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A novel scheme is proposed for sequential cooling of rotation, translation, and vibration of molecules. More generally, this scheme manipulates and controls the states and energies of molecules. The scheme, while somewhat complex, is simpler and more feasible than simply providing a large number of synchronously but independently tunable lasers. The key component is a multiple single frequency laser (MSFL) in which a single narrow band pump laser generates an ensemble of resonant ''stimulated Raman'' (RSR) sidebands (subsequently amplified and selected) in a sample of the molecules to be cooled. Starting with a relatively cold molecular sample (e.g., a supersonic beam of Cs_2), the rotation of molecules is cooled by sequential application of P branch electronic transition frequencies transverse to the molecular beam beginning at higher rotational angular momentum J. Then translation of molecules is cooled by application of multiple low J, P, and R branch transition frequencies which counterpropagate with the molecular beam and are synchronously chirped over their Doppler profiles. Finally, vibration of molecules is cooled by blocking the $R(0)$ line of the 0–0 band. Only this specific order of rotation–translation–vibration appears feasible (using molecules produced by photoassociation of ultracold atoms avoids the requirement for translational cooling). Each step employs true dissipative cooling (i.e., reduction of system entropy in three degrees of freedom) by spontaneous emission and should yield a large translationally cold sample of molecules in the lowest ($v=0$, $J=0$) level of the ground electronic state, suitable for studies such as molecule trapping, ''molecule optics,'' or long range intermolecular states. © *1996 American Institute of Physics.* [S0021-9606(96)01124-5]

INTRODUCTION

There has been tremendous progress in atomic laser cooling[1–3] in recent years, but progress at manipulating even simple molecules during the same period has been comparatively minimal. This is due, in large part, to the increased spectral complexity of molecules and multiple spontaneous decay channels (branching). Coherent manipulation of molecules (e.g., with short pulses) is possible but true dissipative cooling (real reduction of system entropy) requires spontaneous emission. It is well known that attempting to cool molecules by directly applying atomic translational cooling methodology would fail due to optical pumping. This happens when an excited molecule spontaneously radiates to one (of many) nonresonant ground rovibrational states. By changing vibrational or rotational state, the molecule shifts itself out of resonance with the cooling laser and cooling stops. A similar problem occurs in laser cooling of alkali atoms when spontaneous emission occurs to a nonresonant ground state hyperfine level. In this case, however, only one additional (and nearby) laser frequency is needed to counteract this optical hyperfine pumping. For molecules, there are multiple decay channels, making the situation considerably more complicated. Simply using many lasers (one for each possible rovibrational state) might solve the problem of laser cooling molecules, but this would unfortunately lead to a complex ensemble of resonant lasers, that must also be chirped through all Doppler profiles (necessary for maintaining the Doppler resonance condition). Herein, we present a more feasible solution to this problem.

Laser manipulation of molecules has been slow in development although the concept has been known since Kastler's introduction of ''luminorefrigeration.''[4] Over the years, other related concepts have emerged.[5–9] By limiting the number of states (and laser frequencies) involved, there have been a few successful demonstrations of molecule manipulation. Djeu and Whitney seem to have performed the only successful experimental cooling demonstration, one which involved net cooling of rotation and vibration in CO_2 molecules (VV and VR cooling, explained below).[10] Radiative deflection of molecules in a beam has also been demonstrated.[11] Coherent transfer between two molecular states by the STIRAP (stimulated Raman adiabatic passage) process[12] also works. Motivated by the recent renewed interest in manipulating molecules,[13] other new concepts, such as atomic photoassociation,[14–18] shaped pulse or wave packet cooling,[19] and trapping of paramagnetic molecules[20,21] have also emerged. However, none of these methods seem suitable for preparing a large sample of cold molecules, which would be useful for studies of molecule trapping, ''molecule optics,''[22] molecular scattering, or long range intermolecular states.

Before beginning the discussion, a general nomenclature for molecular cooling should be established. We designate the degree of freedom cooled, followed by the type of transition used (e.g., RE is cooling of rotation using an electronic transition). Table I lists the relevant combinations of which we focus on cooling rotation, translation and vibration on electronic transitions: RE, TE, and, VE. Note in particular

TABLE I. Overview of molecular cooling types.

Degree of freedom	Optical transition	Cooling type
External:		
Translation	Electronic/vibration/rotation	TE[a]
	Vibration/rotation	TV
	Rotation	TR
Internal:		
Vibration	Electronic/vibration/rotation	VE[a]
	Vibration/rotation	VV
Rotation	Electronic/vibration/rotation	RE[a]
	Vibration/rotation	RV
	Rotation	RR
Electronic	Electronic/vibration/rotation	EE

[a]Proposed here.

FIG. 1. Block diagram of the MSF laser for the Cs_2 $B\ ^1\Pi_u-X\ ^1\Sigma_g^+$ example (see the text and Table III).
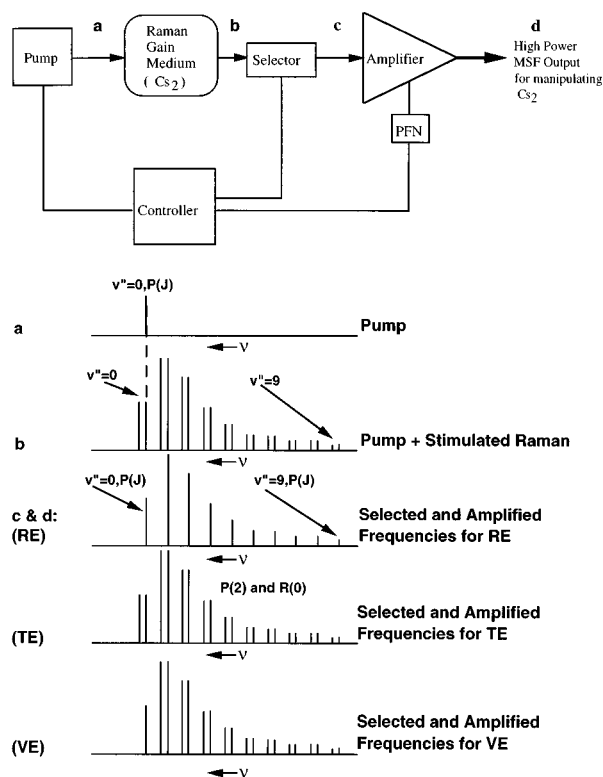
that TE molecular cooling appears to be the only feasible translational cooling technique (TV and TR would be much slower).

Our scheme can be summarized as follows. First, the molecules are rotationally cooled by sequentially exciting P branches for decreasing values of J, driving the population into the lowest J levels. Next, the molecules are translationally cooled with radiation pressure by simultaneously exciting on multiple rovibrational transitions and chirping these excitation frequencies to compensate for the changing Doppler shifts[23,24] of the decelerating molecules. Finally, the molecules are vibrationally cooled by allowing them to be optically pumped into the lowest vibrational level. The overall result is a translationally cold sample of molecules in the lowest rovibrational level.

The method we propose involves the development of a multiple single frequency laser (MSFL) for the generation of multiple transition side bands operating between molecular electronic states (Fig. 1). The MSFL utilizes a single narrow band (master) pump laser (tunable and chirpable) to generate an ensemble of (slave) side bands. These are generated when the pump laser multiply traverses a sample of molecules contained in the Raman gain medium, which in this case is a supersonic molecular beam. Inelastic forward RSR (resonant stimulated Raman) scattering generates the ensemble of weaker, narrow band, copropagating side band beams. Of particular importance to TE cooling, the Doppler detuning of each stimulated Raman sideband (δ_s) is related to the pump laser detuning (δ_p) by,

$$\delta_s = (k_s/k_p)\delta_p,$$

where k_s and k_p are the respective wave vectors of the sideband and pump.[25] This is vital to TE cooling because chirping of the pump laser (within the Doppler profile) results in an ensemble of synchronously chirped sidebands which are all resonant with the same velocity group of molecules (if need be, additional ''repump'' sidebands can be produced by adding a second synchronized pump laser, as discussed in Appendix B). As the molecules decelerate, Doppler compensation therefore occurs simultaneously on all sidebands (k_{si})

when the pump laser detuning is chirped ($\dot{\delta}_p$). This can be seen in the expression for the Doppler compensated detuning rate of the ith sideband ($\dot{\delta}_{si}$), given by,

$$\dot{\delta}_{si} = (k_{si}/k_p)\dot{\delta}_p = k_{si}\dot{V}.$$

Here, the rate of change of velocity for a resonant molecule ($\dot{V}$) is seen to be independent of sideband (k_{si}). The decelerating molecules are always resonant with each sideband.

As an example, we look at laser cooling a beam of Cs_2. In this version of the experiment two (synchronized) pulsed Cs_2 supersonic beams are used; one [long pulse, t (pulse) >11 ms] beam functions as the Raman gain medium, and a second beam using shorter pulses of Cs_2 serves as the ''collisionless'' expanding gas to be RE, TE, and VE cooled. A major requirement in the MSFL approach is the need for a high gain, wide bandwidth optical amplifier, spanning a significant fraction of an electronic molecular band system. Alexandrite, whose tuning range spans the Cs_2 $B-X$ band system, meets this criterion.

After leaving the Raman gain medium (Fig. 1), the RSR side band beams enter a selector and broadband pulsed traveling wave amplifier combination that selects/rejects and amplifies the RSR sidebands. The resultant amplified output is a pulse (>11 ms, ~ 100 W peak power) of ''modeless'' MSFL sidebands. This chirped pulse would suffice for cooling molecules in a supersonic beam (or vapor cell or laser trap). High power output (>1 J/pulse) is important because many
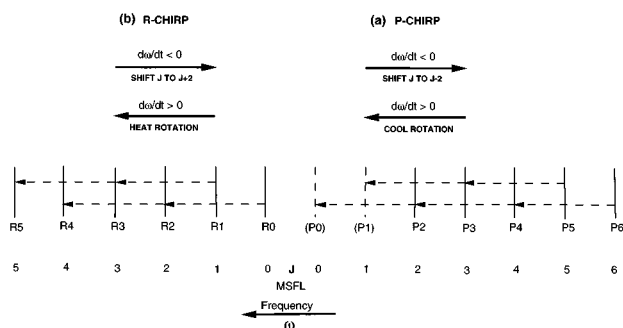
FIG. 2. Illustration of RE cooling and heating using P and R chirp techniques, respectively (bold arrows indicate the MSFL chirp direction, dashed arrows indicate the direction of population transfer).

transitions (some of which are weak) should be saturated.[26] Slower chirp rates and/or reduced initial velocities relax the requirements for saturation of all transitions.

To cool molecules on electronic transitions, only the proposed order RE–TE–VE appears feasible. The most challenging step, TE cooling, can be avoided if one starts with a sample of translationally cold atoms and performs photoassociation[17] followed by RE and VE cooling. On the other hand, directly cooling molecules in a beam would produce many orders of magnitude more cold molecules (and possibly enable molecular trapping as well as a variety of molecular analogs to proven atomic cooling techniques such as ''Zeeman,''[27,28] ''white light,''[29] ''isotropic light scattering,''[30] ''modeless,''[31] ''two-mode,''[32] ''mode-locked,''[33] and ''broadband''[34]).

MOLECULAR COOLING WITH THE THREE STEP RE–TE–VE SEQUENCE: THE Cs_2 $B\,^1\Pi_u$–$X\,^1\Sigma_g^+$ EXAMPLE

Step 1: RE

After selection of an appropriate cooling cycle ($v'=0$, $v''=0$–9, see Appendix A), rotational electronic (RE) cooling of molecules is accomplished with a ''P chirp'' performed by chirping the frequency of the (master) pump laser from high to low J through the P branch of the (0–0) band. The (slave) MSFL sidebands chirp synchronously with the pump from high to low J on all P branches of the cooling cycle ($v'=0$, $v''=0$–9). Such chirps (with the MSFL perpendicular to the molecular beam) can be performed continuously in frequency and time, or in steps.[35] A continuous P chirp ($d\omega/dt>0$) through a P branch is illustrated in Fig. 2(a). Beginning with the MSFL resonant with the $P(6)$ line, population is transferred unidirectionally (dashed arrows) from $J''=6$ to $J''=4$ via *bidirectional* excitation of $J'=5$ followed by *unidirectional* fluorescence to $J''=4$ (e.g., $J''=6\leftrightarrow J'=5\rightarrow J''=4$). After a period of nonresonance ($<1\ \mu$s) the MSFL comes next into resonance with the $P(5)$ line, which transfers population from $J''=5$ to $J''=3$. Finally the $P(4)$ line is reached, which transfers population from $J''=4$ to $J''=2$. The $P(0)$ and $P(1)$ lines do not exist, and there is actually no reason to cool on $P(2)$ and $P(3)$ since $J''=0$ and 2 and $J''=1$ and 3 are coupled in the TE step

(discussed below). At this point (after about 6 μs), most of the population is in rotational levels $J''=0$–3, and the P chirp is terminated (if only RE cooling is desired one could continuously repeat the cycle). Reversing the direction of a P chirp ($d\omega/dt<0$) results in a shift of the rotational population ($J''\rightarrow J''-2$), which does not heat, but does result in a slight cooling. However, all J'' levels (except $J''=5$ and 6, in this case) retain population.

The analogous ''R chirp'' provides the mechanism for RE heating and is illustrated in Fig. 2(b). The R chirp ($d\omega/dt>0$) starts with the $R(0)$ line which transfers population from $J''=0$ to $J''=2$ (excitation followed by fluorescence $J''=0\leftrightarrow J'=1\rightarrow J''=2$) etc., until the limiting high J is reached. Such rotationally hot molecules (which in some cases could be translationally and vibrationally cooled) should exhibit novel collision dynamics but will not be further discussed here. Again, reversing the direction of the R chirp causes a shift of the entire rotational population ($J''\rightarrow J''+2$) which does not cool, but does result in a slight heating. Again, all J'' levels (except $J''=0$ and 1) retain population.

During a P chirp, the MSFL must maintain resonance with each $P(J)$ line for a time long compared to the appropriate radiative lifetime (say 5τ) of the R branch emission for complete population transfer. In general, different levels have different radiative lifetimes (due mainly to variations in vibrational overlap matrix elements: $\langle v'|v''\rangle$) (here, for simplicity we exclude degeneracy, transition moment and the ν^3 dependences). In the present case, assuming saturation of the $P(J'')$ lines, the appropriate population transfer time τ_{psat} of the $B\,^1\Pi_u$ $v'=0$, $J'=J''-1$ level is that corresponding to the total rate of R branch spontaneous emission

$$\tau_{\mathrm{psat}}=\left[\sum_{v''=0}^{9}\mathbf{A}_{v'=0,J'=J''-1;v'',J=J''-2}\right]^{-1}$$

$$\sim\tau_{v'=0}[(J''-1)/(2J''-1)],$$

where $\tau_{v'=0}$ is the (virtually J' independent) radiative lifetime in the absence of saturating lasers.

Spectral overlaps between R and P branches do not present a problem because such overlaps typically involve different J [in the present case of identical nuclei (ortho and para molecules), Q branches may be disregarded].[36] There may still be accidental pumping effects due to spectral blends or perturbed electronic states, but these are not likely to present problems here.

Step 2: TE

The next step, TE cooling, is performed with a much slower Doppler chirp of the MSFL pump laser. This is analogous to the well known atomic laser chirp cooling.[23,24] Immediately following the RE step, TE cooling of either ortho or para molecules is initiated. For the homonuclear alkali dimers with nuclei with odd atomic numbers, selection of the even J lines, $R(0)$ and $P(2)$, for the MSFL output TE cools para molecules. Conversely, selection of the odd J lines, $R(1)$ and $P(3)$, TE cools ortho molecules (for ^{6}Li and ^{40}K,

TABLE II. Molecular data for translational cooling[a] using the alkali $B-X$ bands.

Molecule[b]	T @ 100 Torr (K)	V_0 (M/S)	ΔV (M/S) (10^{-2})	# photons (10^4)	t(rad) (ns)	t(TE) (ms)	a (M/s^2) (10^6)	X min (M)	$\Delta\nu_d$ Doppler shift (GHz)	TE chirp rate (GHz/ms)
^{7}Li$_2$	1350	1270	5.8	2.2	7.8	0.70	3.8	0.21	1.7	1.2
^{23}Na$_2$	980	600	1.8	3.3	6.8	0.90	1.3	0.14	0.78	0.43
^{39}K$_2$	860	430	0.78	5.5	9.7	2.1	0.4	0.23	0.56	0.13
^{85}Rb$_2$	800	280	0.35	8.0	16.6	5.3	0.1	0.39	0.37	0.035
^{133}Cs$_2$	760	220	0.20	11.0	25.0	11.0	0.04	0.61	0.29	0.013

[a]Only allowed electronic transitions have a short enough radiative lifetime for practical translation cooling. Also, numbers in this table reflect arbitrarily choosing V_0 as the initial velocity. A lower initial velocity would result in reduced values for the number of photons, t(TE), $X_{\min}$, $\Delta\nu_d$, and the TE chirp rate.

[b]$V_0 = (2 \ kT/M)^{1/2}$; $a = hk/4\Pi Mt$(rad); $X_{\min} = V_0^2/2a$; t(rad)$= 1/\Sigma_{v''} A_{v',v''}$; $\Delta\nu_d = \nu_{00}(V_0/C)$; t(TE)$= 4 \times$(# photons)$\times t$(rad); TE chirp rate$= \Delta\nu_d/2t$(TE); # Photons$= V_0/\Delta V$.

the para and ortho designations are reversed). Note that two pump lasers would be required to cool para and ortho simultaneously.

Calculations relevant for TE cooling Cs$_2$ and the other alkalis on the $B-X$ bands are presented in Table II. Due especially to the relatively long time needed to perform TE cooling (11 ms for Cs$_2$), significant population transfer by spontaneous emission to high vibrational levels ($v''>9$) of the ground state is the primary population loss mechanism (Appendixes A and B describe techniques for overcoming this loss.)

Step 3: VE

The last step, VE cooling, is illustrated in Fig. 3. In Fig. 3(a), for simplicity, are shown the $R(0)$ and $P(2)$ transitions of the lowest three vibrational levels. With all six transitions in saturation immediately following the TE cooling step, the population is undergoing a radiative *bidirectional* circulation among the seven coupled levels (if all transitions are saturated, populations are purely statistical). Vibrational electronic (VE) cooling to $v''=0$, $J''=0$ is initiated [Fig. 3(b)] by removing (i.e., blocking) the $R(0)$, $v''=0$ MSFL sideband. This causes the entire population to be transferred *unidirectionally* into the $v''=0$, $J''=0$ state. This completes the RE–TE–VE cooling sequence. {Conversely, blocking the MSFL sideband that pumps the $P(2)$, $v''=2$ transition [Fig. 3(c)] VE heats molecules by transferring the entire population to $v''=2$, $J''=2$.}

The time needed for such VE transfers depends primarily on the appropriate effective radiative lifetime ($\tau_{v',J',v'',J''} = 1/A_{v',J',v'',J''}$) of the blocked transition. The corresponding effective radiative lifetimes for blocking $R(0)$ lines of the 0–0, 0–1, and 0–2 bands of Cs$_2$ ($B-X$) are 390, 240, and 300 ns, respectively. For blocking the $P(2)$ lines of the same bands, they are 195, 120, and 150 ns, respectively. Therefore, VE cooling to $v''=0$, $J''=0$ can be taken to be $>99\%$ complete in $\sim 5\tau_{0,1,0,0} \sim 2 \ \mu s$ (in the saturated limit, the untransferred population is given by $e^{-t/\tau_{0,1,0,0}} \sim e^{-5} \sim 1/148 < 1\%$).

The overall RE–TE–VE scheme for cooling Cs$_2$ on the $B-X$ bands is summarized in Table III. The columns give the respective cooling types, pump transitions (with absolute frequencies), selected and amplified transitions, and the esti-

(a) 6 saturated transitions - statistical distribution of population.
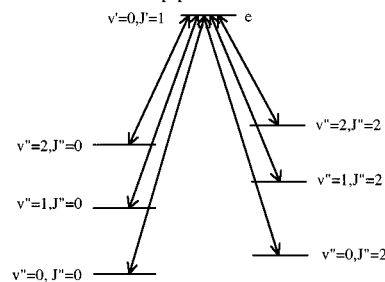
(b) VE cooling (5 saturated transitions): With the $v''=0$, $R(0)$ transition blocked all population is transferred to the $v''=0, J''=0$ state.
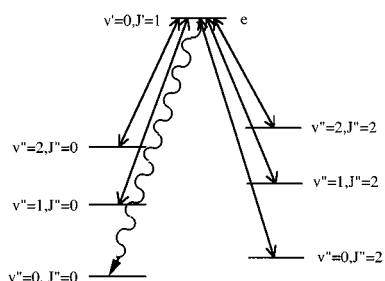
(c) VE (and RE) heating (5 saturated transitions): With the $v''=2$, $P(2)$ transition blocked, all population is transferred to the $v''=2, J''=2$ state.
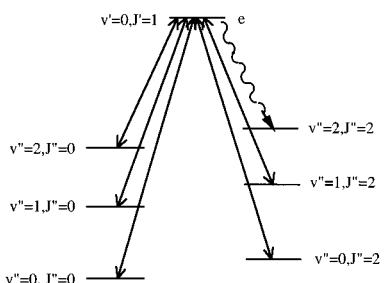
FIG. 3. Internal state cooling (and heating): 6 quantum states example—optically coupled to a single upper state.

TABLE III. Prescribed transitions and timeline for RE, TE, and VE cooling even J (para) Cs_2 using a MSF laser device operating on the $B\ ^1\Pi_u - X\ ^1\Sigma_g^+$ band system.

Cooling type[a]	Pump			Select and amplify		Time line
	X (v'',J'')	$\leftrightarrow$ $\leftrightarrow$	B (v',J')	$\rightarrow$ $\rightarrow$	X (v'',J'')	
RE (continuous)						
step 1 $= P(6)$ (391,191.311)	0,6		0,5		0–9,6	3 μs
step 2 $= P(4)$ (391,193.249)	0,4		0,3		0–9,4	3 μs
TE[b] $R(0)$ and $P(2)$ (391,194.932)	0,2		0,1		0–9, 0 and 2	11 ms
VE (to $v''=0$, $J''=0$) (391,194.932)	0,2		0,1		0,2 1–9, 0 and 2	2 μs
Total frequency change$=3.621$ GHz					Total time$=11.008$ ms	

[a]Absolute (line center) pump laser frequencies are given in GHz.
[b]Repump: 1,2 $\leftrightarrow$ 5,1 $\rightarrow$ 8$-(>13)$,0 and 2 11 ms.
(395,017.252)

mated time for completion of each cooling step. We see that cooling rotation requires chirping over $\sim$3.6 GHz in 6 μs, easily attainable with free running diode lasers.[37] Translational cooling requires a much slower chirp of $\sim$0.3 GHz in 11 ms. And finally, vibrational cooling requires that one of the sidebands be turned off for $\sim$2 μs.

Generally, by making the appropriate choices in the RE, TE, and VE cooling steps, complete population transfer into any given single rovibrational level is possible. The Cs_2 $B-X$ band example constitutes a 40$\rightarrow$1 transfer ($v''=0$–9, and $J''=0,2,4,6)\rightarrow(v''=0$, $J''=0)$. The method, however, should be extendable to include individual magnetic sublevels as well.[38]

In conclusion, we have presented a scheme for the sequential laser cooling of rotation, translation, and vibration in a molecular beam. Rotation is cooled by sequential excitation of P-branch transitions with decreasing J values. Translational cooling takes place via radiation pressure induced by a counterpropagating multiple-single-frequency laser which is frequency chirped for Doppler compensation. Finally, the vibration is cooled by allowing optical pumping to populate the lowest lying vibrational level. The laser light required for this cooling scheme could be generated by long-pulse amplified Raman gain sidebands resulting from molecular excitation by a single frequency pump laser. Our proposed scheme is a promising first step in the extension of laser cooling techniques from the atomic into the molecular domain.

APPENDIX A: THE SELECTION OF TE COOLING CYCLES FOR MOLECULES (THE Cs_2 $B\ ^1\Pi_u - X\ ^1\Sigma_g^+$ EXAMPLE)

Of the three cooling types (RE, TE, and VE), TE cooling presents the greatest challenge because of the relatively long cooling time required (11 ms for Cs_2 $B\ ^1\Pi_u - X\ ^1\Sigma_g^+$). Spontaneous decay to v'' levels outside the cooling cycle is the primary population loss mechanism. This is the molecular analog to optical hyperfine pumping in atoms where an atom decays to a nonresonant ground state hyperfine level and must be repumped back to the original level with another laser. We note that such a decay, resulting in an interruption of the cooling process, can be regarded as a molecular ''quantum jump,'' analogous to interruptions in fluorescence from trapped atomic ions which are ''shelved'' in metastable states.[39–44] There are two strategies for overcoming this spontaneous emission loss: The first uses a high gain amplifier with one pump laser. The second uses a lower gain amplifier, but requires one additional pump laser. Both approaches lead to ''sufficiently closed'' cooling cycles. By sufficiently closed, we mean that an average Cs_2 molecule has much less than unit probability of leaving the cooling cycle ($v'=0$, v'') by spontaneous emission during the TE cooling step.

Rotational electronic cooling does not present a problem because the relevant rotational selection rule ($\Delta J=+/-1$) is sufficiently rigorous to preclude rotational transfers out of a cooling cycle in the time needed for TE (or RE) cooling.

Vibrational electronic cooling also does not present a problem because the times needed to perform significant TE (or VE) cooling are much less than the times needed for significant losses due to spontaneous decay.

Therefore, we focus on strategies for handling ''collisionless'' TE cooling (and exclude losses incurred during RE and VE cooling). For illustration, the Cs_2 $B-X$, $v'=0$ cooling cycle ($v_c' = 0$, $v_c'' = 0$–9) will be used as a working ex-

TABLE IV. Molecule cooling wavelengths (in nm) and range of vibrational states (0 to v''_{max} reached in emission from $v'=0$ with Franck–Condon factors greater than about 10^{-5}).

Molecule	$A-X$ bands	$B-X$ bands
$^7Li_2$	713–997	490–559
	0–12	0–7
$^{23}Na_2$	682–818	492–539
	0–16	0–11
$^{39}K_2$	857–994	650–693
	0–18	0–9
$^{85}Rb_2$	927–1022	681–715
	0–17	0–12
$^{133}Cs_2$	1039–1170	766–790
	0–28	0–9

ample. In the analysis that follows, we examine cooling cycle losses due to spontaneous emission.

In the selection of a molecular cooling cycle, electronic, and vibrational states are chosen that minimize the number of vibrational states involved in the cycle (v'_c, v''_c). For most molecules this is satisfied by the selection of the single, common, upper level $v'_c = 0$ [this minimum occurs naturally in some molecules when two electronic states can be found that have nearly the same R_e ($R'_e \sim R''_e$) (as with the alkaline earth hydrides and halides)]. For the alkali dimer $A-X$ and $B-X$ bands, $R'_e > R''_e$ prevails. Table IV lists the wavelength and v'' ranges that result, with the $v'=0$ restriction at a fixed Franck–Condon factor (FCF) cut off of $\sim 10^{-5}$. Note the

narrow wavelength and v''_c ranges that result for the Cs_2 $B-X$ bands (766–790 nm and $v''=0-9$). Thus for Cs_2 the cooling cycle ($v'=0$, $v'' \sim 0-9$) can be anticipated.

The ''high gain amplifier'' approach

We now examine the conditions under which a cooling cycle can be considered ''sufficiently closed.'' Using Cs_2, the relevant normalized transition probabilities (FCF's for the cooling cycle are given in column 2 of Table V[45] (column 3 is the corresponding running sum over v''). For an average Cs_2 molecule to be TE cooled, it must undergo 1.1×10^5 transitions (from Table II). This means that the probability of spontaneous radiation outside the cooling cycle must be much less than,

$$1/(\text{\#photons for TE}) = 1/(1.1 \times 10^5) = 9.1 \times 10^{-6}.$$

This defines a closure condition for TE cooling. That is, out of 1.1×10^5 transitions, the probability should be much less than 1 for spontaneous transitions to levels outside the cooling cycle. Since the total transition probability (column 3) to $v''=0-9$ is 0.999 990 50, the probability for transitions to $v'' \geq 10$ is $1-0.999\,990\,50 = 9.5 \times 10^{-6}$. A molecule would be expected to make a transition to $v'' \geq 10$ about once ($1.1 \times 10^5 \times 9.5 \times 10^{-6} \sim 1$) during TE cooling (this marginally satisfies the closure condition inequality; in practice the FCF's should be much smaller, e.g., 10^{-7}). Thus if sidebands of sufficient strength can be generated that saturate the *actual*

TABLE V. Normalized transition probabilities (FCF for the Cs_2 $B-X$ bands), running sums, and transition wavelengths for the cooling ($v'=0$, v'') (columns 2, 3, and 4) and repump ($v'=5$, v'') (columns 5, 6, and 7) cycles, respectively.

v''	$|\langle v'=0|v''\rangle|^{2a}$	$\Sigma_{v''}|\langle v'=0|v''\rangle|^2$	λ (nm), cooling	$|\langle v'=5|v''\rangle|^{2a}$	$\Sigma_{v''}|\langle v'=5|v''\rangle|^2$	λ (nm), repumping
0	0.196 472 53	0.196 472 53	766.88	0.015 062 12	0.015 062 12	757.05
1	0.314 356 05	0.510 828 59	769.35	0.127 947 01	0.143 009 13	759.46
2	0.258 715 03	0.769 543 62	771.82	0.161 958 24	0.304 967 37	761.87
3	0.143 975 07	0.913 518 69	774.30	0.000 971 75	0.305 939 12	764.29
4	0.060 042 01	0.973 560 70	776.79	0.108 997 90	0.414 937 02	766.71
5	0.019 804 43	0.993 365 13	779.29	0.013 928 41	0.428 865 42	769.14
6	0.005 344 05	0.998 709 18	781.79	0.053 932 09	0.482 797 52	771.58
7	0.001 037 37	0.999 746 56	784.29	0.090 048 78	0.572 846 30	774.02
8	0.000 204 33	0.999 950 89	786.80	0.006 964 20	0.579 810 51	776.46
9	0.000 039 61	0.999 990 50	789.32	0.035 954 73	0.615 765 24	778.91
10	0.000 007 70	0.999 998 20	791.84	0.120 011 06	0.735 776 29	781.37
11	0.000 001 50	0.999 999 70	794.37	0.129 890 51	0.865 666 80	783.83
12	0.000 000 29	0.999 999 99	796.90	0.081 950 87	0.947 617 67	786.29
13				0.035 954 73	0.983 572 40	788.77
14				0.011 984 91	0.995 557 31	791.24
15				0.003 077 21	0.998 634 52	793.72
16				0.000 962 03	0.999 596 55	796.21
17				0.000 284 24	0.999 880 79	798.70
18				0.000 083 99	0.999 964 78	801.19
19				0.000 024 81	0.999 989 59	803.69
20				0.000 007 33	0.999 996 92	806.19
21				0.000 002 17	0.999 999 09	808.70
22				0.000 000 64	0.999 999 73	811.21
23				0.000 000 19	0.999 999 92	813.72
24				0.000 000 06	0.999 999 97	816.24
25				0.000 000 02	0.999 999 99	818.76

[a]Normalized, $\Sigma_{all\ v''}|\langle v'|v''\rangle|^2 = 1$.

cooling cycle ($v_c' = 0$, $v_c'' = 0-9$; as determined by the closure condition), then TE cooling should be effective. This requires an amplifier of sufficient gain.

The ''low gain amplifier repumping'' approach

Suppose, on the other hand, amplifier gain is not high enough, and one can only achieve MSFL cooling cycle side bands of sufficient strength for an *unclosed* cooling cycle (say $v'=0$, $v''=0-7$). We know that such a cycle would lose population by spontaneous emission to $v'' \geq 8$. Since the probability for transitions to $v'' \geq 8$ is

$$1 - 0.999\,746\,56 = 0.000\,253\,44,$$

an average molecule would be expected to undergo transitions to $v'' \geq 8$ about $1.1 \times 10^5 \times 0.000\,253\,44 \sim 28$ times during this *unclosed* TE cooling cycle.

Therefore, we next select a repump cycle (v_r', v_r'') for the levels $v'' \geq 8$. We note that there are large FCF's for transitions from these levels to $v'=5$. The appropriate transition probabilities for the repump level $v'=5$ are given in column 5 of Table V (column 6 is the running sum). First we consider spontaneous emissions out of the repump cycle ($v'=5$, v''). Using the *same* closure condition previously used for the cooling cycle, we find that the *actual* repump cycle ($v_r'=5$, $v_r''=0-19$) satisfies this criterion. This defines the $v'=5$ repump cycle, which can be divided into three regions of transition probability,

I	$v_r''=0-7$	0.572 846 30
II	$v_r''=8-19$	0.427 143 29
III	$v_r''>19$	0.000 010 41
TOTAL		1.000 000 00

Region I is for *unidirectional* transfers to the cooling cycle levels, region II is for the *bidirectional* repumping levels, and region III is for *unidirectional* losses to $v_r''>19$.

Note that when a molecule leaves the cooling cycle and enters the repump cycle, there is significant probability that it will radiate to region II rather than region I. This inefficiency in repumping must be allowed for with the factor

$$1/0.572\,846\,30 \sim 1.75,$$

which represents how many times a molecule must be excited on the repump cycle to have near unit probability of returning to the cooling cycle (region I).

Therefore, an average molecule effectively enters the repump cycle

$$28 \times 1.75 \sim 50$$

times during the TE cooling cycle. If each time the molecule enters the repump cycle there is a probability of 1.041×10^{-5} for a transition to $v_r''>19$, then the fraction of the molecules lost is

$$1.041 \times 10^{-5} \times 50 = 5.205 \times 10^{-4},$$

meaning that ~99.95% of the molecules stay in the repump cycle and therefore in the cooling cycle as well.

TABLE VI. Molecule cooling efficiency parameters for the alkali metal dimer $B-X$ bands (see the text for definitions).

Molecule	ν_{00} (cm^{-1})	B_e'' (cm^{-1})	ω_e'' (cm^{-1})	ϵ(TE) (10^{-12})	ϵ(RE) (10^{-6})	ϵ(VE) (10^{-2})
^{7}Li$_2$	20 400	0.673	351	100.0	66.0	1.70
^{23}Na$_2$	20 300	0.155	159	30.0	15.0	0.78
^{39}K$_2$	15 370	0.057	92	13.0	7.4	0.60
^{85}Rb$_2$	14 660	(0.026)	57	6.0	3.5	0.40
^{133}Cs$_2$	13 040	0.013	42	3.4	2.0	0.30

Next, we determine the conditions under which repumping would fail. Since each molecule must effectively enter the repump cycle 50 times, if the probability of leaving the repump cycle exceeds

$$1/50 = 0.02,$$

repumping would be expected to fail. Using the probabilities (column 6) in Table V, we find that the total probability for transitions to $v''=0-13$ is 0.983 572 40 and for transitions to $v''>13$ the probability is 0.016 427 60. Therefore, we can specify the *minimum actual* $v'=5$ repump cycle as ($v_r'=5$, $v_r''=8-13$),

I	$v_r''=0-7$	0.572 846 30
II	$v_r''=8-13$	0.410 726 10
III	$v_r''>13$	0.016 427 60
TOTAL		1.000 000 00

Since the total probability for a transition to region III is less than 0.02, the repump cycle is considered sufficiently *closed*.

The total number of photons needed for repumping the ($v_c'=0$, $v_c''=0-7$) cooling cycle can be estimated by considering that the probability of a given molecule scattering (n) photons per repump cycle is

$$P(n) = n \times [(0.410\,726\,10)^{(n-1)}] \times (0.572\,846\,30),$$

$$(n=1,2,\ldots,\infty).$$

The total probability, given by the sum over n, is $\Sigma_{n=1}^{16} P(n) = 1.65$ [we truncate the sum for $n>16$, where $P(n)$ is $<10^{-5}$]. Thus the number of repump photons needed per molecule is,

$$28 \times 1.65 = 46.$$

Although this is much less than the number absorbed from the cooling sidebands (~1.1×10^5 photons), the transition rate for repumping must be comparable to that in the cooling cycle in order that molecules not spend significant time outside the cooling cycle thereby falling behind the frequency chirp. Fortunately, the repump transitions have favorable FCF's, allowing somewhat lower intensities to be used.

Finally, in Table VI are given the molecular TE, RE, and VE quantum cooling efficiency parameters for the alkalis [defined as $\epsilon = (\nu_2 - \nu_1)/\nu_2$, where ν_1 is the frequency of the absorbed photon and ν_2 is the frequency of the spontaneously emitted photon, with $\nu_2 > \nu_1 > 0$]. Note that for Cs$_2$ ϵ(VE)
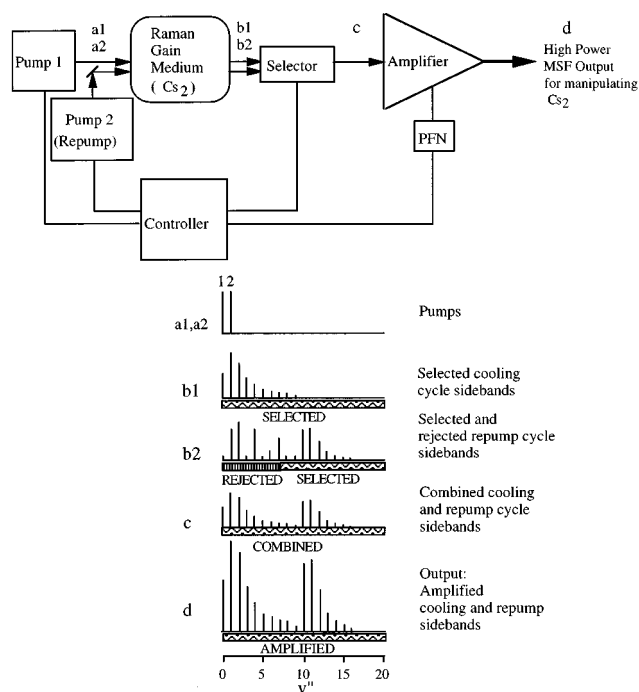
FIG. 4. Block diagram of the MSF laser for cesium dimers, when repumping is needed.

$>1500\epsilon$(RE) and ϵ(RE)$>6\times10^5\epsilon$(TE). Vibrational electronic cooling can be remarkably efficient. In the case of Cs_2, the smallest ϵ(VE) is 0.3%. The actual efficiencies for RE and VE will be $\sim J$ and $\sim\Delta v$ times these parameters. Further, it is worth noting that the theoretical maximum VE cooling efficiency (approaching 100%) can actually occur in the case of ''nested'' electronic states when $E(v_c')$ $= E(v_c''(max))$ (i.e., as $\nu_1\to0$, the upper level v_c' becomes coincident with the highest v_c'').

APPENDIX B: LOW GAIN AMPLIFIER REPUMP MSF LASER DESIGN

The block diagram for the basic MSF laser was given in Fig. 1. However, if repumping is needed, this basic design must be modified. Such a modified block diagram of the major components for the MSF lasers in the case of repumping is shown in Fig. 4. Two CW narrow band pump lasers are synchronized by the controller which also tunes and chirps the pump frequencies. Pump lasers (1) and (2) excite coherent (two-photon) RSR transitions in Cs_2 molecules producing outputs ($b1$) and ($b2$), respectively. The selector removes unwanted repump sidebands from ($b2$) and combines the residual with ($b1$) to give selected output (c). Output (c) is then amplified by the broadband pulsed amplifier to give a burst (>11 ms) of chirped RSR sidebands (d) for cooling and repumping (see Fig. 5).

Raman gain medium operation is analogous to well known ring optically pumped lasers (OPL's).[25,46,47] Gain media consisting of supersonic beam expansions of Na_2 have been shown to have exceptionally low thresholds for lasing $\lesssim100$ μw, with possible improvement to ~100 nw.[47] For
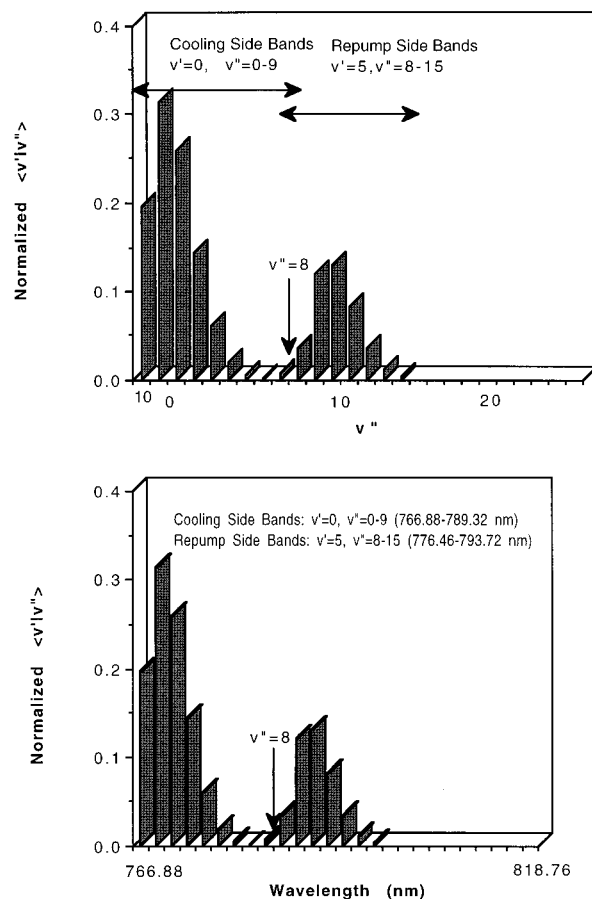

FIG. 5. Cooling and repumping sidebands for the cesium dimer MSFL.

both, the forward RSR gain is greater than that due to population inversion (usually by a factor of 10 to 1000 in the alkalis); hence neither population inversion nor optical cavity are needed.

The selector is a computer controlled, high rejection ($\sim10^6$) dispersive filter and shutter. This device selects the appropriate side bands for cooling (and repumping) (Table III), while rejecting unwanted frequencies.

The selected side bands are amplified by a high gain (10^5-10^7), broadband, multipass traveling wave amplifier (we propose a design similar to that used by Herriott).[48] Long pulse optically pumped, broadband gain media such as alexandrite, titanium sapphire, semiconductors, or dyes with radiative lifetimes in the $10^{-6}-10^{-4}$ s range would be best suited for VE and RE cooling. For quasicontinuous TE cooling, longer pulse durations require gain media with longer lifetimes (such as alexandrite).

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