the different rotational states was computed using equation (8.429) to get the dipole matrix elements. The frequencies were taken from the spectroscopic values [15] and the dipole matrix elements μ_0 were taken from table 8.28.

The calculated energies of the states were accurate to better than 1 MHz. The Stark and Zeeman shifts at low field strengths also matched published values at the 1 MHz level.

2.4. Time propagation

In this section, we describe how the calculations were performed. We also list the important approximations and our estimates for the level of accuracy expected.

The most important approximation is that the centre-of-mass motion of the OH molecule is computed using a classical approximation. This should be an excellent approximation for the parameters in this paper. For example, a 100 μK OH has a de Broglie wavelength of ~ 100 nm whereas the trap size for such a cold OH is ~ 1 mm. Hotter molecules have smaller de Broglie wavelengths and have larger excursions in the trap.

A molecule in state $|F\rangle$ has a magnetic moment μ_F and a potential energy given by $PE = \mu_F |\vec{B}(x, y, z)|$. The force is computed from minus the gradient of the potential energy. Because of the simple form for \vec{B} , the force can be quickly computed by taking a numerical derivative using six closely spaced points. The positions and velocity of the OH is propagated in time using an adaptive step-size fourth-order Runge–Kutta algorithm. This algorithm was checked so that, while the molecule is in a particular state, the total energy drifts by less than 1 μK during the whole simulation.

The stimulated Raman transition was simulated by assuming there was a detuning in units of the magnetic field of an amount B_{Ram} . The transition only couples states $F = 2$ and 4. After a time step of the Runge–Kutta algorithm, the simulation checks whether the OH is in states 2 or 4. If yes, the probability for a transition to the other state is taken to be

$$P_{\text{Ram}} = dt \Gamma_{\text{Ram}} \frac{B_w^2}{(B - B_{\text{Ram}})^2 + B_w^2}, \quad (6)$$

where Γ_{Ram} is the on-resonance transition rate, B_w is the width of the laser driving the transition in units of magnetic field and B is the magnitude of the magnetic field at that time. A random number with a flat distribution between 0 and 1 is compared to P_{Ram} . If the random number is less than P_{Ram} , then a stimulated Raman transition occurs (i.e. the state of the OH is changed from 2 to 4 or from 4 to 2 depending on the initial state). In frequency units, the FWHM of the stimulated Raman transition is $2B_w(\mu_2 - \mu_4) = (0.72 \text{ MHz G}^{-1}) \times B_w$.

If the molecules are in states $F = 3$ or 4, then the molecule can spontaneously decay. After a time step of the Runge–Kutta algorithm, the simulation checks whether the OH is in states 3 or 4. If yes, the probability for a spontaneous emission from F to $F - 1$ is taken to be

$$P_{\text{sp}} = dt \Gamma_{F-1 \leftarrow F} [1 + \alpha(B) C_F \exp(-4 \ln 2 r^2 / w_0^2)], \quad (7)$$

where $\Gamma_{F-1 \leftarrow F}$ is the vacuum decay rate, w_0 is the waist, C_F is the cooperativity from the cavity for this transition and α is the factor due to detuning from the cavity line. The suppression due to $\alpha = (\kappa/2)^2 / [(\mu_4 - \mu_2)^2 (B - B_{\text{min}})^2 + (\kappa/2)^2]$ is not large because there is little detuning across the region of enhanced spontaneous emission. As with the stimulated Raman transition, a random number with a flat distribution between 0 and 1 is compared to P_{sp} . If the random number is less than P_{sp} , then a spontaneous decay occurs.

In both the stimulated Raman transition and spontaneous emission, the momentum kick from the photon is ignored. For the spontaneous emission, this is not a problem because the

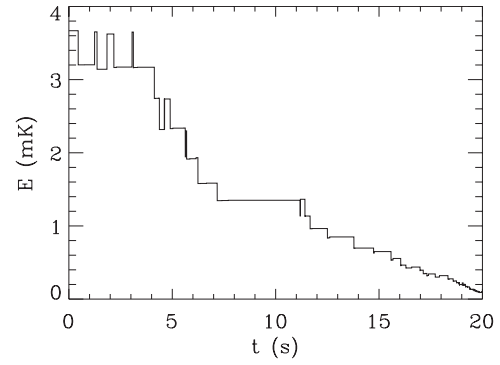


Figure 4. An example of the time dependence of the centre-of-mass energy of the OH molecule as a function of time. The steps are from photon absorption or emission causing a change in the magnetic moment of the molecule.

photon has a momentum less than 1/1000 that of the OH at 100 μK . The stimulated Raman transition is more problematic, because it depends on the geometry of the excitation. If the two stimulated Raman laser frequencies are parallel, then the kicks from the stimulated absorption and emission will essentially cancel so that the momentum kick is negligible. If they are not parallel, then the kick could be roughly 1/5 of the momentum an OH at 100 μK depending on the frequency and geometry. While negligible for the early stages of cooling, it could cause the simulation to be in error for the late stages of cooling.

3. Results

The results from simulations are presented in the following sections.

3.1. Single trajectory example

Figure 4 shows an example of a trajectory that cooled from 3.7 mK to 98 μK . This figure shows a plot of the available energy, $E \equiv (1/2)Mv^2 + \mu(|\vec{B}(\vec{r})| - |\vec{B}(0)|)$, as a function of time. The steps are where a photon is absorbed or emitted.

For this example, the laser width in units of magnetic field was taken to be 1/2 G and the on-resonance transition rate was 70 Hz, the finesse of the cavity was taken to be 4×10^5 and the resonance frequency is ramped from $|\vec{B}(0)| + 30$ G to $|\vec{B}(0)| + 1$ G over 20 s. For these parameters, the cavity waist is 0.44 mm and 0.37 mm, the cooperativity is 1450 and 1030 for the 2 to 3 and 3 to 4 transitions, and the cavity line width is 120 kHz. The cavity line width can be converted to a magnetic field by dividing by $\mu_1 - \mu_0$ (giving 0.5 G) or by $\mu_2 - \mu_1$ (giving 1.2 G) which gives an idea of the accuracy needed for B_{min} .

This example has features common to most cases where the OH starts with a few millikelvin. The steps at early times are widely separated in time but can be a substantial fraction of a millikelvin. The reason for this behaviour is that the stimulated Raman transitions are occurring at large B so that the energy steps, $\Delta\mu\Delta B$, are large, but the probability for going through the region of space where the cavity enhances the spontaneous decay is small so the times

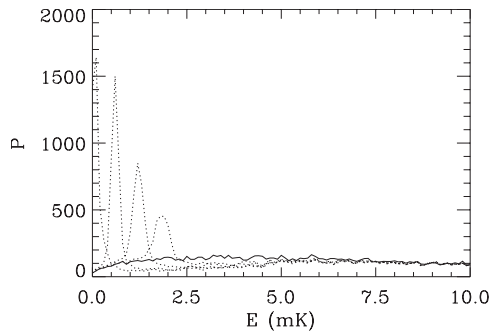


Figure 5. For the same magnetic field, cavity and laser parameters of figure 3, the energy distribution of an OH population as a function of time. The OH is started at the origin with a thermal velocity distribution with average energy 10 mK ($T = 6.7$ mK). The solid line is the initial distribution. The dotted lines are at 5, 10, 15 and 20 s and show $\sim 1/6$ of the molecules being cooled to less than $200 \mu\text{K}$.

between downwards steps is long. In fact, the first spontaneous decay is at roughly 4 s. At later times, there are many steps but with a smaller ΔE because the stimulated Raman transition is at smaller B and the molecule traverses the region of enhanced decay more often because it is colder.

3.2. Initial $L_z = 0$

In this section, we describe the results from calculations where the population is initialized so that the starting position is $r = 0$ and the velocity is a thermal distribution. Because the molecules start at $r = 0$, L_z starts at 0 and tends to remain small. The form of \vec{B} does *not* conserve L_x and L_y . Thus, the molecules do not have to go near the point $r = 0$ at every oscillation. However, this population does go through the waist of enhanced emission more often than a random population that did not have the initial condition $L_z = 0$. Although this situation is unphysical, it has features that are instructive.

In figure 5, we present the energy distribution at various times when the initial average energy is 10 mK. As the resonance energy of the stimulated Raman laser is lowered in B , some of the molecules are caught in the chirp and swept to lower energy. In this example, 15% of the molecules finish with energy less than $200 \mu\text{K}$. The solid line is the starting distribution and the dotted lines are for successively later times. Note that the population with a starting energy greater than ~ 5 mK is hardly affected by the laser.

In figure 6, we show the fraction of molecules that finish with an energy less than $200 \mu\text{K}$ as a function of the initial energy. It is clear that there is little chance of being swept down to lower energy if the starting energy is greater than ~ 4 mK. The initial detuning is 30 G which corresponds to ~ 2.8 mK for the OH ground-state magnetic moment; also, from figure 3 the well depth is roughly 50 G which corresponds to 4.7 mK which means OH with energy higher than this could escape the trap before cooling occurs. Thus, it is not surprising that molecules with higher energy are not substantially cooled. By choosing an initially larger detuning, the highest energy molecules that can be cooled would be increased but then a larger chirp rate would be needed to get the detuning to near 0 after 20 s. The

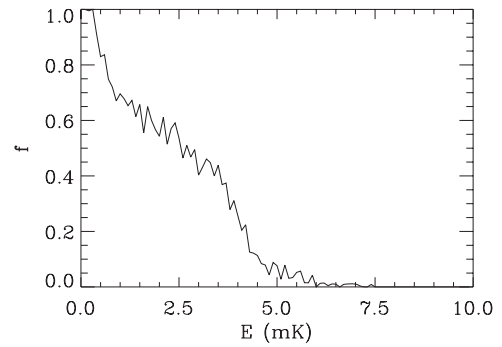


Figure 6. For the same magnetic field, cavity and laser parameters of figure 4, the fraction of OH molecules that start with energy E and finish with less than $200 \mu\text{K}$ at 20 s as a function of the starting energy. This shows that more than 1/2 of the OH molecules that start with less than 2.5 mK will finish with energy less than $200 \mu\text{K}$. Conversely, only a small fraction of the molecules with starting energy greater than 5 mK are cooled.

best choice of initial detuning and chirp rate depends upon the distribution of molecules in the trap.

The results in figure 6 show that the average energy of the molecules will not completely determine the fraction of molecules that can be cooled. The fraction of molecules that can be cooled will strongly depend on the initial energy distribution of molecules. If the energy distribution is pathological by having almost no low energy population, then the fraction of molecules that can be cooled will be strongly reduced.

3.3. Initial $L_z \neq 0$

In this section, we present results when the molecules are not launched from the minimum B . Since there is no clear reason to choose one distribution over another, the calculation in this section focusses on the fraction of molecules at a given starting energy that cool to less than $200 \mu\text{K}$. At each energy, we generate a distribution of starting conditions to approximate a microcanonical ensemble.

The results are shown in figure 7. When the four ‘wires’ are symmetrically placed as in the previous calculation, the fraction that cool shows a similar trend to that in figure 6 but with a somewhat lower fraction of molecules cooling to less than $200 \mu\text{K}$. That the results do not substantially change is important because it means that molecules with a range of L_z can be cooled. But the reduced efficiency can be overcome by a simple change to the magnetic field. The dotted curve shows the fraction that cools when the four wires are not symmetrically placed: one pair at $x = \pm 4.5$ mm, $y = 0$ and the other pair at $x = 0$, $y = \pm 5.5$ mm. The nonsymmetrical placement of the wires leads to a more rapid variation of L_z with time because the magnetic field is not proportional to $x^2 + y^2$ near the z -axis. Because L_z will more rapidly vary with time, L_z more often go through periods where it is small. It is only when L_z is small that the OH can travel through the region $x^2 + y^2 \sim 0$ where the spontaneous decay rate is enhanced.

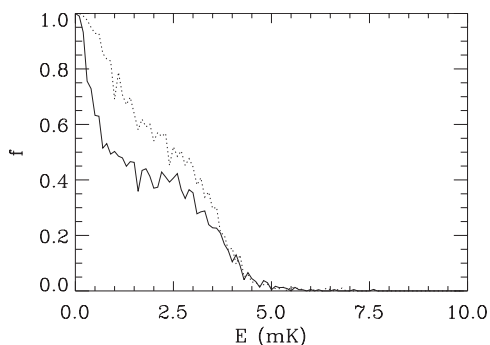


Figure 7. The same information as figure 5 except the molecules are not launched from the origin. The solid curve is when the four ‘wires’ are symmetrically placed as in calculations of figures 1–5. The dotted curve is when the four wires are not symmetrically placed: one pair at $x = \pm 4.5$ mm, $y = 0$ and the other pair at $x = 0$, $y = \pm 5.5$ mm. The nonsymmetrical placement of the wires leads to a more rapid variation of L_z .

4. Less obvious difficulties

In the previous sections, some of the difficulties with implementing this proposal were discussed. In this section, we briefly mention some other possible problems that will need to be addressed.

Black body radiation. Because the timescale for the cooling is 10 s, thermal radiation can cause transitions between the rotational states. This causes problems in two ways. If the molecules interact with thermal radiation, they tend to come into thermal equilibrium with the radiation which will be much higher than the microkelvin temperatures that can be achieved by the laser cooling. The bigger problem is that the thermal radiation can cause transitions to states not in the closed system (e.g. transitions from $F = 3, M = 3$ to $F = 4, M = 3$). The lambda doubling splitting is roughly 1.7 GHz and the transition rate is negligibly small. The main problem will come from the $F = 2, M = 2$ to $F = 3, M = 2$ transition which has an energy splitting of 120 K. The transition rate for this will be roughly $0.3 \text{ Hz}/[\exp(120\text{K}/T) - 1]$. This means the temperature of the thermal radiation will need to be less than ~ 60 K.

Laser transitions to other states. In the calculations, it was assumed that the laser causing the $F = 2$ to 4 transitions is perfectly polarized so that only the $M = 2$ and 4 states are coupled. If this is not the case, then coupling to other M states could cause a loss of population. There are two ways to restrict this loss. One way is to have the laser aligned with the magnetic field. The other is to make sure that the magnetic field minimum is large enough so that transitions to other M are not allowed or is only allowed to weak transitions. To give an example, the $F = 2, M = 2$ state has a magnetic moment of 2.0 MHz G^{-1} and the $F = 4, M = 4$ state has 1.6 MHz G^{-1} . There are two states with $J = 7/2$ and $M = 3$ that could be excited if the laser is not aligned with B -field. One combination is only ~ 6 MHz below the $M = 4$ state and with approximately the same magnetic moment; essentially, this state has the proton flipped compared to the $M = 4$ state. Thus, this state does not have a strong laser transition to the

ground state. The other state has a magnetic moment that is roughly 1.2 MHz G^{-1} but has a strong laser coupling to the ground state. The transition frequency has to be detuned by $(1.6-2) (\text{MHz G}^{-1}) \times 200 \text{ G} = -80 \text{ MHz}$ to cause the desired 2 to 4 transition at a field of 200 G. With this laser detuning, the loss transition $F = 2, M = 2$ to $F = 4, M = 3$ will occur at a field of 100 G. By controlling the range of the magnetic field (in this example keeping it larger than roughly 110 G), the undesired transitions are never in resonance.

Collisions between molecules. The collision between two rotationally excited molecules could cause one molecule to drop to a lower energy state and the other to be ejected from the trap. In [18], calculations for inelastic collisions between OH molecules in an electric field were carried out. The rates with the E -field set to 0 were roughly $10^{-11} \text{ cm}^3 \text{ s}^{-1}$ at $100 \mu\text{K}$. As long as the density is below 10^8 cm^{-3} , it seems that the inelastic rate will not be important. The elastic collision rate between the molecules was calculated to be almost $10^{-9} \text{ cm}^3 \text{ s}^{-1}$ which means collisions might become important if the density gets very high. It is not clear whether this will be beneficial or not because the collisions might allow for a larger fraction of molecules to cool.

5. Conclusions

The results of simulations presented in this paper indicate it may be possible to laser cool the OH molecule. The main idea is to use an external field to provide the momentum kicks. The main case discussed was to use a magnetic field acting on the change in magnetic moment when the internal state changes to remove a substantial amount of energy with relatively few photons. Thus, the long lifetime of the states may not be an insurmountable problem. One of the main positive aspects of this scheme is that the driven transition gives a closed loop and there is no need for a repumping laser. The main negative aspect is that it uses a high- Q cavity that needs to be tuned to two different frequencies and a magnetic field needs to be held (and calibrated) very precisely so the cavity stimulates transitions at the magnetic field minimum. Although the implementation of this method will probably be difficult, there do not appear to be any fundamental processes that would cause this scheme to fail.

Acknowledgments

I greatly appreciate several conversations with R R Jones about lasers and general aspects of the ideas in this paper. This work was supported by the Office of Basic Energy Sciences, US Department of Energy.

Appendix. Other possible methods

Two other possible methods for laser cooling molecules are briefly described. These methods are not worked out with the detail of that in the main text but the description should be sufficient to convey the main idea.

Method 1: electric or magnetic dipole moments. Many molecules have substantial electric or magnetic dipole

moments. In a strong enough field, the moment is proportional to a factor $M_J/[J(J+1)]$ or $|M_J|/[J(J+1)]$. Suppose, the molecule is trapped in the lowest vibrational state and the lowest J state with the highest moment which means $|M_J| = J$.

For this scheme, a laser drives a transition to the first *vibrationally* excited state leaving J and M_J unchanged. Typically, the dipole moment hardly changes upon excitation by one vibrational quanta. This means that the molecule can be excited wherever it is in the trap since the field shifts the vibrationally excited state by the same amount as the ground state. However, the photon emission step will not conserve the dipole moment. There will be some transition back to the state J, M_J which leaves the system unchanged. However, most of the transition will be into the four states: $J, M_J - 1, J + 1, M_J + 1, J + 1, M_J$ and $J + 1, M_J - 1$.

The dipole moments for all of these states are substantially less than that of the original state. This means that each of these states has centre-of-mass potential curves that are *flatter* than the original curve. This could lead to some population loss due to the decrease in the depth of the potential. More importantly it gives a substantial decrease in the temperature. As a second step, four different laser frequencies are used to drive these states back to the vibrationally excited J, M_J state but they are tuned so that the transition occurs at the *field minimum*. Cooling occurs each time the molecule spontaneously decays to the extra four states. Thus, a completely closed system is obtained by using five laser frequencies (depending on the molecule and transition the number of lasers could increase to ~ 10 due to hyperfine interactions). The timescale for each transition is long: approximately the vibrational lifetime. However, each transition causes a substantial decrease in temperature which makes the method viable for molecules with vibrational lifetimes up to a couple 100 ms.

Method 2: frequency-dependent polarizability. Most molecules have the property that the spacing of vibrational levels decreases with the vibrational quantum number. Many atoms have been trapped in a laser field using the ac Stark shift. When the laser is far of-resonance, the ac Stark shift hardly changes for different ro-vibrational states of the molecule. However, when driving close to an allowed transition, the shift is inversely proportional to the detuning. This method uses the change in the frequency-dependent polarizability with the quantum numbers of the molecule to enable laser cooling.

For example, suppose the $v = 0$ to 1 transition is at 3000 cm^{-1} while the $v = 1$ to 2 transition is at 2900 cm^{-1} . If the molecule is in a dressing laser field with photon energy

of 2800 cm^{-1} , the $v = 1$ state will have twice the shift of the ground state. Thus, a weak laser that drives the $v = 0$ to 1 transition when the molecule is at the minimum of the potential caused by the ac Stark shift will cause the molecule to suddenly experience a more strongly binding, steeper potential. When the molecule spontaneously emits back to the ground state, the potential will appear to suddenly get flatter and weaker; this leads to a net cooling because the emitted photon will have a higher energy than the absorbed photon. As with method 1, there are a few different states that the atom can decay into. A few repumping lasers are sufficient to give a closed system.

This method has the advantage that it will work with most molecules with short vibrational lifetimes and you do not lose population during the cycling step. It has the disadvantage that the trapping well will not be deep. However, this disadvantage could turn into an advantage if one starts with very cold molecules because it could be used to bring cold molecules to much colder temperatures.

References

- [1] van de Meerakker S Y T *et al* 2008 *Nature Phys.* **4** 595
- [2] Narevicius E *et al* 2008 *Phys. Rev. A* **77** 051401
- [3] Jones K M *et al* 2006 *Rev. Mod. Phys.* **78** 483
- [4] Kohler T, Goral K and Julienne P S 2006 *Rev. Mod. Phys.* **78** 1311
- [5] Weinstein J *et al* 1998 *Nature* **395** 148
- [6] Junglen T *et al* 2004 *Eur. Phys. J. D* **31** 365
- [7] Gupta M and Herschbach D 2001 *J. Phys. Chem. A* **105** 1626
- [8] Fulton R, Bishop A I and Barker P F 2004 *Phys. Rev. Lett.* **93** 243004
- [9] Strecker K E and Chandler D W 2008 *Phys. Rev. A* **78** 063406
- [10] Lev B L *et al* 2008 *Phys. Rev. A* **77** 023402
- [11] Stuhl B K, Sawyer B C, Wang D and Ye J 2008 *Phys. Rev. Lett.* **101** 243002
- [12] Taylor C L, Zhang J and Robicheaux F 2006 *J. Phys. B: At. Mol. Opt. Phys.* **39** 4945
- [13] Pohl T, Sadeghpour H R, Nagata Y and Yamazaki Y 2006 *Phys. Rev. Lett.* **97** 213001
- [14] Robicheaux F and Fajans J 2007 *J. Phys. B: At. Mol. Opt. Phys.* **40** 3143
- [15] Brown J and Carrington Alan 2003 *Rotational Spectroscopy of Diatomic Molecules* (Cambridge: Cambridge University Press) (see section 8.5.2 for the basic parameterization of $^2\Pi$ states, section 8.5.4 for the parameters for OH and section 9.4.3 (especially iv) for the Zeeman terms and parameters)
- [16] Brune M, Schmidt-Kaler F, Maali A, Dreyer J, Hagley E, Raimond J M and Haroche S 1996 *Phys. Rev. Lett.* **76** 1800
- [17] Andresen J *et al* (ALPHA Collaboration) 2007 *Phys. Rev. Lett.* **98** 023402
- [18] Avdeenko A V and Bohn J L 2002 *Phys. Rev. A* **66** 052718