Topical Review

Ro-vibrational cooling of molecules and prospects

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Abstract

By using a simple spectral shaping technique, optical pumping with laser fields has allowed us to manipulate, on demand, the rotational and vibrational population of di-atomic molecules. We review this method developed first on cold Cs₂ then on ions and discuss its extension to other molecular species as well as its feasibility on a molecular beam. This paves the way to the production of brighter molecular beams and thus a new method of producing cold molecular cloud. We finally present some ideas based on Sisyphus cooling with expected results on neutral as well as ionic molecules.

Keywords: cold molecule, molecular beam, electromagnetic forces

(Some figures may appear in colour only in the online journal)

1. Introduction

The precise control of internal and external degrees of freedom of molecules is very attractive and promises new insights and advances in various domains of physics [1–3] and modern physical chemistry [4–6]. It is well known that, from an experimental point of view, molecules are more difficult to control than atoms because of their complex internal structure. Theoretically, this has stimulated original control schemes, including the control of internal degrees of freedom of (cold) molecules [7–11]. In this context, the transfer and accumulation of molecules into a single rovibrational level of the electronic ground state as been demonstrated [12, 13]. The method follows up the so called ‘luminorefrigeration’ process proposed by Kastler [14] in 1950. This optical pumping is based on a broadband and incoherent optical source designed to modify the distribution of the ro-vibrational populations. The principle is quite simple, general and has been successfully applied to control the vibrational population of Cs₂ [12, 15–20], reduce the vibrational temperature of NaCs [21], to cool internal degree of freedom of molecular ions [22, 23] and control both rotation and vibration of Cs₂ [13]. In all these works, molecules, distributed in several ro-vibrational levels, are optically excited. They then decay, by spontaneous emission toward other levels until they reach a target level which is not accessible to the optical excitation (i.e. ‘dark state’). These methods can be used to enhance the ro-vibrational population in a cold sample or in a molecular beam. The purpose of this paper is to review the basics of this optical pumping method and support it with experimental results on the Cs₂, NaCs, AlH⁺, MgH⁺, HD⁺ cases and new theoretical discussion on RbCs, LiCs or BaF molecules.

Laser cooling of internal degrees of freedom directly raises the question of cooling the external degrees of freedom. Even though we broach the control of the external degrees of freedom, it is not the purpose of this article to review the recent impressive achievements such as one-dimensional transverse laser cooling [24], magneto-optical trapping of a diatomic molecule [25, 26] or evaporative cooling of molecules [27]. However, we shall survey some possible application in terms of translational cooling of cold molecules. In particular we shall discuss how the efficiency of the Sisyphus
cooling method could be enhanced using optical pumping as a repumping step [28].

2. Molecular ro-vibrational cooling

Optical manipulation of molecular gases has a long history, including as a pumping mechanism for lasers such as ZnO [29] lasers. For a long time, it was used to control the polarization (sub Zeeman M-level population) of a sample. This was often performed using destruction of the unwanted states and not really pumping other states toward the one of interest [30, 31]. Along the same lines, some works were devoted to stimulated emission pumping with the intention of producing highly vibrationally excited molecules in their ground electronic state by the suppression of spontaneous emission through selective dissociation of the upper states [32]. Similarly, the selection of rotational and vibrational states are possible by threshold photoionization [33].

Here we focus the attention on the control of rotation and vibration of molecules, that is an optical pumping which transfers populations from different levels toward a single level. In such an operation, a mixed state must be transformed into a pure state. The purity of a state being defined by $\text{Tr}(\rho^2)$, where $\rho$ is the density matrix of the system, such a transformation cannot be realized using a unitary evolution (because $\rho$ would become $U \rho U^\dagger$ and the purity would be conserved). Therefore the process relies on an irreversible, decaying, incoherent or non Hamiltonian step, usually realized by spontaneous emission. In a way, this question is related to the discussion regarding the use of the word ‘cooling’ in ro-vibrational manipulation. If a single populated level is seen as a ‘zero’ temperature system, independently of its potential internal energy, it becomes questionable, from the point of view of the Boltzmann statistics, whether the term ‘cooling’ is appropriated for pure state transfer. Using in this meaning, ‘cooling’ simply means reduction of the (internal) energy. This use is however confusing and actually eclipses strong differences between different ‘cooling’ schemes. In order to avoid such confusion, in this paper the word ‘cooling’ only means an increase of system purity. It corresponds to the only kind of optical pumping that are studied here.

However, before discussing these cooling schemes, let us recall, without entering into details, that optical manipulation preserving purity has been very successful: adiabatic transfer of population (STIRAP: stimulated Raman adiabatic passage) or simple Raman transfer [34, 35] have proved to be extremely efficient to transfer a single level toward another single level [36]. This is now a current technique to transform long-range Feshbach molecules usually formed by magneto-association of laser cooled atoms into ro-vibrational ground state molecules (Cs$_2$, KRb, Rb$_2$, RbCs) [37–44]. Another example of this vein is given in [45] where a sequence of infrared laser pulses is proposed to de-excite a sample of Li$_2$ molecules from the $v = 10$ to their lowest $v = 0$ vibrational level with an overall efficiency of 91%. A different approach of filtering of population of vibration, has been proposed [46, 47]. In these proposals, called ‘purification’ even if no increase of purity is achieved, a laser with a specific choice of wavelength-intensity parameters stabilize the photodissociation of the molecule by creating zero-width resonances in the process. With an adiabatic variation of the parameters along a closed contour around such exceptional points, it is possible to transfer one field-free vibrational state to another. The proposition has been extended to rotational cooling [48] with the aim of total ‘purification’ to reach the ground ($\nu = J = 0$) rovibrational level.

2.1. Theoretical propositions

To return to the subject, several theoretical suggestions regarding optical pumping (cooling) have been proposed to favor spontaneous emission toward the lowest ro-vibrational level as, for instance, the use of an external cavity [7] or the use of strong shaped laser pulses [49]. These methods mainly based on the manipulation of molecules with electromagnetic fields for quantum control using shaped ultrafast laser pulses can also be found in [50] and [51]. They have not been demonstrated experimentally yet and we shall not describe them here but we only mention that one of the first cooling proposals was based on the controlled interplay of coherent strong laser fields and spontaneous emission through quantum interferences between different transitions [8, 10, 49]. A control scheme where the timescale separation between coherent excitation and spontaneous emission is optimized has also been proposed to control the vibrational populations in [52, 53]. In this case, laser cooling of molecules works even if the natural trend (due to spontaneous emission) is preferential to heating rather than cooling.

2.2. Basic idea

We now present the ro-vibrational cooling scheme that has been experimentally realised. It is presented as a guide for experimentalists in order to complete explanation given in [54]. Indeed, we present the protocol to realize ro-vibrational cooling of a molecule that should be followed in order to realize such optical pumping. For the sake of simplicity, we do not consider any hyperfine structure. Its splitting is typically in the MHz range which can be resolved and manipulated by generating side bands in the laser spectrum [24].

The key idea to realize an efficient optical pumping of rotation and vibration toward a target level is to isolate a closed ro-vibronic system using a proper laser spectrum. In this paper, the lowest ro-vibrational target level ($v''_0$, $J''_0$) is frequently chosen but other targets are possible. The first important consideration is the choice of an electronically excited state which, after decay, should populates the initial electronic state only. Then, a bunch of vibrational states around the target one $v'_0$ must be selected by spectral shaping of lasers. The aim is that excited molecules only decay within the same bunch. By making sure that no part of the laser spectrum may excite $v'_0$, the population accumulate in this ‘dark’ level.
Similarly, concerning the manipulation of the rotation: rotational states around the target one \( J_0^0 \) must be isolated. This can be performed by the same laser or by another laser shaping, which must account for the selection rules on rotational transitions. For instance, by selecting only P-branch excitations, we reduce the rotational quantum number at each transition, leading to accumulating the population in the minimal value of the rotational quantum number (such as \( J_0^0 = 0 \) or \( J_0^0 = 1/2 \)).

2.3. Choice of the molecule and electronic transitions

2.3.1. Choosing a proper molecule. Each molecule has its own characteristics and the method must be adapted by making a suitable choice for the electronic states and lasers. This choice is mainly based on the values of the Hön-London and Franck-Condon factors for the spontaneous emission steps. For completeness, we propose an update list (compared to the one given in [28]) providing a review of the produced cold molecular species, in table 1.

2.3.2. Choosing an electronic transition. The electronic transition must have good properties in terms of lifetime, coupling strength, laser accessibility and losses (photo- or pre-dissociation, photo-ionization, ...). However, to properly choose the electronic transition, it is crucial to understand the pumping process whose evolution is governed by the Franck-Condon (FC) factors such as the one given in table 2. It is also important to consider the availability of a broadband light source in the range of the electronic transition wavelengths. For this purpose, table 2 summarize for some (neutral) diatomic molecules the spontaneous emission lifetime as well as the Franck-Condon factors for the ground vibrational transitions between some electronic states.

2.3.3. Calculating or evaluating the Franck-Condon factors: \(|\langle v' | v' \rangle|^2\). The Franck-Condon factors between different vibrational states can be calculated using a computer code (for instance R J Le Roy’s LEVEL program [155]) or simply estimated from a Morse or harmonic potential calculation. In the harmonic approximation of the potential curves, the Franck-Condon factors can be given by the formula (in SI units)

\[
|\langle v' = 0 | v' = 0 \rangle|^2 = \sqrt{\frac{a'' a''}{a' + a''}} e^{-\frac{\mu (r'_v - r''_v)^2 a''}{\hbar (a' + a'')}} ,
\]

where \( \mu \) is the reduced mass, \( a'' \) and \( a' \) are the vibrational angular frequencies and \( r'_v \) and \( r''_v \) the equilibrium positions. This illustrates that favorable Franck-Condon factors requires electronic state with similar curvature (\( a'' \approx a' \)) and equilibrium points (\( r'_v \approx r''_v \)).

2.3.4. Understanding absorption-emission process using the Franck-Condon factors as illustrated in figure 1. The vibrational dependence of any \( v' \leftrightarrow v'' \) optical transition between two electronic states is commonly given by the corresponding FC factor, as illustrated in figure 1. It is possible to roughly anticipate the evolution of a vibrational population using the figure 1. Let us consider an initial level \( v_0^0 \). Once excited to a \( v' \) state, it spontaneously and efficiently decays at the inner Condon turning point toward \( v_0^0 = 0 \) (through point B). This possibility of excitation to this specific \( v' \) state also lead to efficiently populate much higher vibrational levels by a decay at the outer Condon turning point (through point C). Such a dispersion effect of population is prejudicial to vibrational pumping. This analysis already highlights the fact that the excitation process must be studied carefully.

2.4. Vibrational pumping

Starting from a broad vibrational distribution, the goal is to optically pump this population toward a single target level \( v_0^0 \). The general idea is to create a closed system of several manipulable vibrational levels and keep \( v_0^0 \) untouched. \( v_0^0 \) thus becomes a dark state in which molecular population accumulates after a series of excitation-spontaneous emission cycles. The manipulation itself is achieved by shaping the laser spectrum in order to choose appropriate frequencies exciting the most favorable transitions.

2.4.1. Finding a proper scheme for vibrational detection. A non-selective broadband detection scheme may help to first detect all the molecules [156]. However a vibrationally selective detection technique, as Resonance-enhanced multiphoton ionization (REMPI), is useful to determine the modification of the vibrational distribution. The REMPI technique typically involves a resonant single or multiple photon absorption to an electronically excited intermediate state followed by another photon that leads to molecular ionization. The produced ions can be detected by standard time-of-flight techniques and ion—or electron—detectors. Other methods like light induced fluorescence (LIF) can also be used but are generally more noisy than REMPI, and thus requires many experimental cycles to get an acceptable signal-to-noise ratio.

2.4.2. Choice of the target level \( v_0^0 \). In principle, any vibrational level can be chosen as the target state. This has been demonstrated experimentally in [16]. However there are some obvious limitations such as the available laser bandwidth, the initial molecular distribution and the losses such as pre-dissociation, ionization, decay toward others states, etc.

An important criterion to understand how molecules evolve in their internal degrees of freedom lies in the position of point A (see figure 1). Point A corresponds to a vibrational level \( v_0^0 \) that, after laser-excitation toward \( v' = 0 \), does not deexcite to many other vibrational levels. It can be considered as an ‘attractor’. Thus one of the most efficient choices to realize such optical pumping is to pump populations in \( v_0^0 \) using mainly excitations toward \( v' = 0 \). However some FC, such as the one between \( v' > 10 \) and \( v' = 0 \) in figure 1, are too small to induce efficient excitation. Therefore to optimize the pumping scheme, \( v' \leftrightarrow v'' \) absorption transitions with
Table 1. Slow and cold molecule list with $T < 1 \text{ K}$ with an estimation of their temperature $T$ and number $N$. For each species, the only reference given corresponds to the pioneering work and with no isotopic difference.

| Method                          | Molecule                  | $T(\mu \text{K})$ | $N$   |
|---------------------------------|----------------------------|-------------------|-------|
| Feshbach, RF [55, 56]           | $^{85,87}\text{Rb}_2$ [57–59], Cs$_2$ [60], $^{40}\text{K}_2$ [61], Li$_2$ [62–64], Na$_2$ [65], $^{40}\text{K}\text{Rb}$ [66], $^{41}\text{K}\text{Rb}$ [67], Cr$_2$ [68], Li$_3$ [69], NaK [70] | 0.1 | 100 000 |
| Photoassociation [71]           | Cs$_2$ [72], H$_2$ [73], Rb$_2$ [74], Li$_2$ [75], Na$_2$ [76], K$_2$ [77–79], He$_2^*$ [80], Cs$_2$ [81], KRB [82], RbCs [83], NaCs [84], LiCs [85] | 100 | 200 000 |
| Three body collision            | Rb$_2$ [74], Li$_2$ [62, 86] | 0.2 | 2 000 000 |
| Laser cooling                   | SrF [24], YO [25], CaF [87] | 0.3 |       |
| Cryogeny (Buffer Gas) [88]      | CaH [89], VO [90], CaF [91], PbO [92, 93], O$_2$ [94], NH [95], ND, C$_2$H, MaH [96], ND$_3$, H$_2$CO [97], YBF [98], NH, NH$_3$, O$_2$, ThO, Naphthalene [99], BaF, SrO, YbF, YO [88] | 400 000 | $10^{12}$ |
| Field Slowing: Stark [100]      | CO [101], NH$_3$, ND$_3$ [102, 103], OH [104, 105], OD [106], H$_2$CO [107], NH [108], SO$_2$ [109], C$_2$H$_2$N [110], YBF [111], LiH [112], CaF [113] | 10 000 | 1 000 000 |
| Rydberg                         | H$_2$ [114–117]            |                 |       |
| Optical Zeemann                 | C$_2$H$_4$ [118], NO [119] |                 |       |
| Beam collision                  | NO [121], KBr (13K) [122], ND$_4$ [123] | | 400 000 |
| Beam dissociation               | NO [124]                   |                 | 1 600 000 |
| Rotating or centrifugal slowing | O$_2$, CH$_4$F, SF$_6$ [125, 126], CHF$_3$ [127], perfluorinated C$_6$H$_6$ [128], CH$_3$F, CF$_3$H, CF$_3$CCH [129] | | 1 000 000 |
| Velocity filtering              | H$_2$CO [107], ND$_3$ [130], D$_2$O [131], CHF$_3$ [132], CF$_3$H [133], CH$_3$CN [134], H$_2$O, D$_2$O, HDO [135], NH$_3$, CH$_3$I, C$_2$H$_5$CN, C$_2$H$_4$Cl [136] | 1 000 000 | $10^9$ |
| Sympathetic cooling [137–139]   | BeH$^+$, YbH$^+$ [140], AF350$^+$ = C$_{16}$H$_{14}$N$_2$O$_8$S$^+$ [141], MgH$^+$ [142], O$_2^-$, MgO$^-$, CaO$^+$ [143], H$_2^+$, H$_3^+$ [144], BaO$^+$ [145], NeH$^+$, N$_2^-$, OH$^-$, H$_2$O$^-$, HO$^-$, ArH$^+$, CO$_2^+$, KrH$^+$, C$_3$F$_4^+$, R6G$^+$ [139], Cyt$_{12}^{15+}$, Cyt$_{17}^{17+}$ [146], GAH$^+$ = C$_8$H$_{18}$O$_4$ [147] | 20 000 | 1000 |
| Nanodroplet [148–153]           | Mg$_{10–33}$, HCN, Ne$^-$, Kr$^-$, ArHF, tetracene-Ar, HCN-H$_2$, HD, D$_2$, Ag$_8$-Nex, Ar$_N$, Kr$_N$, Xe$_N$ ($N = 1 – 135$), NaCs, LiCs, HF-(H$_2$), OCS-(H$_2$)$_N$ ($N = 1 – 17$), | 1 000 000 | 10 |
C, S, O, H, Cl, amino acid, 3-hydroxyflavone, xanthine, [Na(H2O)2]n+ (n = 6–43) [154], HF-N2O, Mg-HF, Mg-(HF)2, CH3H2O, Cs2(H2O)3Br, CF3I, CH3I, ...

Table 2. Some properties of some neutral diatomic molecules taken from [28]. The molecules are ordered by the rounded value of the state. An initial level is excited to a \( v' \) state can spontaneously decays at the inner Condon turning point toward \( v'' = 0 \) (through point B) or to much higher vibrational at the outer Condon turning point (through point C). Only the case, where \( v'' = 0 \), and with excitation toward \( v' = 0 \) (point A), does not modify the population because spontaneous decay occurs mostly into the same initial level.

\[ v' \neq 0 \] must be considered and controlled. A ‘combi’ of selected laser frequencies must be designed to induce transitions that produce an efficient optical pumping from the initially populated levels to the target. A possible set of excited states can be furnished by considering the highest values of the FC factors (with the target vibrational level). However, due to the limited laser bandwidth, it is important to limit the transfer of populations to high vibrational levels (see the point C of figure 1) that are not affected by the laser. Thus it is better to favor excitation in levels that correspond to the ‘lower branch’ of the FC parabola. With such a choice, once a \( v' \) molecule is excited, it decays either in the ‘lower branch’ of the FC parabola, i.e. in lower vibrational levels than the initial one or it decays in the ‘upper branch’ of the FC parabola i.e. in same \( v' \) level and we just repeat the process.

An experimental demonstration is given in figure 2 where the target state \( v'' = v'' = 1 \) level, the initial population covers \( v'' = 0 \) = 10 and the available laser linewidth is some hundreds of cm⁻¹.

2.4.3. Spectral shaping realization for vibrational pumping

The optimization has to be done according to the chosen objective or cost function. If the number of absorbed photons has to be minimized or if the efficiency has to be maximized, it is better to only excite states having very good Franck–Condon factor toward \( v'' = v'' = 0 \) even if the excitation probability is low. On the contrary, if the speed of the process has to be optimized, for instance for a molecular beam where the
interaction time is short, the choice of transitions that can be excited efficiently is also important.

**Choice of the laser system.** The laser must be sufficiently intense and cover all the needed vibrational transitions. Indeed, the optical pumping is usually limited by the finite laser spectral bandwidth $\Gamma$. The required irradiance density $I/\Gamma$, where $I$ is the laser irradiance, can be evaluated from a simple two-level model having a spontaneous emission rate $\gamma$. In such a model, the absorption rate $\gamma$ at the resonance wavelength $\lambda$ is given, including the Franck–Condor (FC) and angular factors (AF), by $\gamma \sim 300000 \lambda^{-3}$ W m$^{-2}$ FC AF. Typically, for $\Gamma = 2\pi(10$ MHz), a 1W laser with 10 nm linewidth (corresponding to roughly $I/\Gamma = 2\pi$ (10 000 GHz) at 500 nm) focused on 1 mm leads to an excitation rate of one photon absorbed every $3 \mu$s. Thus the full optical pumping probably takes hundred of microseconds.

As in the scheme we are describing, the coherence of the light is not concerned, any sufficiently collimated source to be shaped and focused on the molecular sample can be used. We then have to choose a laser system featuring a broad spectrum. One interesting possibility is the use of a super-continuum laser, nowadays spanning 0.4–2.3 μm with a uniform power density of 50 mW nm$^{-1}$ [157]. It may be simpler to use distinct (diode) laser to drive the desired transition. Broadband laser diode, or (tapered) amplifier, with or without anti-reflected coating are one of the simplest and cheapest solutions [17] since they have a small bandwidth (tens of nm) and a high spectral power density.

**Choice of shaping system.** The only requirement for shaping is to isolate the desired transition frequency from the unwanted ones. Thus, shaping is not mandatory if the source itself has the required characteristics with a proper choice of the laser wavelength properly tuned (as demonstrated in the NaCs case studied later [21]). Similarly (non-shaped) black-body radiation has been used in cooling ions [22, 23].

In other cases, the suppression of the optical frequencies related to the chosen dark state is realized through a spectral shaping of the broadband laser. It requires a typical spectral resolution on the order of the vibrational frequency $\omega''$ divided by the number of levels involved. Optical shaping is usually not an issue because, even in including heavy atoms, vibrational frequencies are higher then hundreds of GHz. The simplest shaping is a basic cut-off of a part of the light spectrum by a simple interference filter [17]. For an arbitrary shaping, a 4-f imaging system can be set up (see figure 3). An important aspect is the quality of the removal of the unwanted transition
frequencies performed by the shaping. Standard liquid crystal spatial light modulator (SLM) have gaps between cells and an on-off ratio at the percent level, which may create an imperfect dark state [16]. Therefore, it is preferable to use a spatial mask such as rotatable micro-mirrors or even simple opaque elements having near 100% on-off ratio between wanted and unwanted transition frequencies.

### 2.5. Rotational cooling [13]

Optical pumping of rotation is difficult to achieve because the rotational degree of freedom can not be manipulated independently from the vibrational one. The vibrational pumping modifies the rotational quantum number, just as the rotational pumping modifies the vibrational quantum number. As a consequence, a global rovibrational cooling can only be achieved through an interplay between both processes, except for exceptional cases such as NH or AlH* having FC factors near unity.

#### 2.5.1. Finding a proper detection scheme for the rotation

It is possible that techniques used for vibration (such as REMPI) do not resolve the rotational spacing. Therefore, other methods must be employed. A narrow-band laser must selectively excite the rotational levels $J'$ of the initial $v_0$ level toward a given $v'$, $J'$ level. If this laser is pulsed in a fast enough way, it is possible to directly detect (through photo-ionization for instance) the excited $v'$ population after a subsequent ionization. It may be simpler to use depletion spectroscopy [158] that consists in monitoring the rotational populations $v_0'$. To improve the signal-to-noise ratio, the use of background free signal may be helpful, as it is for spontaneous-decay-induced double resonance (SpIDR) based on detection of a vibrational level populated by the deexcitation of the $v'$ level [159].

#### 2.5.2. Choosing the pumping scheme

**Selection rules** Whereas the vibrational state can be strongly modified after a single optical transition (even if depending of FC factors), the rotational population cannot change drastically for parity reasons and dipolar selection rules $\Delta J = J' - J'' = -1, 0, 1$ (called P, Q, R branches).

Precisely, we recall that the amplitude of a transition between a ground $|J''\Omega'M''\rangle$ and an excited $|J'\Omega'M'\rangle$ rotational state is proportional to the product of the the Clebsch–Gordan coefficients $(J'\Omega', 1(\Omega' - \Omega))|J''\Omega''\rangle$ $(J'M', 1 - p|J'M'\rangle$ times the amplitude of the local laser polarization vector in the $\sigma_\ell \in \{\sigma_+, \sigma_0 = \pi, \sigma_-\}$ polarization base, where $p = M'' - M'$. The spontaneous emission probability is calculated in a similar way but with the extra factor coming from the cube of the energy difference. Here $M$ is the projection of $J/\hbar$ along the quantization axis usually given by the local electric or magnetic field at the particle position and $\Omega$ its projection along the internuclear axis.

Assuming unpolarized light and equidistribution of the $M''$ population leads to the well known HönL-London angular factors $(2J' + 1) |J'\Omega', 1(\Omega' - \Omega)|J''\Omega''\rangle|^2$ for the transition probabilities.

**Population transfer to high $J''$ values**. One simple method to transfer population to high $J''$ values is to remove the frequency corresponding to the P and Q transitions $(\Delta J = -1, 0)$ or similarly to drive only the R branch $(\Delta J = 1)$. The absorption step is then optimized to increase the rotational quantum number.

**Population transfer to low $J''$ values**. To transfer population to low $J''$ values, i.e. to realize laser cooling of the rotation, we need to shape the laser by removing the frequencies that correspond to the Q and R transitions $\Delta J = 0, 1$ (or similarly to drive only P branch $\Delta J = -1$). Thus, the absorption step is optimized to reduce the rotational quantum number.

**Laser polarization**. We mention that the lowering scheme, i.e. the scheme using $J' = J'' - 1 \leftrightarrow J'$ transitions, may lead to some difficulties because $(J'M', 1 - p|J'M')$ can be null. In other words, a well defined laser polarization has a dark state that may stop the cooling process. The solution might be to randomize the light polarization by
sending lasers to several axes or to modify the sample polarization by a ‘random’ (non coherent) external field [24, 160, 161].

Sample polarization. It is good to mention that the transfer of the initial populations toward $J' = 0$ automatically polarizes the molecular sample. This is due to the reduction of the number of the $2J' + 1$ projections of the total angular momentum $J'$ on a given quantization axis to zero.

2.5.3. Choice of the absorption-spontaneous emission system. The simplest choice for the absorption-spontaneous emission system is to shape the rotational cooling laser in the same way as the vibrational one. The same principles of accumulation into a dark state can be used if the population evolution is limited to a closed ro-vibronic system. It might be more ingenious to find optical transitions that are different from those chosen for vibrational cooling. For instance, the choice of an electronic state having better Franck-Condon factors toward $v_0^\prime\prime$, as suggested in the case of $\text{Cs}_2$ [15], can simplify the interplay between rotational and vibrational cooling.

Choice of the laser. The rotational spacing is much smaller than the vibrational one. As a consequence, it might be useful to choose a dedicated laser for the rotational cooling. In the case of heavy molecules, such as demonstrated in the $\text{Cs}_2$ [70], the rotational spacing is too small to be resolved using standard shaping method as described in figure 3. So a narrowband (diode) laser is used. However, for lighter molecules, the standard shaping methods with GHz-shaping resolution [162] can be applied and a shaped broadband diode should be sufficient.

Choice of the shaping method. If the standard methods of spectral shaping are too inaccurate, the spectral shaping can be realized dynamically by scanning the narrowband laser over the appropriate frequency range. This control has to be faster than the typical vibrational cooling time. A sawtooth shape may facilitate the pumping by following the population redistribution: for instance by addressing the laser frequency to lower and lower $J$ values during the cooling process. In [13] the amplitude, center, speed and repetition of the frequency scan are controlled by a function generator that drives the current of the laser diode.

2.5.4. Estimation of the efficiency. Studying the $J$ lowering scheme does not alter the generality of the method and we shall thus focus on this scheme here. Typical Hönl-London factors are 1/4 for P and R branch and 1/2 for the Q one. Thus an ‘absorption-emission’ step, driving only the P Branch, lowers the $J$ value with a probability $p = 3/4$. If all the transitions, including the one used in the vibrational cooling, are $J$ lowering (but without dark state in $J$ for the vibrational cooling step), the $J$ population exhibits a random walk. This random motion modifies the rotational quantum number by $np$ after $n$ spontaneous emissions in both rotational and vibrational pumping steps.

However, it is possible that the vibrational cooling transitions are not ‘rotationally’ shaped, that is the vibrational cooling laser, even if shaped for vibrational cooling, still covers all rotational transitions. In such a case the vibrational cooling will counteract the control of the rotation and will create extra random walk in the process increasing the rotational quantum number by a probability of $5/16$ at each step. To avoid such nasty heatings only a couple of vibrational cooling processes can occur between rotational cooling ones. In such a case, the efficiency depends on the number of steps required to cool the vibration and an optimized vibrational cooling (in terms of photon numbers) scheme may be needed.

2.6. Discussion based on $\text{Cs}_2$ case

We will now illustrate the method on the case of the cooling of $\text{Cs}_2$ molecules. The initial sample is translationally cold (size $\sigma = 1$ mm, temperature $T = 100 \mu$K) but its vibrational and rotational distributions are spread over several levels (typically $v' = 0 \rightarrow 10$ and $J'' = 0 \rightarrow 5$) of the ground electronical state $X^\Sigma^+_g$.

The first step is the choice of the electronic transition. The $\tilde{\alpha} \tilde{g}^o$ is strongly perturbed by spin-orbit coupling which produces both triplet states and highly excited vibrational levels. Population transfer from a given (triplet) electronic state to another (singlet) one has been realized [20], but this makes the system more complex. Therefore, the $B^3\Pi^+_u$ and $C^3\Pi^+_u$ states look preferable and both may be used. However the $\chi \rightarrow C$ transitions lay in the energy range near 16000 cm$^{-1}$, which is unfortunately out of reach for our laser (10000–14300 cm$^{-1}$) but could be attained, for instance, by a laser diode. Cooling scheme using this state is discussed in [19]. Furthermore the C state, lying in higher energy than the B state, can dissociate or populate other states that the sole X one. For vibrational cooling, we thus use the B state and excite the transitions using a broadband laser. Depending on the experiment, we use a femtosecond laser or a cheaper but still efficient diode laser [17]. The laser linewidth is somewhat limited to tens to hundreds cm$^{-1}$, which is barely enough to isolate a closed ro-vibronic system. It reduces the efficiency of the process to ~80% for vibrational cooling [12] and 40% for rotational cooling [13]. With a larger spectral width, an efficiency of 99.9% vibrational cooling step [19] should be reached according to numerical simulations.

The laser used for vibrational cooling has a 1 mm-waist with a $\sigma$ polarization and an effective spectral power density of 1 mW/cm$^{-1}$. The laser used for rotational cooling has a spectral power density of 1.5 mW/cm$^{-1}$, and a 2 mm-waist. Numerical simulations based on the resolution of kinetic Monte-Carlo rate equations [28, 163] show a general good agreement with experimental results as it is shown for vibrational cooling in figure 2 and rotational cooling in figure 4. Starting with the experimental populations, the simulation consists in cooling the vibration by accumulating the population in $v'' = 0$, and cooling rotation using a $P$-branch (hatched area in figure 4(a)). Figure 4(b) shows a good agreement between simulation and experiment since, in
Numerical simulation of the rovibrational cooling of Cs2. The arrows cooling laser. The J = 0 population has clearly increased. (b)

cooling. The hatched area represents the frequency spectrum of the

represents the final experimental populations.

both theory and experience, the population in (v′ = 0, J′ = 0) represents 40% of the population initially pumped in v′ = 0 in 10 ms.

2.7. Optimization

Several approaches can be implemented to optimize the spectral shaping as already discussed in [54]. At some stage, they require a simple criterion to keep or reject the transition frequencies. For example a criterion that we often used was to keep the highest FC factors between the target vibrational level and the excited states. In general, it is thus useful to have access to the FC factors to optimize the pumping process. It is convenient to think of the optical cycle as divided in two steps: the excitation (absorption) and the spontaneous emission. Using generic notation of X for the lower state and B for the excited one (as used effectively in the Cs2 case) and in a perturbative approach (low laser intensity), the distribution of molecules in the various vibrational levels is described in absorption by

\[ P_{\nu_X}^{(n+2)} = P_{\nu_X}^{(n+1)} + \sum_{\nu_B} A_{\nu_X\nu_B} P_{\nu_B}^{(n)} \]

\[ P_{\nu_B}^{(n+1)} = \sum_{\nu_X} A_{\nu_B\nu_X} P_{\nu_X}^{(n)} \]

and in emission by

\[ P_{\nu_X}^{(n+2)} = P_{\nu_X}^{(n+1)} + \sum_{\nu_B} E_{\nu_X\nu_B} P_{\nu_B}^{(n+1)} \]

\( P_{\nu_X}^{(n)} \) and \( P_{\nu_B}^{(n)} \) respectively denote the population of the vibrational levels \( \nu_X \) and \( \nu_B \) of the ground and the excited electronic states at the stage number \( n \) of the process. \( A_{\nu_X\nu_B} \) denotes the absorption rate at which molecular populations are transferred from one vibrational level \( \nu_X \) to any \( \nu_B \) accessible by our laser bandwidth. Similarly, \( E_{\nu_X\nu_B} \) denotes the molecular population decay by spontaneous emission from one vibrational level \( \nu_B \) to \( \nu_X \). These rates are proportional to:

\[ A_{\nu_X\nu_B} \propto FC_{\nu_X\nu_B} (D_{\nu_X\nu_B})^2 I_{\text{laser},\nu_X\nu_B} \]

\[ E_{\nu_X\nu_B} \propto FC_{\nu_X\nu_B} (D_{\nu_X\nu_B})^2 \alpha_{\nu_X\nu_B}^3 \]

FC_{\nu_X\nu_B}, D_{\nu_X\nu_B}, \alpha_{\nu_X\nu_B} \text{ and } I_{\text{laser},\nu_X\nu_B} \text{ correspond respectively to the Franck-Condon coefficient, the dipole moment, the transition angular frequency and the laser intensity at the vibrational transition. The criterion for an efficient transfer is that } P^{(0)} \text{ has to get closer to } P_0, \text{ a target distribution defined by } (P_0) = \delta_{\nu_0}. \text{ The simplest optimization is by looking after just one cycle of absorption-spontaneous emission by minimizing } \| P^{(2)} - P_0 \| \text{ lead to choose } A_{\nu_X\nu_B} = 0 \text{ [54]. Therefore, } \nu_0 \text{ is a dark state and cannot interact with the laser. This simple derivation makes rigorous the choice of dark states: it is enough to remove transitions that can excite the target level. More complex derivations or simulations, as performed below, can extend this discussion to cases with more than one cycle.}

2.8. Results on NaCs

Vibrational cooling on heteronuclear molecules has been realized on NaCs [21] soon after the first demonstration of the technique on the Cs2 homonuclear molecule. The lack of gerade-ungerade symmetry in heteronuclear molecules enables other electronic transitions and different schemes are possible. Results of the NaCs cooling scheme are given in figures 5 and 6.

The initial vibrational population of the electronic ground state X′Σ+ was \( v \approx 4–6 \). The optical pumping approach was based on the use of simple, commercially available multimode diode lasers selected to optically pump population into X′Σ+ (\( v = 0 \)). The ground state molecules are pumped through a 300 mW CW laser covering the 979–991 nm region. This laser is able to excite low vibrational levels toward the AΣ+−b3Π complex. Due to the spin–orbit coupling, the excited molecules can also decay toward the a3Σ+ states where the same laser can re-excite them. In order to increase the efficiency, high vibrational levels are excited using a 1.5 W second laser with ~6 nm linewidth.
Both lasers have 1 mm waists and were not shaped.

The authors also investigate the impact of the cooling process on the rotational state distribution of the vibrational ground state. They observe that an initial distribution, $J_{0} = 2$, is only moderately affected resulting in a final distribution $J_{0} = 4$.

2.9. Extension to other molecular species like Rb$_{2}$, RbCs or LiCs

Optical pumping has also been used in other contexts such as the ACME Collaboration on ThO [164, 165] and preliminary results have been obtained by Marcassa’s team on Rb$_{2}$. They demonstrate continuous production of vibrationally cooled Rb$_{2}$ [166] in three steps. First, they use a dedicated photoassociation laser to produce molecules in high vibrational levels of the $X^1\Sigma^+$ state. Second, a broadband fiber laser at 1071 nm is used to transfer the molecules to lower vibrational levels via optical pumping through the $A^1\Sigma^+$ state. This process transfers the molecules from vibrational levels around $v^{1\Sigma^+} = 113$ to a distribution of levels where $v^{1\Sigma^+} < 35$. Then molecules may be further cooled using a broadband superluminescent diode near 685 nm with a shaped frequency spectrum. The resulting vibrational distributions are probed using resonance-enhanced multiphoton ionization with a pulsed dye laser near 670 nm.

When studying RbCs potential curves, it appears that the RbCs case is far from being ideal. Indeed, the A and B states are affected by spin–orbit coupling and their excitation would lead to losses. Furthermore the position of point A (as defined in figure 1) of the X-B transition is near $v_A^1 \approx 3$ which makes cooling toward $v^1 \approx 0$ difficult. One possibility is to optically pump toward $v_A^1 = 3$ and then transfer it, for instance by STIRAP, to $v^1 = 0$.

On the contrary, LiCs seem a very promising candidate. The use of the A state has been considered in discussion following [15]. Even without taking into account the (important) spin–orbit coupling the position of point A is $v_A^1 = 6$ which prevents, or would make quite difficult, an
optical pumping toward $v^* = 0$. On the contrary, the B state seems ideal with a very convenient wavelength (627 nm where diode lasers or pulsed dye lasers exists) and good FC factors. The B state can decay to the A state, but the small energy separation, and the cubic dependence in the spontaneous emission rate, makes this decay negligible compared to the decay toward the X state. Using the B state, an efficient coherent control cooling scheme has been suggested by Koch’s group \[52, 53\]. Using the same FC factors, we have simulated a vibrational optical pumping using a 1 W laser with a Lorentzian spectral profile of 1000 cm$^{-1}$ centered at 690 nm with a 0.3 mm waist in order to cover the sample. Evolution of the population of the lowest vibrational levels versus time starting with an equidistribution of the first 11 levels are given in figure 7. We observe that after 450 ms, near 90% of the molecules are cooled in the $v = 0$ level.

2.10. Extension to molecular beam: BaF case

In addition to the study of trapped cold molecules, we have also present here some unpublished consideration on another interesting and common configuration: a molecular (supersonic) beam. The main difference is the temperature of the molecular gas, typically 1 K, and the non-zero velocity which limits the interaction time with the laser. For simplicity, we choose molecules with FC \(\approx 1\), therefore, the vibrational redistribution almost disappears. Such a situation can be illustrated with Barium monofluoride (BaF) molecules (see table 2 : $\lambda = 860$ nm, FC = 0.95) seeded in an Ar supersonic carrier beam which thermal mean velocity is 560 m s$^{-1}$. The BaF molecules are distributed among a few tens of J levels and a few vibrational levels as shown in the REMPI spectrum obtained in our group and shown in figure 8. The ro-vibrational population distribution follows the Boltzmann
The gain of population in the ro-vibrational ground state achievable by optical pumping—in other words the increase of brightness beam—may reach \( \frac{k_B T_v k_B T_r}{\hbar h c_\nu} \sim 570 \) (a reliable approximation when the numerators are greater than the denominators, i.e. when many vibrational and rotational levels are initially populated).

Efficient vibrational cooling can be provided by a \( \sim 10 \) nm non-shaped broadband laser (such as femtosecond laser, diode lasers or self-seeded tapered amplifier) tuned to the \( v'' \leftarrow v' = v'' - 1 \) transitions between the \( \Sigma^+ \) and \( \Pi \) states (either \( \Pi_{1/2} \) or \( \Pi_{3/2} \)). Indeed, due to the high diagonal FC factor, the decay almost conserves the vibrational quantum number. Such absorption-spontaneous emission emission cycle remove one quanta of vibration.

For rotational cooling, however, the frequency cut-off resolution has typically to be better than \( B_v \), which is technically accessible to a commercial Bragg volume grating. For our simulation, we choose an initial transverse size of 1 mm for the molecular beam. Figure 9(a) shows the numerical evolution of the 15 first rotational levels (\( v = 0, J \) equally distributed) pumped by an effective spectral power density of 150 mW cm\(^{-1}\), which is realizable experimentally. With a pumping time of typically 200 \( \mu s \), BaF molecules accumulate in the lowest ro-vibrational level (\( v'' = 0, J'' = 1/2 \)) with an efficiency of \( \approx 50\% \), a limitation mainly imposed by the parity selection rules. The remaining 50% are pumped in the other lowest level (\( v'' = 0, J'' = 3/2 \)). In figure 9(b), we also show that the transverse temperature, that is the divergence of the beam, clearly impacts the efficiency. The latter decreases for fast transverse molecules because they simply fly out of the interaction zone with the laser, thus reducing the number of optical transition cycles.

### 2.11. Ions

The use of a tailored incoherent broadband light source for rotational cooling of molecular ions was proposed more than ten years ago [167, 168]. However the successful realization of this method is based on optical pumping of trapped molecules by blackbody radiation (similar ideas were also studied for neutral molecule in Meijer’s group [169] and also in [170, 171]).

The Drewsen’s group realized rotational laser cooling of vibrationally and translationally cold molecular ions [22]. They demonstrated rotational cooling of vibrationally and translationally cold MgH\(^+\) ions, using a laser-cooling scheme based on excitation of a single rovibrational transition as shown in figure 10. As shown in figure 11, a gain of nearly 15 in the rotational ground-state population of the electronic ground state is obtained and leads to a relative population of the ro-vibrational ground of 37%, which is equivalent to a thermal distribution at about 20 K.

At the same time, the Schiller’s group demonstrate similar cooling of the rotational degree of freedom of HD\(^+\) using two lasers achieving nearly 80% rovibrational ground-state population [23] (see figure 12). They then control
transfer of population into a selected state using optical excitation of individual transitions (see figure 13) [172].

Another type of internal cooling of ions have been considered by Odom’s group using the pulse shaping technique [173]. They first propose the use of pulse-shaped broadband femtosecond lasers to optically cool rotational and vibrational degrees of freedom of molecules. Compared to MgH+ or HD+ schemes that cool rotation with ro-vibrational excitations, this approach, as the one used for the neutral molecules, utilizes an electronic transition which enables an internal cooling several orders of magnitude faster thanks to the fast electronic decay timescale. The authors have demonstrated this method on AlH+ using an electronically exciting broadband laser to simultaneously drive cooling resonances from many different rotational levels as indicated in figure 14. No vibrational heating occurs because of the extremely high Franck–Condon factor between the vibrational grounds states. Rotational cooling is achieved in 140 ms from room temperature to 4 K with the ground-state population increasing by a gain of 30 [174]. Such an approach is potentially applicable to homonuclear molecules.

Combining these ideas, it has been suggested that laser induced rovibrational cooling of non di-atomic molecules can also been achieved. Softley’s group propose that it should be possible for the linear polyatomic ion C₂H₆⁺ using the laser-induced blackbody-assisted rotational cooling [175]. Although pure rotational transitions are forbidden in this non-polar species, a vibrational bending mode is infrared active and overlaps the blackbody spectrum. Hence the lifetimes of state-selected rotational levels are found to be short compared to the typical timescale of ion trapping experiments. The rotational-cooling scheme proposed involves pumping with only two broadband infrared lasers (Δν = 0.4–3 cm⁻¹) tuned on Q-branch transitions of the 2Δ₅/2 − Δ₃/2 and 2Σ⁺ − Δ₁/2 bands. This should lead to >70% of total population in the lowest rotational level at 300 K and over 99% at 77 K.

We mention that non optical internal state cooling is also a very active way of research. Recent works follow this way for BaCl⁺ [176] on MgH⁺ [177] using sympathetic vibrational cooling either with ultracold calcium atoms or helium buffer gas.

3. Cooling of external motion

A natural extension of internal state cooling is external state cooling. The complex internal structure of molecules complicates the creation of ultracold molecular gases using traditional methods such as laser cooling, in particular because the spontaneous decay produces molecules in many states. As ro-vibrational cooling methods circumvent this key bottleneck, we think that this review can also briefly cover the topic of cooling of external degrees of freedom of molecules. We only focus on potential methods able to fill the gap between the (milli-)Kelvin range and the micro-Kelvin range.

3.1. Cooling external degree of freedom

Summarizing and extending the discussion presented in [28], we quickly review some suggested methods aiming at realizing cooling of translational degrees of freedom of molecules before detailing the Sisyphus method often supporting the use of ro-vibrational cooling.

Among the most naturals ideas to cool molecules, it is obvious to think about evaporative cooling or collisions with dense and colder species, such as trapped laser cooled atoms or ions, in a so called sympathetic cooling scheme. Such a
thermalisation technique has been demonstrated with molecular ions [142] and sympathetic cooling of neutral molecules with trapped ions seems possible [178]. However reactive or inelastic collisions strongly limit the efficiency of the process [179, 180]. A noticeable counter-example is OH radicals which has been successfully cooled using evaporative cooling [27]. Another idea is to cool the translation with transfer of photon momentum as standard laser cooling of molecules that was achieved by [24]. To circumvent the general modification of the internal state occurring after the spontaneous emission step, this method requires to choose very well suited molecules (SrF, YO, CaH, …) that have a quasi-closed-level system thanks to a high Franck–Condon factor (see also table 2) [25, 181]. In such schemes, ro-vibrational cooling could be used to limit the losses.

Finally, another cooling method, the so-called one-way [182–188] or Sisyphus [181, 189] cooling, consists in converting the kinetic energy into potential energy using external

Figure 12. Rovibrational levels representation to perform rotational cooling of HD⁺ molecular ions. Here \( p_N \) is the population of the 6 first rotational levels of the fundamental vibrational level \( (v = 0) \).

Figure 13. (a) Initial distribution of the rotational levels of HD⁺ ions sample. (b) Experimental and theoretical results for rotational cooling of HD⁺. Distribution of the 5 first rotational levels of molecular ions without (grey squares) and with (red circles) rotational cooling. Black and blue squares represent two different simulations of the experiment.
The principle, sketched in figure 15, relies on external forces that remove kinetic energy by transferring it into potential energy. The irreversibility of the process is ensured by a spontaneous emission of photon, and the whole operation can be repeated by optically pumping the molecule back to its original state.

3.2. One-way cooling

In contrast to standard laser cooling based on photon momentum transfer, in a one-way or Sisyphus cooling, the reduction in temperature per spontaneous emission step is typically a few mK compared to a few μK. The Sisyphus cooling process requires less cycles and is therefore less sensitive to the modification of the internal state occurring after spontaneous emission.

One-way optical pumping can be a way to cool if the optical pumping is performed at the top of a potential [191]. It has not been demonstrated efficiently yet, however, optical pumping of decelerated molecules can already produce trapped molecules [183–186]. For instance, accumulation of Stark-decelerated NH molecules in a magnetic trap has been realized [187]. Similarly, magnetically slowed calcium monofluoride (CaF) has been trapped using a two-stage optical pumping [192].

3.3. Sisyphus cooling

The Sisyphus cooling process, first proposed by Pritchard [193], has represented a milestone in the history of laser cooling by being responsible, through polarization induced light shifts, for breaking the Doppler limit in magneto-optical traps (MOT) [189]. For molecules, the Sisyphus effect has recently been demonstrated in Rempe’s group and enables the first efficient laser cooling of a polyatomic molecule from 400 mK down to 30 mK with a phase-space density increased by a factor of 30 [194]. In this experiment CH₃F molecules remain electrically trapped, and microwave transition between vibrational states provides the energy transfer [195] as shown in figure 16.

This promising experiment already indicates the possibility to reduce the temperature below the mK range in tens of seconds. One of the difficulties is to find molecules with short enough spontaneous emission times for excited states (hundreds of milliseconds is a maximum) in order to have a fast enough cooling. In [196] it has been suggested to put an optical cavity around a magnetically trapped OH sample in order to accelerate the spontaneous decay in order to have a faster cooling.

3.3.1. Choice of the molecular states

Each molecule has its own characteristics and the cooling strategy should be adapted to each of them by making suitable choices for the trap, the electronic states and the lasers. In table 2, a list of some diatomic molecules is given showing that the Sisyphus method can be implemented for most of the current produced cold molecular species. For the choice of the lasers or trap, a key parameter is the AC or DC electric, magnetic or electromagnetic trapping capability of the molecule. Once
3.3.2. Strategy of removal elementary steps

Sisyphus transfer can be obtained in several ways and using different strategies such as spontaneous or induced transfers. Spontaneous transfer can occur if the excited state ($U_2$) has a long enough lifetime so that the particle moves in the trap before its spontaneous decay [197–199] as described in figure 15. For other cases, such as described in figure 16, the Sisyphus step is performed by applying a laser, or RF-microwave, excitation that transfers the molecule to an excited state that will then decay toward $U_1$. This can be realized by possibly shaped broadband laser covering the whole sample.

Another method consists in catching the particle when it has almost zero kinetic energy. This selection can be realized spectroscopically or spatially by applying the laser only at this position.

For all methods a temperature variation per cycle of $\Delta T \approx 0.3 T$ is expected [28] and the temperature decays exponentially with a decay time of the order of 5 times the ‘oscillation’ period. In this way, a cooling by a factor 10000, say from 100 mK to 10 μK, takes only 30 cycles. This has to be compared to the few thousands of cycles needed for standard laser cooling [24] and clearly highlights the potential of the Sisyphus method.
The Sisyphus method is very easy to implement for trapped quasi closed systems [200–203] and can improve standard laser cooling. For trapped species, the photon transition rate can be very slow and the scheme is particularly suitable for particles that require deep-UV lasers for electronic excitations. It also enables the use of pure ro-vibrational transitions or quasi-forbidden electronic transitions.

3.4. Optimized strategy: 1D, 2D or 3D cooling?

Optimizing the cooling strategy is very complex and often linked to objectives that can be cooling time, final temperature, density or phase space density. Consideration on the interaction time, the power broadening of the transition or the velocity dependence of the transition rate can lead to much lower energy or spatial resolution than naively expected. A reliable estimation of the efficiency of a strategy has to be performed through a detailed simulation as performed in [28].

Although defining a global and optimal strategy is difficult, some general considerations can be made. For instance, when the decay processes populate a lot of levels, for instance due to bad Franck-Condon factors, and optically pumping is not efficient enough, it must be preferred the solution of single photon cooling [204, 205]. 1D cooling is simple and very efficient. 1D transitions can be controlled using light polarization on the polarization axis, [195, 206]. A 3D...
extension of the 1D process can be achieved by a rotation of phase space method like in [206]. But, the discussion concerning 1D motion cannot be generalized to the (2D) or 3D case. Indee, even if figure 15 is still valid, r designs the radial coordinate in 2D or 3D motion, due to the angular momentum, the particles can miss the center and \( r_{\text{repump}} \) could be non zero leading to low energy removal per cycle. To avoid this strong difficulty, it is possible to create asymmetries in the potential.

3.4.1. Trapped NH case. The case of NH molecule, studied in [28], can be understood from a sketch of its relevant levels and transition strength shown in figure 17. The A-X transition in NH is almost perfectly diagonal and the \( v' = 0 - v'' = 0 \) band has a Franck-Condon factor better than 0.999 [187].

The use of a magnetic trap with zero field at the center leads to difficulties because with degenerate energy levels near the trap center (i.e. at low temperature), the spectral or spatial selectivity for the transitions is no longer ensured and excitation of undesirable levels during the process occurs.

Therefore a bias field of \(-0.1\) T that lefts the level degeneracy is really useful. Furthermore, it creates a preferential quantization axis along which it is convenient to make lasers propagate with a well-defined (usually circular) polarization, which helps choose the desired transitions. As explained earlier, an asymmetric configuration is needed to avoid angular momentum conservation and to have ergodic trajectories (in this example \( \mu \) of the order of \( X \) along X and \( 0.83 \) \( T \) \( cm^{-1} \) along Y has been chosen). Because of the exponential decay of the temperature and as a result of the sample size, it is found that the power, the detuning, as well the as the FWHM Lorentzian laser linewidth of the Sisyphus laser should decrease exponentially with the same time constant. However it does not appear useful and necessary to reduce the waist of the lasers. In order to repump particles at low enough energy, the spectrum of the repumping laser (see figure 17) is flat and the frequency corresponding to particles in \( M' = 1 \) at a potential energy of \( 0.4k_B T \) is cut off.

The numerical simulation, summarized in figure 18, shows that the temperature drops by a factor 1000 and the phase-space density increases by a factor 10⁷ in only one second, with almost no losses.

With the very high FC factor of NH, the vibration is frozen, but many molecules do not have a so good property (see table 2). With no good FC factor, except the solution of single photon cooling, another possibility is to perform a Sisyphus cooling in the ground state using only ro-vibrational transitions as shown in figure 16. Finally, Sisyphus cooling can be very efficiently combined with ro-vibrational cooling in order to bring the molecule back to its original internal state using ’shaped’ light absorption as a ’repumping step’ as symbolized by the shaped spectrum in figure 15.

3.4.2. Trapped \( C^-_2 \) case. As another example, we have very recently proposed a scheme for laser cooling of negatively charged molecules that could have an impact on the study of molecular anions, charged particle sources and antimatter physics. We have carried out a detailed computational study with \( C^-_2 \), the most studied molecular anion. \( C^-_2 \) energy levels and required optical transitions are shown in figure 19. A solution to avoid \( C^-_2 \) losses through photo-detachment or decay in high vibrational levels of ground-state is to use the slower X-A transition and not the fast X-B one. We simulated a 1D Sisyphus-type cooling in an 1.5 cm long Penning-like trap whose principle is illustrated in figure 19(b): due to the axial motion induced by the electric trapping potential (with a period of 300 \( \mu s \) in the simulation), particles move between the low (0.2 T) and the high (2 T) magnetic fields at both ends of their axial range, thus continuously loosing kinetic energy. Two cooling lasers, at 2.533 \( \mu \)m and 2.536 \( \mu \)m, as well as a single broadband (6000 MHz) laser repumping losses in X (\( v'' = 0, N'' = 2, J'' = 3/2 \)) are used. As shown in figure 20, in a few tens of ms, the axial temperature is expected to decrease from 60 K to a few K. The lost population mainly goes to \( X(v'' = 1) \), but with the help of two lasers, at 4.57 and 4.59 \( \mu \)m, this state can be repumped, thereby leaving less than 0.5% of the anions in \( X(v'' = 2) \).

3.4.3. Continuous deceleration. Sisyphus cooling can also be used as an all-optical method for cooling or decelerating molecules traveling repeatedly through uphill potentials [28] similar to the single photon cooling ideas proposed in references [208, 209]. Such cooling can be longitudinal to the beam or transverse to it. We have performed preliminary studies on the transverse cooling of our BaF molecular beam using similar Sisyphus methods as demonstrated on atomic Cs atoms in [210], or proposed with Yb atoms in [211], which looks promising.

4. Conclusion

Optical pumping of the internal degrees of freedom increases the purity of any kind of molecular or atomic sample. Improving the brightness of a molecular beam is consequently an accessible application. We have particularly described how optical methods are able to efficiently transfer an initial rovibrational distribution to a single rovibrational level. They all deal with light source inducing efficient absorption/spontaneous emission cycles that lead to population redistribution. Broadband diodes and frequency shaping are cheap and the scheme can often be easily implemented. The amount of possible cooling schemes, using optical, magnetic, electric or gravitational forces combined with laser (or radio-frequency) transitions of any kind (Raman, coherent, stimulated, pulsed, shaped, multiphotonics, black-body ...) is so large and methods so versatile that it can be implemented to several species ranging from simple atoms or ions to polyatomic molecules, that are difficult to laser cool, such as (anti-)hydrogen. We also proposed to combine Sisyphus and optical pumping methods to realize efficient cooling of external degree of freedom. This can pave the way to full laser cooling of molecules in cells or beams, one of the biggest challenges in the cold
molecule community whose efforts attempt to explore many-body physics, quantum chemistry, quantum information, and precision measurements [1, 139, 212].

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