CHEMICAL LASERS: A THERMODYNAMIC ANALYSIS OF A SYSTEM IN DISEQUILIBRIUM[*]

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The application of energy and entropy cycles to the analysis of chemical lasers is discussed and illustrated by explicit results for six reactions. Measures of the actual and the limiting efficiency (and bounds on these efficiencies) are derived and computed. In particular, it is shown that the nascent rotational excitation of the reaction products is available (on thermodynamic grounds) for lasing. The entropy changes during the different stages of lasing are computed (invoking the state property of the entropy) as the difference between the initial and final values. Explicit algorithms for computing the different entropies are provided.

1. Introduction

This paper has two distinct goals. On the theoretical side we consider the application of thermodynamic-type arguments to a bulk, macroscopic system which is not in thermal equilibrium. From a more down to earth point of view we apply the thermodynamic arguments to analyze the operation of chemical lasers [1—3] pumped by (any one) of the following reactions

$F + H_2 \rightarrow H + HF$	(I)		$F + DH \rightarrow H + DF$	(IV)
$F + D_2 \rightarrow D + DF$	(II)		$Cl + HI \rightarrow I + HCl$	(V)
$F + HD \rightarrow D + HF$	(III)		$O + CS \rightarrow S + CO.$	(VI)

The formal and computational goals are interwoven in the discussion. Chemical lasers are used, as an example of a system in thermal disequilibrium, to illustrate the theoretical arguments. Conversely, the thermodynamic analysis provides additional insight into the workings of the chemical laser. It should however be explicitly stated that we are more concerned with the method rather than with deriving entirely new results. What we present (and illustrate) is an alternative point of view and many of our conclusions have been previously derived via different approaches.

The key concept in the discussion is that of the entropy as a state function [4—11]. The system need not be in thermal equilibrium in order that the entropy be well defined. It is sufficient that the state be reproducible. The information-theoretic approach to statistical mechanics has argued this point for some time. The novel point here is that we shall not treat purely schematic situations nor will we recover known, equilibrium, results. Rather, we provide actual working expressions for a molecular gas in disequilibrium and, in the final step, come up with numbers. We do limit ourselves however to the (important but restrictive) case of a system which is uniform in space.

The methods used in this paper were previously employed by us in the study of microscopic disequilibrium [7, 11—14]. There we have shown how one can characterize the population of molecular energy levels and how such non-equilibrium distributions can be assigned an entropy. We follow the same approach in the present application.

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Since the gas is (by assumption) spatially uniform, its state (at any given instant) is specified in terms of the distribution of the internal and translational energies of the molecules. The entropy of the gas will then be defined in terms of these distributions. A particularly important property which we will repeatedly invoke is the following: Among all systems of a given mean energy, the one in thermal equilibrium has the highest entropy. We shall demonstrate this assertion later (section 2) as well as provide the necessary algorithms for the explicit computation of the entropy. From this point on, however, we shall assume that there is a measure, called entropy, which can be computed, if the distribution function of the molecular energy states is known. As an example we can take the nascent products of an exoergic chemical reaction. Chemical lasers and chemiluminescence type techniques [15–18] have established the distribution of the unrelaxed reaction products. Hence, the distribution of nascent reaction products can be assigned an entropy. If these nascent products were to relax adiabatically (and without the presence of a buffer gas) they would eventually reach a state of thermal equilibrium. While this (equilibrium) state would have the same mean energy as the nascent products it would necessarily have a higher entropy.

For the purpose of the analysis we have adopted the following (oversimplified) scheme for the operation of a chemical laser [15–17]. We start from the reactants (in thermal equilibrium) in the presence of a large excess of an inert, buffer, gas. The buffer gas is assumed to retain its temperature throughout. (The mean energy content of the buffer gas is thus constant. It serves as the heat reservoir.) Our discussion is thus limited* to an isothermal operation of the laser. Collisions between the reactants lead to the formation of nascent product molecules. Consider now these newly formed products before they had time to engage in subsequent collisions with the molecules of the buffer gas. The mean energy of these nascent product molecules equals the mean energy of the *reactive* reactant molecules. For the reactions under consideration (and most other reactions) the mean energy of the reactive reactants exceeds the mean energy of all reactants. The difference is the, so called, activation energy of the reaction [16] (at the given temperature). The magnitude of this increase in energy content in going over from thermal reactants to nascent products is quite small for the exoergic reactions under consideration. Leaving the details to the appendices, fig. 1 shows the (mean) energy content at 300 K for reaction (V).

The exoergicity of the reaction is released partly as internal energy of the products and partly as relative translational energy. Collisions with the buffer gas molecules rapidly equilibrate the translational motion and relax the rotational energy. We assume that the rotational relaxation is sufficiently efficient so as to equilibrate all the rotational states in any given vibrational manifold [15,17]. Any excess energy (over the thermal mean) released into the translational and/or the rotational energy of the nascent products is thus very quickly relaxed (in our model, not necessarily in reality [19,20]). This excess energy is removed into the buffer and is not available to extract as work. A
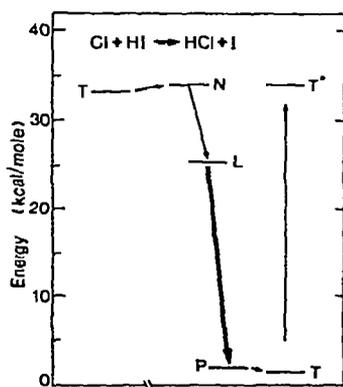

Fig. 1. Energy cycle for reaction (V) at 300 K. Starting with thermal reactants (T, on the left) the energy increases (by the activation energy) on going to the nascent, (N), unrelaxed products. The energy loss on going to the lasing products (L) occurs due to the translational and rotational relaxation of the nascent products. Lasing occurs between the lasing and post-lasing (P) products. The residual vibrational excitation of the post-lasing products is relaxed during their thermalization to give the equilibrated, thermal products (T). T* designates the 'heated products' stage, (discussed in section 2), where the thermal products are raised in temperature until their (mean) energy content equals that of the nascent products. The explicit expressions used in the computations are given in appendix C.

* This limitation is adopted only for simplicity. One can readily modify the formulation so as to incorporate heating and cooling of the buffer medium. See O. Kafri and R.D. Levine, Optics Commun. 12 (1974) 118.

central question is whether such losses are, in principle, unavoidable. Must one, no matter what, lose a fraction of the exoergicity if the system is to operate as a laser? It turns out that the answer is yes and that the actual losses (in our model) exceed the thermodynamic threshold. In other words, the available work (under ideal operating conditions and when there is complete translational and rotational relaxation), is less than the maximal amount allowed by thermodynamics.

We refer to the distribution of product molecules which retained the relative vibrational populations of the nascent products but is in translational and rotational equilibrium (with the buffer gas) as the lasing products. The (mean) energy of the lasing products (shown in fig. 1 as L) is available for chemical laser action. It should be clear that our different 'stages' have no particular significance from a kinetic point of view. There is no intended implication that all (or some) of the product molecules are in the 'lasing products' stage at any given instant of time. In the same way that not all products are simultaneously 'nascent'. These constructs simply represent thermodynamic stages, i.e., states of the system whose energy and entropy can be readily computed and interpreted. The 'state property' of the energy and entropy means that the changes as a mole of reactants is converted to a mole of products can be computed as a sum of the changes between the consecutive stages.

As has been discussed before [1,21], lasing in a diatomic gas does not require vibrational population inversion. We shall return to these considerations in section 3. Here we merely note that while in principle lasing can proceed until the vibrational distribution has been thermalized, in practice, due to losses, this is not the case. We allow for this possibility by the inclusion of a 'post lasing' stage. This corresponds to a highly relaxed vibrational population distribution but one which is still not in complete thermal equilibrium with the buffer gas. We characterize this distribution by its mean vibrational energy content (cf. appendices).

The final stage is that of products in equilibrium with the buffer gas. The (small) energy difference between the post lasing and the thermalized products stages is again taken up by the buffer gas.

The following is then a very schematic summary of the model of a chemical laser. An energy-rich system in disequilibrium (the reaction products) is coupled (via collisions) to a heat reservoir (the buffer gas). A fraction of the excess energy of the system (excess over the energy content at equilibrium with the reservoir) is extracted as pure work[*]. The complementary fraction is dissipated into the reservoir. The following sections consider the construction and interpretation of the energy and entropy cycles for such a process.

The concepts of entropy and (mean) energy of the system are sufficient for the discussion of available energy, section 2. The discussion there is carried out with special reference to isothermal operation, to conform to our simple model of the laser. Section 3 considers a thermodynamic treatment of lasing at a particular vibrotational transition and section 4 extends the treatment to lasing at several frequencies. All the algorithms used in the actual computational work have been collected in three appendices.

2. Entropy and pumping efficiency [9,10]

Chemical lasers are similar to electrochemical cells in that they convert chemical energy directly into work. In this section we consider their maximal efficiency, i.e., the fraction of chemical energy that could, in principle, be converted to work. We shall show that (as in the case of cells) the maximal possible (or 'pumping') efficiency is quite high, usually above 90%. We shall then turn to the model discussed in the introduction to find that rotational relaxation is avoidable (on thermodynamic grounds) and that the rotational excitation of the nascent products can be extracted as pure work.

We consider an energy rich system (the nascent reaction products) coupled to a heat reservoir (the buffer gas). Work is done by the system until it is in equilibrium with the reservoir. Let the amount of energy released by the reaction be E_p [per mole; see eq. (11) below]. What fraction of this energy is available as work?

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[*] We have assumed here that the laser light being well collimated and well defined in frequency carries practically no entropy and hence is (thermodynamically) equivalent to pure work [9,23,24].

During the process the reservoir maintained its temperature T. If the entropy transferred from the system to the reservoir is ΔS_M, the energy Q transferred from the system to the reservoir is, at least, $T\Delta S_M$. (The inequality, i.e. $Q \geqslant T\Delta S_M$ follows from conventional arguments since the coupling of system and reservoir need not be reversible). Hence, the amount of energy of the system available as work is $E_p - T\Delta S_M$. The efficiency is thus

$$\eta = (E_p - T\Delta S_M)/E_p = 1 - T\Delta S_M/E_p. \tag{1}$$

Thus far there was no real need to depart from very conventional arguments. We now want however to relate the entropy change of the reservoir to the entropy change of the system. It is at this point that we depart from the classical tradition since, in the initial, energy rich, state the system is not in thermal equilibrium and hence cannot be assigned an 'equilibrium' entropy.

The distribution of nascent products can be characterized as follows[*] The chemical reaction leads to formation of products in different quantum states i. The (relative) rates of formation of these product states can be measured. The bulk chemical change corresponds, on the molecular level, to many, many binary reactive collisions. Hence the relative rates of formation correspond to the probabilities of formation of the different product states. Each quantum state i of the products can then be assigned a probability $P(i)$ which is the fractional rate of formation of state i. When the experiment is repeated, the same probabilities will be assigned. (Since the number of reactive collisions is so very high, probabilities equal the observed frequencies.) Hence, the distribution of nascent products can be characterized by an 'information-theoretic' [4—11] entropy

$$S[i] = -R\sum_i P(i) \ln P(i). \tag{2}$$

Here R is the gas constant and the logarithm is to the natural base. The square bracket notation indicates that the entropy was computed as a sum over quantum states. We show in appendix C how to reduce (2) to a 'working' expression for an explicit computation. We shall also show that for thermal equilibrium (2) reduces to the known expression for the entropy of a gas. At this point it is sufficient to note that the entropy is positive (for $x < 1$, $\ln x < 0$) and is defined even when $P(i) \to 0$ (since $x \ln x \to 0$ as $x \to 0$). The maximal value of the entropy obtains when all the probabilities are equal.

The highest possible efficiency obtains when the entropy increase of the reservoir is just balanced by the change ΔS_p

$$\Delta S_p = S_N - S_T \tag{3}$$

in entropy of the system. Here S_N and S_T are the entropies of the nascent and thermalized products respectively. This highest value is denoted η_p:

$$\eta_p = 1 - T\Delta S_p/E_p \tag{4}$$

and obtains when $\Delta S_M = \Delta S_p$.

We now prove that

$$\Delta S_p = S_N - S_T \leqslant E_p/T. \tag{5}$$

The equality applies only when the nascent products are also in equilibrium (at the temperature T). The efficiency (η_p) is thus nonnegative and vanishes only when no work can be extracted, (i.e., when the nascent products have the same distribution as the thermalized products. This necessarily implies $E_p = 0$).

The entropy S_N is computed, in principle, from eq. (2) where $P(i)$ is now the (quantum state) distribution of the nascent products. Similarly, we introduce $U(i)$,

$$U(i) = \exp(-E_i/RT)/Q, \tag{6}$$

as the distribution of the thermalized products. Q is the (ordinary, equilibrium) partition function defined so that

$\Sigma_i U(i) = 1$. The entropy S_T is defined by eq. (2) as well, with $U(i)$ as the distribution. Explicitly

$$S_T = -R \sum_i U(i) \ln U(i) = -R \sum_i U(i) \left[-(E_i/RT) - \ln Q \right] = T^{-1} \sum_i E_i U(i) + R \ln Q. \tag{7}$$

The last line is the standard expression for the entropy of a system in thermal equilibrium [6].

To prove the result (5) we employ the ubiquitous inequality [11]

$$\ln x \leqslant x - 1, \tag{8}$$

(with equality for $x = 1$). It thus follows that

$$-\sum_i P(i) \ln [P(i)/U(i)] = S_N + \sum_i P(i) \ln U(i) = \sum_i P(i) \ln [U(i)/P(i)] \leqslant \sum_i P(i) \{[U(i)/P(i)] - 1\} = 0,$$

and hence that

$$S_N \leqslant - \sum_i P(i) \ln U(i). \tag{9}$$

The inequality (9) provides a general bound on the entropy in terms of the actual distribution (i.e., $P(i)$) used to define S_N and some arbitrary normalized distribution *, $U(i)$.

To derive the explicit bound (5) one merely needs to insert (6) for the [in (9), arbitrary] distribution $U(i)$. This gives

$$S_N \leqslant T^{-1} \sum_i E_i P(i) + R \ln Q = S_T + E_p/T. \tag{10}$$

Here E_p is the difference in the energy content of the nascent and the thermalized products,

$$E_p = \sum_i E_i P(i) - \sum_i E_i U(i). \tag{11}$$

Another very useful bound on S_N is

$$S_N \leqslant S_{T^*}. \tag{12}$$

Here S_{T^*} is the entropy of the thermalized products at such temperature T^* that their energy content equals the energy content of the nascent products. To prove (12) we merely insert in (9) the distribution

$$U^*(i) = \exp(-E_i/RT^*)/Q^*. \tag{13}$$

Here T^* is determined by the implicit equation [cf. (11)]

$$E_p = \sum_i E_i U^*(i) - \sum_i E_i U(i), \tag{14}$$

where $U(i)$ is the thermal distribution (6) (at the buffer gas temperature T). E_p is available from thermochemical data.

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* In fact it is sufficient that $\Sigma_i U(i) \leqslant 1$ for (9) to hold.

An upper bound on ΔS_p,

$$\Delta S_p \leqslant S_{T*} - S_T \tag{15}$$

and a lower bound on the pumping efficiency η_p

$$\eta_p = 1 - T(\Delta S_p/E_p) \geqslant 1 - T(S_{T*} - S_T)/E_p \tag{16}$$

can thus be obtained, even in the absence of any information on the distribution of the nascent products. Standard algorithms for the (equilibrium) entropy S_T are available [6] but common experience with the magnitude of entropies of hot gases is sufficient to indicate that $S_{T*} - S_T$ is, typically, of the order of 10–20 eu even for highly exothermic reactions so that η_p is seldom significantly below unity.

There are therefore two entropy differences that characterize the energy available from the nascent products. One, $\Delta S_p = S_N - S_T$, is the entropy difference between the nascent and thermalized products. $T\Delta S_p$ is the minimal energy loss to the reservoir or $\eta_p = 1-T\Delta S_p/E_p$ is the highest possible efficiency. $T\Delta S_M$ is the actual energy loss or $\eta = 1-T\Delta S_M/E_p$ is the actual efficiency. In the model of the chemical laser outlined in section 1, the major energy loss to the reservoir is the excess (over thermal) translational and rotational energy of the nascent products. Chemical reactions seldom release less than about 1/3 of their exoergicity into translation and rotation and since E_p is roughly equal to the exoergicity we have that, typically, $(T\Delta S_M/E_p) > 1/3$. On the other hand, for these reactions $\Delta S_p < \Delta S_M$ so that not all the energy that is thermodynamically available is actually extracted as laser light. Clearly, the fault is with the mechanism that allows more dissipation of energy into the reservoir than is thermodynamically essential. Are there however any compensating aspects? What purpose can the excessive entropy loss $(\Delta S_M - \Delta S_p)$ serve. To explore this point we consider in section 3 lasing at a particular transition.

Detailed algorithms for computing the energies and entropies are provided in the appendices. Table 1 is a summary of the magnitude of the different measures employed in this section.

Table 1
Pumping parameters of chemical lasers[a)]

	E_p	ΔS_p	ΔS_M	η	η_p	S_N	S_T	S_{T*}	T^*
$F + H_2 \rightarrow HF + H$	33.1	5.6	37.0	0.66	0.95	124.9	119.3	134.7	5650
$F + D_2 \rightarrow DF + D$	33.2	6.9	44.0	0.60	0.94	129.4	122.5	138.1	5490
$F + HD \rightarrow HF + D$	32.3	7.0	45.3	0.58	0.93	128.2	121.2	136.5	5530
$F + HD \rightarrow DF + H$	33.8	6.6	50.1	0.55	0.94	127.2	120.6	136.3	5610
$Cl + HI \rightarrow HCl + I$	32.5	8.2	30.1	0.72	0.92	139.0	130.8	146.3	5390
$O + CS \rightarrow CO + S$	90.0	16.6	184.3	0.38	0.94	148.7	132.1	155.3	13260

[a)] Entropies in entropy units (eu $\equiv$ cal mol^{-1} deg^{-1}). Energies in kcal mol^{-1}. Temperatures in K. For computational details see appendices A and C.

3. Population inversion and amplification of light

That it is not possible for a macroscopic body to decrease its energy by laser emission (or light amplification) can be seen as follows. Consider an energy rich macroscopic body within an enclosure. Let the body emit light. The body loses energy and hence entropy. The entropy of the isolated enclosure (cooler body plus light) cannot decrease. It follows that entropy must be associated with the emitted radiation. It is possible for a body to lose energy as radiation only when this radiation carries its appropriate share of entropy.

Ordinary radiation is not equivalent to pure work since it has to be assigned an entropy, depending on its spectral width and angular (spatial) distribution. Only a coherent (well collimated and with a narrow frequency range) pencil of radiation carries no entropy [9,23,24]. Amplification of light (or lasing) requires that the emitted radia-

tion be coherent and so equivalent to pure work. Hence, a macroscopic body cannot lose its entire excess energy as laser emission.

Once it is realised that laser light carries practically no entropy and is equivalent to work, the restriction above is obvious from the second law. A macroscopic body cannot undergo a process where the only net effect is that the body cools down while an equivalent amount of energy is available as work*.

Lasing is possible if the entire available energy is not extracted as light energy but some of it is 'wasted', [9,10, 26], say, by delivering it to a cold heat reservoir. As an example we consider lasing at a particular p-branch (v, $J \rightarrow v - 1, J + 1$; fig. 2) transition of a diatomic molecule.

We consider the nascent diatomic reaction products after completion of translational and rotational relaxation (the 'lasing products'). Let $P(v, J)$ be the population of the vibrotational levels so that the vibrotational entropy is**

$$S[v, J] = -R \sum_{v, J} P(v, J) \ln [P(v, J)/(2J + 1)]. \tag{17}$$

When the populations change by a small amount ($\delta P(v, J)$) the corresponding change in the entropy is

$$\delta S = -R \sum_{v, J} \{1 + \ln [P(v, J)/(2J + 1)]\} \delta P(v, J) = -R \sum_{v, J} \ln [P(v, J)/(2J + 1)] \delta P(v, J). \tag{18}$$

The first term does not contribute since the change in the populations must be such that the total number of molecules is unchanged

$$\delta \sum_{v, J} P(v, J) = \delta(1) = 0 = \sum_{v, J} \delta P(v, J). \tag{19}$$

Let a small fraction, δP, of molecules emit light while making a $v, J \rightarrow v-1, J + 1$ transition. Here $\delta P = \delta P(v-1, J + 1) = -\delta P(v, J)$. The change in the entropy (per mole) is δS_L,
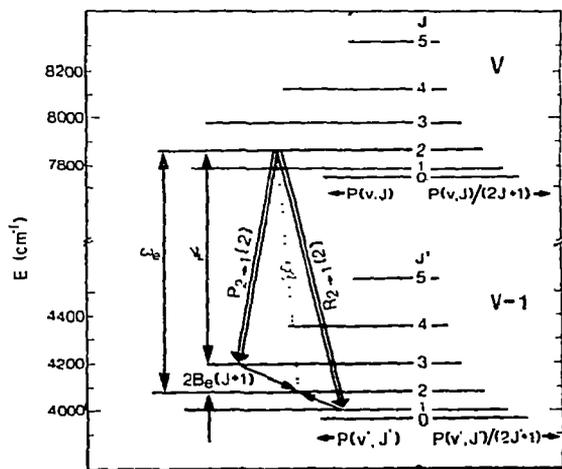

Fig. 2. The funneling mechanism for lasing when the rotational relaxation is fast. Shown are P- and R-branch transitions in HF. $[P_{v \rightarrow v-1}(J)$ denotes the $v, J \rightarrow v - 1, J + 1$ transition. The vibrational population in the drawing corresponds to $P(v) = P(v-1)$ (i.e., $T_v \rightarrow +\infty$).] Following the radiative transition is the rotational relaxation (where v is unchanged) and then the (conceptual) pumping back where only v but not J is changed.

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* This is possible for a system at a negative temperature [9,25–26]. However, a macroscopic body cannot possess a negative temperature. That does not exclude a more limited situation where a particular transition is assigned a negative temperature, as discussed below.

** The degeneracy factor, $(2J + 1)$, can be traced to the summation over the $2J + 1$ (so called 'magnetic') states within each level J, cf. appendix C.

$$\delta S_{\rm L} = \frac{\delta S}{\delta P} = \frac{\delta S}{\delta P(v-1,J+1)} - \frac{\delta S}{\delta P(v,J)} = R \ln \left[P(v,J)/(2J+1)\right] - R \ln \left[P(v-1,J+1)/(2J+3)\right]. \quad (20)$$

If the transition is to lase we must have $\delta S_{\rm L} \geqslant 0$ for otherwise the emitted light would have to carry away entropy (of, at least, $-\delta S_{\rm L}$, per mole) and ordinary fluorescence would result. The condition for lasing is thus [10]

$$P(v,J)/(2J+1) \geqslant P(v-1,J+1)/(2J+3) \quad (21)$$

as previously derived [1, 21, 22] from non-thermodynamic considerations.

The entropy change, $\delta S_{\rm L}$, upon lasing reflects the changes in the vibrotational populations. Since during the lasing the gas loses energy one can introduce a 'lasing temperature', $T_{\rm L}$, as the coefficient of proportionality between the increase in energy ($-h\nu_{\rm L}$, where $\nu_{\rm L}$ is the transition frequency) and increase in entropy ($\delta S_{\rm L}$), $-h\nu_{\rm L} = T_{\rm L}\delta S_{\rm L}$ or

$$\delta S_{\rm L} = -h\nu_{\rm L}/T_{\rm L}. \quad (22)$$

Lasing thus corresponds to a 'negative' temperature $T_{\rm L}$. (It should be clear, however, that $T_{\rm L}$ is simply a convenient measure for $\delta S_{\rm L}$.) Lasing is possible as long as $T_{\rm L}$ is negative and terminates when the populations are such that the equality in (21) obtains, i.e., when $\delta S_{\rm L} \to 0$ or[*] $T_{\rm L} \to -\infty$. Figs. 3 and 4 show $T_{\rm L}$ for different transitions in the HF chemical laser for two different situations. One is that of complete rotational relaxation when[**]

$$P(v,J) = P(v)\,P(J|v), \quad (23)$$

$$\sum_{J} P(J|v) = 1, \quad (24)$$

$$P(J|v) = Q_{\rm R}^{-1}(2J+1) \exp\left[-hcB_e J(J+1)/RT\right]. \quad (25)$$

This is the case extensively treated in this paper. For comparison sake, fig. 4 shows $T_{\rm L}$ for a nascent rotational distribution when $P(J|v)$ is of the form[†] [14,27]

$$P(J|v) = (2J+1)\left[E - E_v - E_J(v)\right]^{1/2} \exp\left[-\theta_0 - \theta_{\rm R} E_J(v)/(E - E_v)\right]. \quad (26)$$

It is seen that $T_{\rm L}$ is higher (i.e., nearer to -0) for the nascent rotational distribution. Writing (20) and (22) together as

$$\frac{P(v,J)}{(2J+1)}\left(\frac{P(v-1,J+1)}{(2J+3)}\right)^{-1} = \exp\left(-h\nu_{\rm L}/RT_{\rm L}\right), \quad (27)$$

it is clear that a higher $T_{\rm L}$ implies a higher $\delta S_{\rm L}$ for the transition.

When the rotational distribution is in thermal equilibrium (21) is equivalent to

$$2hcB_e(J+1)/RT \geqslant \ln\left[P(v-1)/P(v)\right], \quad (28)$$

where the inequality applies when $\delta S_{\rm L} > 0$ (or $T_{\rm L} < 0$) and the equality applies 'at threshold', i.e., when $\delta S_{\rm L} = 0$. It is thus not necessary to have vibrational population inversion (i.e., $P(v) > P(v-1)$) in order to achieve lasing. In

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[*] Recall that the negative temperature axis goes from $-\infty$ (which is barely hotter than $+\infty$) to -0 (which is the highest possible temperature).

[**] $P(J|v)$ is the population of the rotational states within a given vibrational manifold. B_e is the rotational constant and $Q_{\rm R}$ is the (rotational partition) function that insures that $P(J|v)$ is normalised as in (24). To simplify the notation we assume that the rotational constant (and hence $Q_{\rm R}$) are independent of v. This assumption is not essential and was not used in the computations.

[†] E is the energy available to the reaction products while E_v and $E_J(v)$ are the vibrational and rotational energies. $\theta_{\rm R}$ is a parameter of the distribution, and θ_0 is defined such that $P(J|v)$ is normalized as in (24).
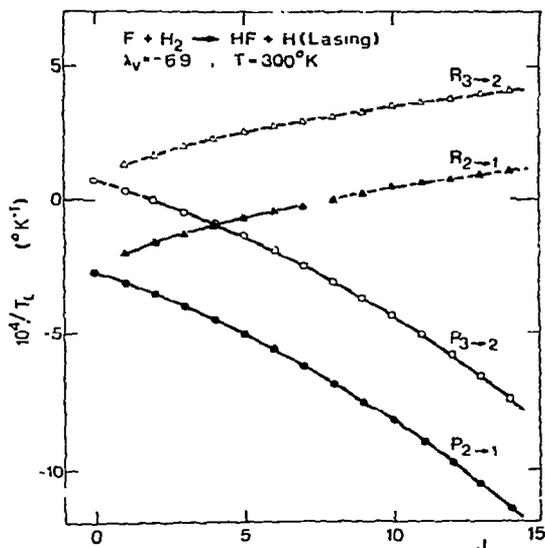
Fig. 3. The lasing temperature, T_L, versus J in the HF chemical laser for P- and R-branch transitions from a relaxed rotational distribution. (For computational details see appendix A.)
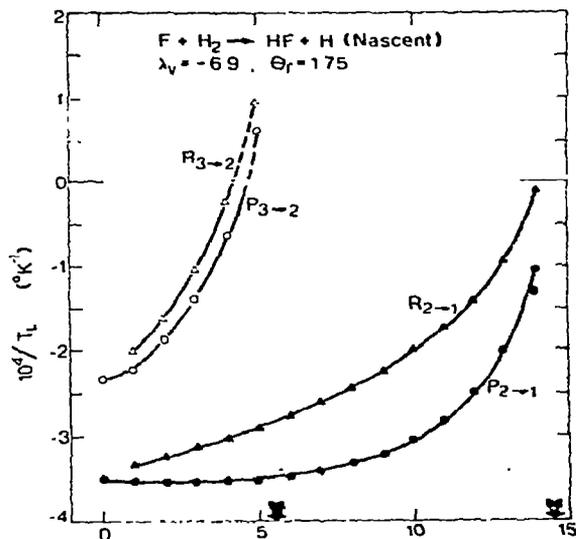
Fig. 4. T_L versus J in the HF chemical laser for a nascent rotational distribution, for comparison with fig. 3. The arrows indicate the highest J level populated by the reaction for $v = 2,3$, respectively.

fact, if we characterize the ratio $P(v - 1)/P(v)$ by an empirical temperature T_v (i.e., ln $[P(v)] = hc\omega_e/RT_v$), eq. (28) can be written as

$$2B_e(J + 1)/\omega_e \geqslant T/T_v. \tag{29}$$

To summarize: Lasing only requires a 'line' (or 'partial') inversion, i.e., $T_L < 0$ (or $\delta S_L > 0$). If there is complete inversion (i.e., $T_v < 0$ or $\delta S_v < 0$), lasing (for P-branch transitions*) is possible at any positive temperature T.

In principle, lasing is possible when the entropy of the body does not decrease as it emits light. How is this requirement implemented for the present mechanism? When light emission occurs the rotational equilibrium (in both the v and $v - 1$ manifolds) is disturbed. The population of the v,J level is depleted while that of the $v - 1$, $J + 1$ level is enhanced. To restore equilibrium we can imagine the following cycle. The excess population in the $v - 1, J + 1$ level is deactivated (by collisions, say) to the $v - 1,J$ level. During this stage, energy of $2hcB_e(J + 1)$ (per mole) is transferred to the buffer gas and its entropy thus increases by δS_R,

$$\delta S_R = 2hcB_e(J + 1)/T. \tag{30}$$

Note that since the rotational population is in equilibrium with the buffer gas, δS_R is defined as the entropy decrease of the diatomic gas due to the decrease in its (mean) rotational energy. In fact, by definition

$$-\delta S_R = \frac{\delta S}{\delta P(v - 1,J)} - \frac{\delta S}{\delta P(v - 1,J + 1)} = -R \ln\left\{\frac{P(v - 1,J)}{(2J + 1)}\left(\frac{P(v - 1, J + 1)}{(2J + 3)}\right)^{-1}\right\} = -2hcB_e(J + 1)/T. \tag{31}$$

---

* For R-branch $(J \to J - 1)$ transitions $\delta S_R = -2B_e J/T$ and the condition (21) now reads $(2B_e J/\omega_e) < -T/T_v$. Lasing in the R-branch is possible only for complete vibrational inversion.

Finally, to restore the initial state, we need to pump the excess population from the $v - 1, J$ to the v, J level. This will correspond to increasing the vibrational energy content by $hc\omega_e$ (per mole). The corresponding change in the entropy is

$$\delta S_v = \frac{\delta S}{\delta P(v,J)} - \frac{\delta S}{\delta P(v-1,J)} = -R \ln \left\{ \frac{P(v,J)}{(2J+1)} \left(\frac{P(v-1,J)}{(2J+1)} \right)^{-1} \right\} = -R \ln [P(v)/P(v-1)]. \qquad (32)$$

Here again, since pumping corresponds to an increase in energy by $hc\omega_e$, we can define T_v by $hc\omega_e = T_v \delta S_v$ or

$$\delta S_v = hc\omega_e/T_v. \qquad (33)$$

From (20), (31) and (32)

$$\delta S_L = \delta S_R - \delta S_v \qquad (34)$$

Hence, only if the entropy loss to the buffer gas during the rotational 'hole filling' (δS_R) is larger than the entropy increase due to vibrational pumping (δS_v) will lasing take place. The entropy increase during the lasing (δS_L) is compensated for by the decrease when collisions with the buffer gas restore the rotational equilibrium*.

We have thus provided the following thermodynamic interpretation of lasing in a diatomic gas in rotational equilibrium. During the lasing the rotational equilibrium is perturbed. A 'hole' is created at the emitting level while an excess appears at the final level. Collisions with the buffer gas restore the rotational equilibrium and, in so doing, reduce its entropy (with a compensating increase in the entropy of the buffer gas). If this decrease is sufficient to overcome the entropy increase which occurs when the vibrational energy content is restored, lasing is possible. The entropy loss which occurs while the nascent products relax to the lasing products is not essential from a thermodynamic point of view. It represents avoidable losses.

The relation (34) provides an 'entropy cycle' for lasing at a particular frequency. In conventional thermodynamics such cycles are expressed as $\Sigma_i Q_i/T_i \geqslant 0$, where Q_i and T_i are the heat transfer and temperature at the ith stage of the cycle. Using (22), (30) and (33), the entropy cycle (34) can be written as

$$\omega_L/T_L = \omega_e/T_v - 2B_e(J+1)/T, \qquad (35)$$

where $\omega_L = \omega_e - 2B_e(J+1)$. The equality in (35) reflects our central assumption that rotational relaxation is sufficiently efficient to maintain the rotational populations ($P(J|v)$) in (thermal) equilibrium with the buffer gas. If this is not the case $\delta S_R \geqslant 2B_e(J+1)/T$. Thus, while (34) is invariably true**, (35) is restricted to the case when the rotational distribution is thermal; it reads in general

$$\delta S_L/hc = -\omega_L/T_L \leqslant 2B_e(J+1)/T - \omega_e/T_v. \qquad (36)$$

The right hand side of (36) provides an upper bound for δS_L. The only parameter not readily available is T_v [defined by (33)]. Once the nascent vibrational population has been measured (and this is somewhat easier than the characterization of the nascent vibrational distribution) T_v can be readily computed for any pair of vibrational levels.

Lasing is possible, from a thermodynamic point of view when $\delta S_L \geqslant 0$ (or $T_L^{-1} \leqslant 0$). Of all the variables in the right hand side of (36), only T can be readily varied†. One can then define the 'threshold temperature', T_{th}, as that value of T for which $\delta S_L = 0$. Clearly $\delta S_L > 0$ for any $T < T_{th}$, for P-branch transitions. For R-branch transitions, where $J' = J - 1$, $\delta S_R < 0$ since energy is transferred from the buffer gas to the lasing system in order to restore rotational equilibrium. Hence δS_L can be positive for R-branch transitions only if $P(v) > P(v-1)$. When this condition obtains, $\delta S_L > 0$ for any $T > T_{th}$.

In general, T_{th} is defined by $\delta S_L = 0$ or

$$P(v,J)/(2J+1) = P(v',J')/(2J'+1). \qquad (37)$$

---

* Similar considerations apply for an R-branch transition.
** One can readily verify that (34) is simply the statement that for a cyclic process there is no net change in the entropy.
† This is the basis of the zero gain method [18]. For this, and other, techniques see [15,18].

Using the equality in (29) this implies (for P-branch transitions)

$$2B_e(J + 1)/\omega_e = T_{th}/T_v. \tag{38}$$

For practical computations it is more useful to introduce the parameter λ_v which is often sufficient to characterize the entire nascent vibrational population in the form

$$P(v) = \tfrac{5}{2} (1 - f_v)^{3/2} \exp(- \lambda_0 - \lambda_v f_v). \tag{39}$$

Here $f_v = E_v/E$ is the fraction of the reactants energy available as vibration and λ_0 insures that $\Sigma P(v) = 1$. Then (37) can be rewritten as

$$T_{th} = [E_J(v) - E_{J'}(v')] /R \{- \lambda_v(f_v - f_{v'}) + \tfrac{3}{2} \ln [(1 - f_v)/(1 - f_{v'})] \}. \tag{40}$$

Fig. 5 shows computed values of T_{th} for both P and R transitions in the F + H$_2$ laser. As is very evident the J-dependence is quite different for the two types of transitions [18]. For P-branch transitions, where δS_M increases with increasing J, δS_L increases with J, and for the example shown, lasing is possible at all temperatures. For the R-branch transitions, where δS_M decreases at increasing J, lasing is possible (at 300 K) only for the lowest rotational levels. Additional considerations and explicit computational agorithms are provided in the appendices. To avoid any misunderstandings we mention explicitly that (in contrast to T_v) λ_v is a v-independent parameter [7, 14,17].
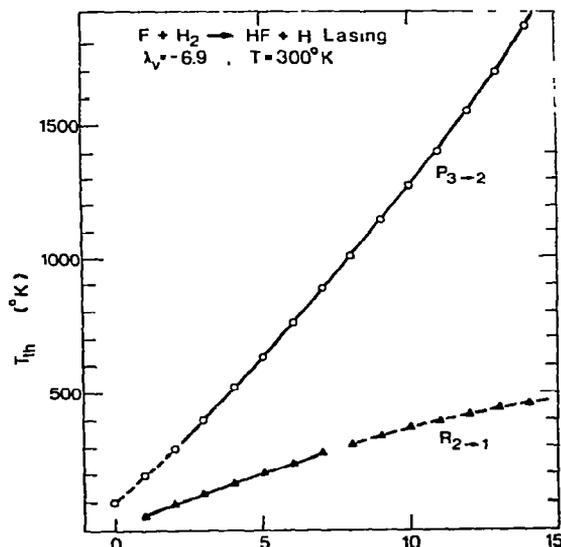

Fig. 5. The threshold temperature, T_{th}, for lasing in the HF chemical laser, versus J. Transitions for which lasing is possible at 300 K are connected by a solid line. (For computational details see appendix A.)

4. Efficiency

In an actual chemical laser, radiation is emitted at several frequencies. Let $\chi(v,J)$ be the number of photons emitted in the $v,J \to v - 1, J + 1$ transition (per mole of nascent products). The work available (as coherent radiation) is[*]

$$W = \sum_{v,J} \chi(v,J) \, hc \, [\omega_e - 2B_e(J + 1)]. \tag{41}$$

---

[*] We are overlooking the possibility of R-branch lasing (at low J). This introduces no essential modifications. Also, in the appendix, we shall use more realistic (vibrating rotor) energy levels in evaluating (41).

The actual efficiency is η

$$\eta = W/E_p \tag{42}$$

and the energy released as heat to the buffer gas is Q_M

$$Q_M = T\Delta S_M = E_p - W. \tag{43}$$

There are two contributions to Q_M. The major one is $(E_N - E_L) + (E_{PL} - E_T)$, the energy difference between the nascent and lasing products and between the post-lasing and thermal products. This is the energy wasted during the (thermodynamically) inessential relaxation processes. The other one is Q_R,

$$Q_R = hc \sum_{v,J} \chi(v,J)\, 2B_e(J + 1), \tag{44}$$

the energy transferred to the buffer gas while maintaining the rotational equilibrium during lasing,

$$Q_R = T\Delta S_R; \qquad \Delta S_R = \sum_{v,J} \chi(v,J)\, \delta S_R. \tag{45}$$

In terms of E, the energy available in the lasing products,

$$E = Q_R + W = hc \sum_{v,J} \chi(v,J)\, \omega_e, \tag{46}$$

the efficiency can be written as

$$\eta = W/E_p = (W/E)(E/E_p) = p(W/E) = p(1 - T\Delta S_R/E). \tag{47}$$

Here

$$p = E/E_p = (W + Q_R)/(W + Q_M) \tag{48}$$

is the reduction in efficiency due to the relaxation of the nascent (to the lasing) and of the post-lasing (to the thermal) products.

As expected, the overall efficiency of the lasing to post-lasing process, W/E, is not the sum but the weighted sum of the efficiencies of the individual transitions. Using (41) and (46)

$$W/E = \sum_{v,J} \eta(v,J)\, e(v,J). \tag{49}$$

Here $\eta(v,J)$ is the efficiency of a particular transition

$$\eta(v,J) = (hc\omega_e - T\delta S_R)/hc\omega_e = 1 - 2B_e(J + 1)/\omega_e \tag{50}$$

and $e(v,J)$ is the fraction of the available energy (E) provided by that transition,

$$e(v,J) = \chi(v,J)\, hc\omega_e/E. \tag{51}$$

For the lasing to post-lasing stage, one can define the pumping entropy (cf. (32)) by

$$\Delta S_v = \sum_{v,J} \chi(v,J)\, \delta S_v, \tag{52}$$

so that (34) now reads

$$\Delta S_L = \Delta S_R - \Delta S_v. \tag{53}$$

Here, using (22) and (41)

$$\Delta S_L = - \sum_{v,J} \chi(v,J) \, h\nu_L/T_L = - W \sum_{v,J} \omega(v,J)/T_L. \tag{54}$$

$\omega(v,J)$ is the fraction of the available work provided by the particular transition

$$\omega(v,J) = \chi(v,J) \, h\nu_L/W. \tag{55}$$

Combining (49), (53) and (54)

$$W/E = \eta_v (1 - T \sum_{v,J} \omega(v,J)/T_L)^{-1}. \tag{56}$$

Here η_v is the overall vibrational pumping efficiency

$$\eta_v = 1 - T\Delta S_v/E. \tag{57}$$

The denominator in (56) is the reduction of the actual efficiency (W/E) below the pumping efficiency because of the operation at a finite gain [9, 10].

It is at this point that the 'state property' of the entropy is of critical importance. Rather than compute ΔS_v as in (52), i.e., along the 'path' from the lasing to the post-lasing products, we can simply put

$$\Delta S_v = S_L - S_{PL}. \tag{58}$$

Here S_L and S_{PL} are the entropies of the distributions of the lasing and post-lasing products, computed using (2), with the explicit details provided in the appendices. Since the precise specification of the post-lasing state is subject to an assumption about the mean vibrational energy content left after lasing is completed it is important to note that $S_{PL} \geqslant S_T$ where S_T is the entropy of the thermal products so that

$$\Delta S_v \leqslant S_L - S_T, \qquad \eta_v \geqslant 1 - T(S_L - S_T)/E. \tag{59}$$

The results of explicit computations for the six reactions are collected in tables 2—4 and in figs. 1 and 6—10. Table 2 provides the thermodynamic measures that govern the efficiency. Tables 3 and 4 provide the actual measures that are displayed in figs. 6—11, and which were used to derive the results shown in table 2. Details of the computations are provided in the appendices.
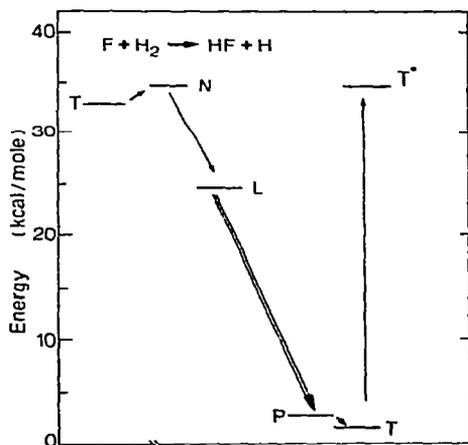

Fig. 6. An energy cycle for the reaction (I). (Same notation as in fig. 1. For computational details see appendix C.)
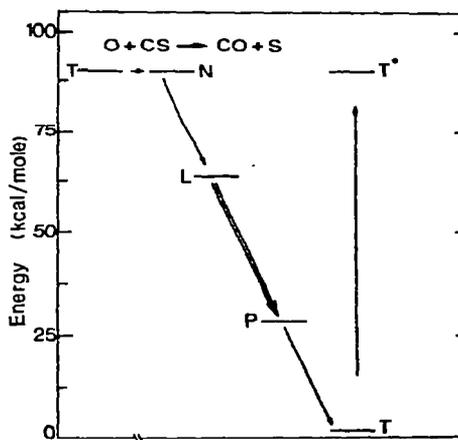

Fig. 7. An energy cycle for the reaction (VI). (Same notation as in fig. 1. For computational details see appendix C.)
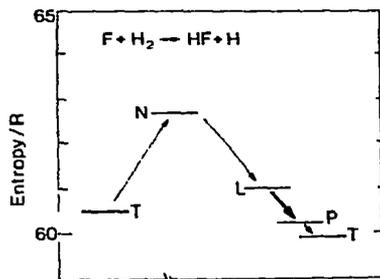
Fig. 8. An entropy cycle for the reaction (I). (Same notation as in fig. 1. For computational details see appendix C.)
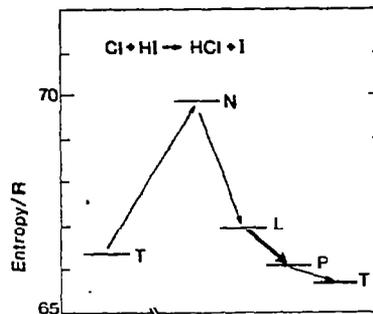

Fig. 9. An entropy cycle for the reaction (V). (Same notation as in fig. 1. For computational details see appendix C.)
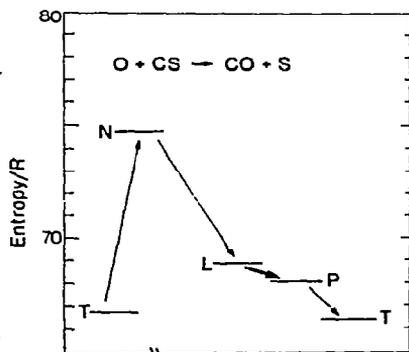

Fig. 10. An entropy cycle for the reaction (VI). (Same notation as in fig. 1. For computational details see appendix C.)
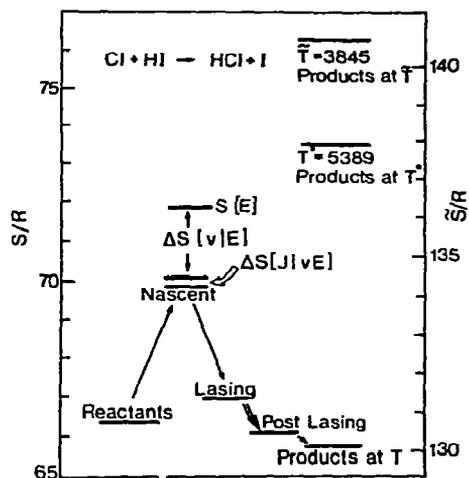

Fig. 11. A detailed entropy cycle for the reaction (V). (For the definitions and computational procedures, see appendix C, under the heading 'nascent products'.) Here, and in fig. 9, $\theta_R = 1.1$.

Table 2
Vibrational parameters [a]

	E_p	E	η	ΔS_v	η_v	λ_v
$F + H_2 \rightarrow HF + H$	33.1	23.2	0.66	2.2	0.97	−7.7
$F + D_2 \rightarrow DF + D$	33.2	20.8	0.60	2.3	0.97	−5.7
$F + HD \rightarrow HF + D$	32.3	19.9	0.58	2.6	0.96	−6.7
$F + HD \rightarrow DF + H$	33.8	19.4	0.55	2.7	0.96	−5.5
$Cl + HI \rightarrow HCl + I$	32.5	23.8	0.72	2.4	0.97	−8.0
$O + CS \rightarrow CO + S$	90.0	62.2	0.38	4.9	0.98	−7.7

[a] Here $\Delta S_v = S_L - S_T$; $\eta_v = 1 - T\Delta S_v/E$. Other details as in table 1.

Table 3
Parameters of energy cycles [a]

	$E_N = E_{T*}$	E_L	E_{PL}	E_T
F + H$_2$ → HF + H	34.6	24.7	2.7	1.5
F + D$_2$ → DF + D	34.7	22.3	2.3	1.5
F + HD → HF + D	33.8	21.4	2.7	1.5
F + HD → DF + H	35.3	20.9	2.3	1.5
Cl + HI → HCl + I	34.0	25.3	2.0	1.5
O + CS → CO + S	91.5	63.7	29.0	1.5

[a] Energies in kcal mol^{-1}.

Table 4
Parameters of entropy cycles [a]

	S_R	S_N	S_L	S_{PL}	S_T	S_{T*}	$-S_N[u/tE]$
F + H$_2$ → HF + H	120.4	124.9	121.5	120.0	119.3	134.7	4.0
F + D$_2$ → DF + D	122.2	129.4	124.8	123.2	122.5	138.1	3.3
F + HD → HF + D	120.6	128.2	123.8	121.9	121.2	136.5	2.5
F + HD → DF + H	120.6	127.2	123.3	121.2	120.6	136.3	3.8
Cl + HI → HCl + I	132.1	139.0	133.2	131.5	130.8	146.3	4.0
O + CS → CO + S	133.2	148.7	137.0	135.6	132.1	155.3	2.9

[a] Entropies in eu.

5. Summary

The use of entropy cycles for computing the thermodynamic parameters relevant to chemical laser action has been discussed and illustrated. In particular, the 'state function' property of the entropy has been used to evaluate the entropy change during a process in terms of the difference between the initial and final values of the entropy.

Acknowledgement

Appendix A: The calculation of T_L and T_{th}

Most of the results presented in the various figures and tables of this paper are based on the vibrating rotor (VR) level scheme for diatomic molecules [7]. Measuring the energy from the ground vibrational level of the diatomic molecule

$$E_v = hc\omega_e v \left[1 - x_e(v + 1)\right], \tag{A.1}$$

$$E_J(v) = hcB_v J(J + 1), \tag{A.2}$$

where $B_v = B_e - (v + \frac{1}{2})\alpha_e$.

For $v,J \rightarrow v - 1,J'$ transitions we have

$$\Delta E_v = E_v - E_{v-1} = hc\omega_e(1 - 2x_e v) \tag{A.3}$$

and

$$\Delta E_J(v) = E_J(v) - E_{J'}(v - 1) = -2B_v(J + 1) - \alpha(J + 1)(J + 2), \quad (\text{P branch}, J' = J + 1),$$

$$= 2B_v J - \alpha J(J - 1), \quad (\text{R branch}, J' = J - 1). \tag{A.4}$$

The lasing temperature T_L in the P or the R branch is determined by

$$\frac{P(v,J)}{P(v - 1,J')} = \frac{P(v) P(J|v)}{P(v - 1) P(J'|v - 1)} = \frac{2J + 1}{2J' + 1} \exp\{-[\Delta E_v + \Delta E_J(v)]/RT_L\}. \tag{A.5}$$

For $P(v)$ we have taken the nascent vibrational distribution of HF molecules generated by the reaction $F + H_2 \rightarrow HF + H$, which can be represented as [7, 17]

$$P(v) = P_0(v) \exp(-\lambda_0 - \lambda_v E_v/E), \tag{A.6}$$

where

$$P_0(v) = [(E - E_v)^{3/2}/B_v]\bigg/\bigg(\sum_{v=0}^{v^*} (E - E_v)^{3/2}/B_v\bigg)^{-1}. \tag{A.7}$$

E is the total energy available for the reactions products, λ_v is the vibrational temperature parameter and λ_0 ensures the normalization

$$\sum_{v=0}^{v^*} P(v) = 1, \tag{A.8}$$

where v^* is the maximal v consistent with $E_v \leqslant E$. The vibrational temperature parameter, λ_v, characterizes the deviation of the actual distribution $P(v)$ from a microcanonical distribution $P_0(v)$ (see appendix C). Large and negative λ_v values correspond to large population inversions and high gains [17,28,29]. For the $F + H_2 \rightarrow HF + H$ reaction $\lambda_v = -6.9, E = 34.6$ kcal/mole and $v^* = 3$ [17]. Note that (39) is equivalent to (A.6) if we take $B_v = B_e$ and replace in (A.7) summation over v by integration over E_v. This corresponds to the passage from the VR model to the RRHO approximation (appendix C).

In order to demonstrate the effect of rotational thermalization on the inversion, T_L was computed for two different rotational distributions.

(a) The *thermal rotational distribution*

$$P(J|v) = Q_R^{-1}(v)(2J + 1)\exp[-E_J(v)/RT], \tag{A.9}$$

with $T = 300$ K. $P(J|v)$ depends only weakly upon v via B_v which appears in (A.4) for $E_J(v)$ and in the rotational partition function $Q_r(v) \approx RT/hcB_v$. From (A.5), (A.6) and (A.9) we find

$$T_L = [\Delta E_v + \Delta E_J(v)]/R\{\lambda_v \Delta E_v/E + \Delta E_J(v)/RT - \frac{3}{2}\ln[(E - E_v)/(E - E_{v-1})]\}. \tag{A.10}$$

The values of T_L for the $P_{3\rightarrow2}, P_{2\rightarrow1}, R_{3\rightarrow2}$ and $R_{2\rightarrow1}$ bands of HF are shown in fig. 3.

(b) The *non-relaxed rotational distribution* which characterizes the rotational level populations of the nascent products. This distribution can be described by (see (26))

$$P(J|v) = (2J + 1)[1 - E_J(v)/(E - E_v)]^{1/2}\exp[-\theta_0 - \theta_R E_J(v)/(E - E_v)], \tag{A.11}$$

where θ_R is a rotational temperature parameter characterizing the deviation of $P(J|v)$ from the microcanonical rotational distribution $P_0(J|v) \propto (2J+1) [1 - E_J(v)/(E - E_v)]^{1/2}$, θ_0 ensures the normalization

$$\sum_{J=0}^{J^*(v)} P(J|v) = 1,$$ (A.12)

where $J^*(v)$ is the highest rotational level in the v manifold, i.e., the highest J which satisfies $E_J(v) \leqslant E - E_v$. As distinguished from the thermal distribution (A.9), (A.12) depends strongly upon v. This fact is reflected both by the range of $P(J|v)$ [i.e., by $J^*(v)$] and by the decrease in the value of J at which $P(J|v)$ obtains its maximum when v increases. For the F + H$_2$ → HF + H reaction $\theta_R = 1.75$ [27]. Insertion of (A.6) and (A.11) into (A.5) leads to

$$T_L = [\Delta E_v + \Delta E_J(v)]/R \{\lambda_v E_v/E + \theta_R [(E_J(v)/(E - E_v)) - E_{J'}(v-1)/(E - E_{v-1})]$$

$$- \tfrac{1}{2} \ln \{[E - E_v - E_J(v)]/(E - E_{v-1} - E_{J'}(v-1)]\}\}.$$ (A.13)

From figs. 3 and 4 it is seen that $|T_L^{-1}|$, which measures the degree of inversion, is (for most transitions) smaller for the nascent rotational distribution (A.11). This is due to the fact that, as distinguished from the case of thermal rotations (A.9), the nascent rotational distributions at different vibrational manifolds do not 'overlap' each other.

The threshold (zero gain) temperatures shown in fig. 5, are determined by (A.10) in the limit of $T_L \to \infty$. Hence

$$T_{th} = \Delta E_J(v)/R \{- \lambda_v E_v/E + \tfrac{3}{2} \ln [(E - E_v)/(E - E_{v-1})]\}.$$ (A.14)

Note that (A.14) is more general than $\Delta E_J(v)/\Delta E_v = T_{th}/T_v$ in the sense that when several vibrational levels are involved T_v (but not λ_v) is a function of v.

Appendix B: Funneling

The simplified laser model employed in this paper rests on two central assumptions. First, rotational energy transfer is fast enough to ensure complete rotational relaxation before the start of the laser pulse and to prevent 'hole burning' in the rotational distributions during the pulse. Second, vibrational relaxation is sufficiently slow to ensure that during the pulse the vibrational populations are modified only because of the radiative transitions. At the start of the laser pulse the vibrational distribution is that of the nascent products, i.e., it is usually 'highly inverted' and T_L is negative for most P-branch and few R-branch transitions, fig. 3. Since the rotational distributions (in all vibrational manifolds) are thermal, the inversion (and the gain) is high for the low $P(J \to J + 1)$ transitions. They are the first to reach threshold and to start lasing. [$P(J \to J + 1)$ always overcomes (and hence, quenches) the $R(J \to J - 1)$ transition.] Due to lasing the vibrational populations are continuously changing and the general trend is to decrease $P(v)/P(v - 1)$, or, in terms of (29), T_v^{-1} is continuously increasing. Therefore, as time progresses, the lasing condition (29) can only be fulfilled for continuously increasing values of J. The fast rotational relaxation 'funnels' the rotational populations and the laser radiation towards higher and higher J. This description was suggested by Berry [17] in order to explain the temporal evolution of the lasing transitions in the HF laser. The thermodynamic considerations presented in section 3 can provide a rough idea about the rotational levels from which the bulk of the radiation takes place. It should be stressed however that our considerations are subject to the validity of the lasing mechanism suggested above*.

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* It should be also mentioned that the phenomena of progression of the laser pulse toward high J may, sometimes, be the result of a different mechanism. If there is no heat bath, e.g., the buffer gas pressure is low, and heat conduction to the walls is negligible the lasing molecules are warmed up by the energy released in the pumping reaction. This leads to a temperature rise accompanied by an increase in J of the highest gain transitions [30,31].

The energy change associated with the passage from the lasing to the post-lasing stage is E,

$$E = \sum_{v} [P_L(v) - P_{PL}(v)] E_v, \tag{B.1}$$

where, at least in principle, the post lasing distribution may be identical to the thermal product distribution*.

For the laser model just described, E can also be expressed as

$$E = \sum_{v} \chi(v) (E_v - E_{v-1}), \tag{B.2}$$

where

$$\chi(v) = \sum_{J} \chi(v,J) = \sum_{v' \geqslant v} [P_L(v') - P_{PL}(v')]. \tag{B.3}$$

$\chi(v,J)$ is the number of photons emitted from the v,J level (per mole) [see (41)]. $\chi(v)$ is, therefore, the number of photons emitted in the $v \to v-1$ band (per mole). The second equality in (B.3) accounts for cascading from higher to lower vibrational levels.

The light emitted as laser radiation, i.e., the work, is given by (section 4)

$$W = E - T\Delta S_v = \sum_{v,J} \chi(v,J) [E_v - E_{v-1} + E_J(v) - E_{J+1}(v-1)], \tag{B.4}$$

where $\Delta S_v = S_L - S_{PL}$, (or $S_L - S_T$), and only $J \to J+1$ transitions are considered. From (B.2) and (B.4) we obtain

$$T\Delta S_v = \sum_{v,J} \chi(v,J) [E_{J+1}(v-1) - E_J(v)]. \tag{B.5}$$

In the VR model

$$E_{J+1}(v-1) - E_J(v) = 2B_v(J+1) + \alpha_e(J+1)(J+2). \tag{B.6}$$

In order to estimate the 'average J' from which lasing transitions will take place, we approximate (B.5) by replacing every B_v by B_1 (i.e., B_v for $v=1$), and neglecting the second order correction in (B.6). (Note that due to cascading the $v=1 \to 0$ band is usually the most intense one.) Thus

$$\langle J+1 \rangle = \sum_{v,J} \chi(v,J)(J+1) \approx T\Delta S_v/2B_1. \tag{B.7}$$

Since B_v decreases with v, $T\Delta S_v/2B_1$ is a lower bound on $\langle J+1 \rangle$.

Table 5 presents estimates of $\langle J \rangle$ for the chemical lasers pumped by reactions I–IV, for which experimental data exist [17]. Since, as mentioned before, the post lasing distribution is somewhat artificial, we have taken two estimates for ΔS_v: $\Delta S_v^{(1)} = S_L - S_{PL}$ with $\alpha = 0.1$ (see appendix C) and $\Delta S_v^{(2)} = S_L - S_T \cdot J_{m.p.} \approx \sqrt{RT/2hcB_1} - \frac{1}{2}$ is the most probable rotational level at the buffer gas temperature, $T = 300$ K. J_{exp} indicates the range of J values over which P-branch transitions were observed experimentally. It is seen that both estimates of $\langle J \rangle$ fall within this range.

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* The values shown in figs. 6–11 represent only one possible choice. The definition of the post-lasing distribution is somewhat arbitrary. See appendix C.

Table 5
The rotational distribution during lasing

	$\Delta S_v^{(1)}$ (c.v.)	$\Delta S_v^{(2)}$ (c.v.)	$\langle J \rangle_{(1)}$	$\langle J \rangle_{(2)}$	J_{exp}	$J_{m.p.}$
$F + H_2 \rightarrow HF + H$	1.5	2.2	3	5	4–11	2
$F + D_2 \rightarrow DF + D$	1.6	2.3	7	10	4–14	3
$F + HD \rightarrow HF + D$	1.9	2.6	4	6	4–11	2
$F + HD \rightarrow DF + H$	1.9	2.7	8	12	5–13	3

Appendix C: Explicit algorithms for the energy and entropy at different stages

In this appendix we present the explicit expressions used to calculate the entropies and energies of the various stages illustrated in figs. 1 and 6–11 and tables 1–5.

The stages considered are: (1) Thermal reactants; atoms A and molecules BC in thermal, but not chemical, equilibrium at temperature T. (2) Nascent products; the products of the A + BC $\rightarrow$ AB + C reaction before any relaxation took place. (3) Lasing products; the vibrational distribution is assumed to be the same as for the nascent products but the rotational distribution of the AB molecules and the translational motions of AB and C are taken to be thermal, at the heat bath (buffer gas) temperature T. (4) Post lasing products; the products at the end of the laser pulse. (5) Thermal products; molecules AB and C in thermal equilibrium at temperature T. (6) Heated products; the products at the temperature T^* corresponding to the same average energy as the nascent products.

The center of mass motion is not modified by the reaction. Since in the thermal reactant stage the center of mass motion is thermal it will remain thermal throughout the passage from the thermal reactants to the thermal products. Thus, with the exception of the last stage (heated products), we shall disregard the center of mass motion from our considerations.

The energy distribution in each stage can be characterized by the probability distribution function (pdf), $P(E_T, v, J)$, where E_T is the relative translational motion of the atom–diatom pair (A + BC or Ab + C), v is the vibrational state of the diatom and J its $(2J + 1)$-fold degenerate rotational level. Keeping in mind that E_T is a continuous variable, then $P(E_T, v, J)\,dE_T$ is the probability of finding an atom–diatom system with relative translational energy in the range E_T, $E_T + dE_T$ and with the molecule in the v, J level. In certain cases it is more convenient to represent the state of the system by alternative (but equivalent) pdf's. For example, in characterizing the nascent products of highly exoergic reactions (typical for chemical lasers), we shall see that $P(E, v, J)$ is a more convenient pdf. Here, $E = E_T + E_v + E_J(v)$ is the total energy of the triatomic (atom + diatom) system.

Except in the stage of the nascent products the translational, rotational and vibrational motions are independent and $P(E_T, v, J)$ will be used. The entropy S and the energy E of the system are given by [7,16,32]

$$S = S[E_T, v, J] = -R \int_0^\infty dE_T \sum_{v=0}^\infty \sum_{J=0}^\infty P(E_T, v, J) \ln [P(E_T, v, J)/\rho(E_T, v, J)], \tag{C.1}$$

$$\langle E \rangle = \int_0^\infty dE_T \sum_{v=0}^\infty \sum_{J=0}^\infty P(E_T, v, J) [E_T + E_v + E_J(v)]. \tag{C.2}$$

The square bracket on the l.h.s. of (C.1) serve to denote the summation variables; they do not contain functional arguments. The density of states factor $\rho(E_T, v, J)$ results from the continuous character of the translational motion. It is given by [7, 32]

$$\rho(E_T, v, J) = (2J + 1)\,\rho_T(E_T), \tag{C.3}$$

where

$$\rho_T(E_T) = (2^{1/2} \pi^2 \hbar^3)^{-1} \mu^{3/2} E_T^{1/2} \tag{C.4}$$

is the density of translational states (per unit volume) corresponding to the relative atom–diatom motion with reduced mass μ. [For reactants $\mu = \mu_R = m_A m_{BC}/(m_A + m_{BC})$, $\mu_P = m_{AB} + m_C/(m_{AB} + m_C)$.]

When the three types of motion are not coupled to each other we have

$$P(E_T, v, J) = P(E_T) P(v) P(J). \tag{C.5}$$

Hence, the entropy and the energy can be written as sums of three independent contributions [8]

$$S = S[E_T] + S[v] + S[J], \tag{C.6}$$

$$S[E_T] = -R \int dE_T \, P(E_T) \ln [P(E_T)/\rho_T(E_T)], \tag{C.7}$$

$$S[v] = -R \sum_v P(v) \ln P(v), \tag{C.8}$$

$$S[J] = -R \sum_J P(J) \ln [P(J)/(2J + 1)]. \tag{C.9}$$

and similarly

$$\langle E \rangle = \langle E_T \rangle + \langle E_v \rangle + \langle E_J \rangle. \tag{C.10}$$

In fact, due to the v-dependence of $E_J(v)$, there is always some coupling between the vibrational and rotational motions; i.e., $P(J)$ in (C.5) should be replaced by $P(J|v)$, and $S[J]$ in (C.6,9) by $S[J|v]$ (see below). However, this coupling has only a minor effect on the rotational entropy and energy. Thus, while in all computations (A.1) was used for E_v, we have sometimes taken $E_J(v) = B_{\bar{v}} J(J + 1)$, where $B_{\bar{v}}$ is an averaged rotational constant (see below).

When the total (triatomic) energy E is sharply defined (as in stage 2, below), it is more convenient to employ the representation

$$P(E, v, J) = P(E) P(vJ|E) = P(E) P(v|E) P(J|vE), \tag{C.11}$$

where $P(v|E)$ and $P(J|vE)$ are conditional pdf's normalized according to (A.7) and (A.12), respectively. The entropy is expressed now as

$$S = S[E, v, J] = -R \int dE \sum_{v=0}^{v^*} \sum_{J=0}^{J^*(v)} P(E, v, J)/\rho(E, v, J)], \tag{C.12}$$

where $\rho(E, v, J)$ is identical, apart from the notation, to $\rho(E_T, v, J)$. It should be noted that both representations of S lead to identical results; this will be shown explicitly for the nascent products.

The density of states can be factorized into [7,8]

$$\rho(E, v, J) = \rho(E) P_0(vJ|E) = \rho(E) P_0(v|E) P_0(J|vE), \tag{C.13}$$

where

$$\rho(E) = \sum_{v=0}^{v^*} \sum_{J=0}^{J^*} \rho(E, v, J). \tag{C.14}$$

$P_0(vJ|E)$, etc., are normalized (conditional) density of states functions whose definitions follow from (C.13) and

(C.14). From (C.3), (C.4), (C.13) and (C.14), we obtain

$$P_0(v,J|E) = N(2J + 1) [E - E_v - E_J(v)]^{1/2},$$ (C.15)

where N is a normalization factor (in the RRHO approximation $N = 15\, h^2 c^2 \omega_e B_e / 4E^{5/2}$). Similarly

$$P_0(v|E) = \sum_{J=0}^{J^*(v)} P_0(vJ|E)$$ (C.16)

$$\approx (E - E_v)^{3/2} B_v^{-1} \left(\sum_{v=0}^{v^*} (E - E_v)^{3/2} B_v^{-1} \right)^{-1}$$ (C.17)

$$\approx (5/2) hc\omega_e (E - E_v)^{3/2}/E^{5/2},$$ (C.18)

and

$$P_0(J|vE) = p_0(vJ|E)/P_0(v|E) \simeq N' [E - E_v - E_J(v)]^{1/2}/(E - E_v)^{3/2},$$ (C.19)

where (C.17) and (C.19) result from treating J as a continuous variable while (C.18) is the (classical) RRHO approximation where we take $B_v = B_e$ and integrate instead of summing over v. (Note that $dv = dE_v/hc\omega_e$.) $P_0(v|E)$ and $P_0(vJ|E)$ are recognized as the pre-exponential factors in (39) or (A.6) and (26) or (A.11) respectively. Substitution of (C.11) and (C.13) into (C.12) yields

$$S[E,v,J] = S[E] + S[v|E] + S[J|vE],$$ (C.20)

where

$$S[E] = -R \int dE\, P(E) \ln [P(E)/p(E)],$$ (C.21)

$$S[v|E] = \int dE\, P(E) S[v|E] = -R \int dE\, P(E) \sum_{v=0}^{v^*} P(v|E) \ln [P(v)|E)/P_0(v|E)],$$ (C.22)

$$S[J|vE] = \int dE\, P(E) \sum_{v=0}^{v^*} P(v|E) S[J|vE]$$

$$= -R \int dE\, P(E) \sum_{v=0}^{v^*} P(v|E) \sum_{J=0}^{J^*} P(J|vE) \ln [P(J|vE)/P_0(J|vE)].$$ (C.23)

It can be shown that $S[E] \geqslant 0$ while $S[v|E] \leqslant 0$ and $S[J|vE] \leqslant 0$. Only if $P(v|E) = P_0(v|E)$ we have $S[v|E] = 0$. This is the case of a microcanonical distribution at any given E. Since in a state of thermal equilibrium every small energy shell is microcanonically populated, then $S[v|E] = 0$. Similarly $S[J|vE] = 0$ only when $P(J|vE) = P_0(J|vE)$. The non-negative (zero only at equilibrium) quantities $S[v|E]$ and $S[J|vE]$ provide measures of deviation from equilibrium, they are called 'entropy deficiencies' [7,14,32].

We turn now to an explicit treatment of each stage of the cycles.

C.1. Thermal reactants

In this stage every degree of freedom is separately in equilibrium with the heat bath. Although the representation $P(E_T,v,J)$ with (C.5)–(C.10) is convenient we shall first consider the $P(E,v,J)$ representation to prepare the way for the next stage.

We consider exoergic reactions and choose a common energy scale for reactants and products, with its zero at the ground vibrational level of the products.

The total energy distribution $P(E)$, in (C.11), is canonical

$$P_R(E) = \rho_R(E) \exp\{-E/RT\}/Q_R,$$ (C.24)

where

$$\rho_R(E) = 0, \qquad \text{for } E - E_v - E_J(v) < \Delta D_0,$$

$$= \sum_{v,J} (2J+1)\,\rho_{T,R}\,[E - \Delta D_0 - E_v - E_J(v)], \qquad \text{otherwise},$$ (C.25)

where R symbolizes 'Reactnats'. $\Delta D_0 > 0$ is the exoergicity of the reaction ('zero point to zero point' difference) and Q_R is the partition function. $\rho_{T,R}$ denotes the density of translational states of the reactants.

$$Q_R = \int_0^\infty \rho_R(E) \exp(-E/RT)\,dE = \exp(-\Delta D_0/RT)\,Q_{T,R}Q_{v,R}Q_{R,R}.$$ (C.26)

The Q factors in the last equation are the partition functions for the (relative) translational motion of A + BC (per unit volume), the rotation of BC and the vibration of BC, respectively.

$$Q_{T,R} = \int_0^\infty dE\,\rho_{T,R}(E_T) \exp(-E/RT) = (\mu_R RT/2\pi\hbar^2)^{3/2},$$ (C.27)

$$Q_{R,R} = \sum_J (2J+1) \exp(-E_J/RT) \approx RT/hcB_R,$$ (C.28)

$$Q_{v,R} = \sum_v \exp(-E_v/RT) \approx [1 - \exp(-hc\omega_R/RT)]^{-1}.$$ (C.29)

The expressions on the r.h.s. of (C.28) and (C.29) correspond to the RR and HO approximations, respectively. B_R and ω_R stand for the rotational constant and the vibrational frequency of the reactant molecule.

As mentioned before, in equilibrium, $P(\omega|E) = P_0(\omega|E)$, hence $S[\omega|E] = 0$ and it is easily seen that

$$S[E,v,J] = S[E] = \langle E\rangle/T + R \ln Q_R = (\langle E_T\rangle + \langle E_R\rangle + \langle E_v\rangle + \Delta D_0)/T + R\,[-\Delta D_0/RT + \ln(Q_{T,R}Q_{R,R}Q_{v,R})]$$

$$= S[E_T] + S[v] + S[J],$$ (C.30)

where $S[E_T] = \langle E_T\rangle/T + R \ln Q_{T,R}$, etc. The resolution $P(E_T,v,J) = P(E_T)\,P(v)\,P(J)$ will also yield (C.30). Since in thermal equilibrium

$$S[E_T] \gg S[J] \gg S[v]$$ (C.31)

we can ignore the vibrational contribution to the entropy of the thermal reactants.

In the subsequent stages, however, the changes in the vibrational entropy are the most relevant ones, and will not be neglected.

For the energy of the reactants we have

$$\langle E\rangle \approx \Delta D_0 + \tfrac{5}{2}RT,$$ (C.32)

where the average vibrational energy of the reactants was neglected (among all the molecules involved in reactions I–VI only CO and CS have non-negligible vibrational energies at ordinary temperatures).

C.2. Nascent products

Since the total energy is conserved in the reaction, the nascent products will have the same total energy as that of the reactive reactants. (The reactive reactants are those which can pass over the activation barrier.) Thus, $P(E)$ of the nascent products is determined, in principle, not only by $P(E)$ of the thermal reactants but also by the reaction rate constant $k(E)$. However, for highly exoergic reactions with low activation barriers, (like reactions I–VI) which take place at ordinary temperatures we have $E_a \ll \Delta D_0 \approx E$ and it can be assumed that $P(E)$ of the reactive reactants is sharply (with respect to E) peaked at $E \approx \Delta D_0 + E_a + \frac{5}{2} RT$. Making the additional assumption that the shape of $P(E)$ of the reactive reactants (and therefore also $P(E)$ of the nascent products) is similar to that of the thermal reactants, we obtain

$$P_N(E) = P_R(E - E_a),$$ (C.33)

with $P_R(E)$ given by (C.24), (N denotes "Nascent"). Hence

$$S_N[E] = -R \int_0^\infty dE\, P_N(E) \ln [P_N(E)\rho_P(E)]$$ (C.34)

$$= -R \int_0^\infty dE\, P_R(E - E_a) \ln [P_R(E - E_a)/\rho_R(E - E_a)] + R \int_0^\infty dE\, P_R(E - E_a) \ln [\rho_P(E)/\rho_R(E - E_a)].$$

Changing variables from $E - E_a$ to E and noting that $P_R(E) = 0$ for $E < \Delta D_0$ it is easily verified that the first term is simply $S_R[E]$, the entropy of the thermal reactants.

The second term represents the entropy increase due to the fact that on the product side E, and therefore the density of states, is much larger. This second integral can be evaluated numerically. However, since $P_R(E)$ is narrow (its spread in E is about RT) and $\rho_P(E)$ changes only slowly with E, the integral can be approximated by the average value of the integrand. (The two procedures were numerically compared and good agreement was obtained.) Since at ordinary temperatures the vibration of the reactants is essentially $v = 0$ then $P_R(E) \propto E^{3/2} \exp(-E/RT)$, and $\langle E \rangle \approx \frac{5}{2} RT$. Thus, replacing the integral by the value of the integrand at $E = \Delta D_0 + E_a + \frac{5}{2} RT$ yields finally

$$S_N[E] = S_R[E] + R \ln [\rho_P(E)/\rho_R(\Delta D_0 + \frac{5}{2}RT)]$$

$$= S_R[E] + R \ln [(\mu_P/\mu_R)^{3/2} (B_R/B_P)(2/5\, hc\omega_P) E^{5/2}/(\frac{5}{2}RT)^{3/2}].$$ (C.35)

We have used here (C.14) (in the RRHO approximation), for ρ_P (E is large), and (C.25) for ρ_R (only $v = 0$ is populated).

An additional, negative, contribution to $S[E,v,J]$ of the nascent products comes from the entropy deficiency $S[v,J|E]$. This can be further decomposed into $S[v|E] + S[J|vE]$. All the reactions studied here can be characterized by product vibrational and rotational distributions of the form of (A.6) and (A.11), respectively [7,12,17,27]. (The only exception is the unknown product rotational distribution in reaction VI for which we take (A.11) with $\theta_R = 0$.) Taking into account that the width of $P_N(E)$ is much smaller than E we obtain

$$S[v|E] \approx S[v|E] = \lambda_0 + \lambda_v \langle E_v \rangle/E.$$ (C.36)

Similarly

$$S[J|vE] \approx S[J|vE] = \theta_0 + \theta_R \langle E_J/(E - E_v) \rangle.$$ (C.37)

Note that $\langle f_v \rangle = \langle E_v \rangle/E$, is the average fraction of reaction energy which appears as product vibrational energy. For reactions I–VI $\langle E_v \rangle/E \approx 0.7$ and $-\lambda_v \approx 5-8$.

To summarize, $S_N[E,v,J]$ is the sum of the terms on the l.h.s. of (C.35), (C.36) and (C.37).

The average energy of the nascent product is

$$E_N \approx \Delta D_0 + E_a + \tfrac{5}{2}RT. \tag{C.38}$$

C.3. Lasing products

At this stage the translational and rotational motions have already been relaxed to the buffer gas temperature but the vibrational motion is still non relaxed, i.e., $P(v)$ is given by (A.6). We use now the resolution (C.5) with

$$P(E_T) = \rho_T(E_T) \exp\left(- E_T/RT\right)/Q_T, \tag{C.39}$$

$$P(J) = (2J + 1) \exp\left(- B_{\bar{v}}J(J + 1)/RT\right)/Q_R, \tag{C.40}$$

where $B_{\bar{v}}$ is the averaged vibrational constant. In the calculations $\bar{v}$ was taken as the most populated vibrational level. (From this point on we shall only deal with the products and the symbol P will be omitted.)

The entropy of the lasing products is

$$S_L = S[E_T] + S[v] + S[J], \tag{C.41}$$

with

$$S[E_T] = \langle E_T \rangle/T + R \ln Q_T = \tfrac{3}{2}R + R \ln Q_T, \tag{C.42}$$

$$S[J] = \langle E_R \rangle/T + R \ln Q_R = R + R \ln Q_R, \tag{C.43}$$

$$S[v] = -R \sum_{v=0}^{v^*} P(v) \ln P(v). \tag{C.44}$$

Note that since $S[v]$ and $S[v|E]$ are different quantities, $S[v]$ is not given now by (C.36). (Furthermore $S[v|E] \leqslant 0$ while $S[v] > 0$.)

The average energy of the lasing products is given by

$$E_L = \langle E_T \rangle + \langle E_J \rangle + \langle E_v \rangle \tag{C.45}$$

$$= \tfrac{5}{2} RT + \langle E_v \rangle. \tag{C.46}$$

Note that $\langle E_v \rangle \gg RT$, for the lasing products.

C.4. Post lasing products

Due to funneling, lasing does not terminate when all $P(v)$ are equal. Ignoring V–R,T relaxation and spontaneous emission, the post lasing vibrational distribution ($P(E_T)$, $P(J)$ are thermal) is determined by the cavity (Schawlow–Townes) threshold condition. We employed here an approximation suggested elsewhere [17]. There, it was assumed that at the end of the laser pulse

$$P(v) = C \alpha^v, \qquad \alpha < 1, C = (1 - \alpha)/(1 - \alpha^{v^*+1}), \tag{C.47}$$

where v^* is the highest v populated initially by the reaction. Note that if $\alpha \ll 1$, $P(v)$ is, to a very good approximation, a Boltzmann distribution

$$P(v) = \alpha^v(1 - \alpha) \tag{C.48}$$

with an effective vibrational temperature T_v defined by

$$\alpha = \exp\left(- hc\omega_e/RT_v\right). \tag{C.49}$$

Following [17] we assumed $\alpha = 0.1$ for reactions I–V. For the $0 + CS \rightarrow CO + S$ reaction we have simply taken $\alpha = 0.82$, so that $(E_L - E_{PL})/E_P = 0.38$, which is the efficiency reported for the CO laser in [33].

It should be emphasized that the post lasing stage is somewhat artificial, since towards the end of the pulse, vibrational relaxation is always significant.

C.5. Thermal products

In this stage the vibrational distribution joins the rotational and translational modes and is at equilibrium at the buffer gas temperature T. ($P(v)$ is given by (C.48) and (C.49) with $T_v = T$.) For $T = 300$ K both $S[v]$ and $\langle E_v \rangle$ are negligible and we take

$$S_T = S[E_T] + S[J] = \tfrac{5}{2}R + R \ln Q_T Q_R,$$ (C.50)

$$E_T \approx \tfrac{5}{2}RT,$$ (C.51)

where Q_T is the partition function of the relative translational motion of AB + C and Q_R is the rotational partition function of AB.

C.6. Heated products

The heated products stage corresponds to the maximum entropy distribution discussed in section 2. Namely, a canonical distribution whose average energy is equal to that of the nascent products. Two kinds of 'heated product' distributions are considered in fig. 11 and the tables.

In the first place a distribution describing the hypothetical situation where all the product degrees of freedom (except the three associated with the center of mass motion of AB + C), are in thermal equilibrium at a temperature T^*. The value of T^* is determined by the requirement that the average energy of the 'heated products' will equal that of the nascent products (excluding the center of mass energy). Using (C.38) and the HO model we find

$$E_{T^*} = \Delta D_0 + E_a + \tfrac{5}{2}RT = \tfrac{5}{2}RT^* + hc\omega_p \exp(-hc\omega_p/RT^*)/[1 - \exp(-hc\omega_p/RT^*)].$$ (C.52)

Since T^* is generally of the order of 10^3–10^4 K, i.e., $hc\omega_p \approx RT^*$, the vibrational contributions to the energy and the entropy cannot be neglected.

The entropy of this stage is given by

$$S_{T^*} = \tfrac{5}{2}R + R \ln Q_T(T^*) Q_R(T^*) + R\langle E_v \rangle/T^* - R \ln [1 - \exp(-hc\omega_p/RT^*)],$$ (C.53)

where $Q_T(T^*)$ and $Q_R(T^*)$ are given by (C.27) and (C.28), respectively with μ_P, B_P and T^* instead of μ_R, B_R and T, respectively. $\langle E_v \rangle$ is equal to the second term in (C.53).

Note that the situation described in this stage cannot be achieved experimentally, because the center-of-mass motion cannot be kept at the lower temperature T. However, as was emphasized in section 2 S_{T^*} and E_{T^*} provide useful bounds on the efficiency of chemical lasers. In fact, we may also consider a more realistic process by allowing the center of mass motion to exchange energy with the relative and internal motions of AB + C. In this case the average energy of the heated products, including the center of mass energy, will equal that of the nascent product, i.e.,

$$E_{\tilde{T}} = \Delta D_0 + E_a + 4RT = 4R\tilde{T} + hc\omega_p \exp(-hc\omega_p/R\tilde{T})/[1 - \exp(-hc\omega_p/R\tilde{T})]$$ (C.54)

where, to account for the center of mass energy, $\tfrac{3}{2}RT$ and $\tfrac{3}{2}R\tilde{T}$ were added to the l.h.s. and r.h.s. of (C.52), respectively.

The entropy of these heated products is the sum of (C.53) with T^* replaced by $\tilde{T}$ and

$$S_{\tilde{T}}(\text{c.m.}) = \tfrac{3}{2}R + R \ln Q_{\text{c.m.}}(\tilde{T}),$$ (C.55)

where $Q_{c.m.}$ is an ordinary translational partition functions of a mass $m = m_A + m_B + m_C$. As the bounds on the efficiency associated with S_{T^*} are more significant than those associated with $S_{\overline{T}}$, we have shown $S_{\overline{T}}$ only in fig. 11. For all other reactions only S_{T^*} was computed.

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