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Molecular Constraints Implied by Kinetic Coupling Schemes and Maximal Work in Chemical Lasers

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Abstract

The efficiency of molecular lasers is known to be enhanced when certain relaxation processes (which dissipate some energy) are allowed to take place. We consider a thermodynamic interpretation of such observations with special applications to chemical lasers operating in the limits of slow and fast rotational relaxation. Specifically it is shown that kinetic coupling schemes which reflect the hierarchy of rate processes in a nonequilibrium molecular system can be expressed as thermodynamic constraints on the internal state distribution function. The lower the number of constraints the higher is the work which can be extracted from the nonequilibrium populations. The lower laser efficiency in the absence of rotational relaxation is due to the existence of an isolating constraint on the vib-rotational populations of the lasing molecules.

Introduction

Experiments [1, 2] and numerical simulations [3] show that the efficiency of a chemical laser is significantly enhanced in the presence of a buffer gas. A kinetic interpretation [4] (the 'funnel effect' [1], see below) invoking a competition between stimulated emission and the (pressure dependent) rotational relaxation is available. The purpose of this paper is to offer a corresponding thermodynamic interpretation. The discussion illustrates the general approach to systems in molecular disequilibrium [5, 6] which is based on the maximal entropy formalism [7]. The increase of the laser efficiency with the buffer gas pressure is shown to reflect the additional work which is available from a system when a constraint is removed.

The constraints which are introduced in the discussion of thermodynamic work processes [8–10] are typically macroscopic (e. g. pistons, catalysts). A novel feature of the present discussion is that work is obtained by the removal of a molecular (i. e. a kinetic or mechanistic) constraint. Specifically, the constraints to be discussed are conditions on the distribution of the molecules over their internal energy levels.

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In a laser system the work is extracted as light which due to its spectral characteristics (well collimated beam over a very narrow frequency range) can be regarded as thermodynamic work [11].

Section 1 is a discussion of the work available upon (partial) removal of the constraints on the system. The maximal entropy formalism enables us to introduce the molecular constraints in a simple fashion and to demonstrate their role not only analytically but also in a graphic fashion. A particular feature of the discussion is that it is not limited to systems coupled to a heat bath [12]. The particular constraints which are removed due to the presence of a buffer gas are formulated in section 2, which applies the point of view of section 1 to the physical system of interest.

On the microscopic level we are concerned with the following physical picture. A fast chemical reaction creates a disequilibrium population of molecules in their vibrational and rotational states. In the low pressure regime lasing is possible on any allowed[1] molecular line for which there is an excess population in the upper state. Laser emission depletes the upper state and hence terminates when the populations in the upper and lower state become equal (or, in practice, when the excess in the upper state falls below the threshold density required by losses etc [2, 4]). Collisional processes (whose rate is proportional to the pressure) are too slow as compared to the rate of laser emission in order to drain the upper state or to feed the lower state. The entire system acts as a collection of independent two-level systems. For each molecular laser line the sum of the populations in the upper and lower states is constant (on the time scale of interest).

As the pressure is increased, collisional relaxation begins to take place. The critical observation here is that rotational energy transfer is several orders of magnitude more effecient than vibrational energy transfer [1, 13]. Hence rotational relaxation can but vibrational relaxation typically cannot compete with the (unimolecular) lasing process [1]. In the limit where rotational energy transfer is quite efficient any depletion of an upper state due to lasing[2] is immediately restored by the collisional process and any excess of the lower state is immediately removed. The net result of this "cooperative" lasing mechanism is an efficient draining of the population of the upper vibrational state into the lower one.

The low pressure constraint that on any lasing line the total population (sum of upper and lower states) must be constant is thus removed in the higher pressure regime.

In the limit of strong rotational coupling the rotational distribution is thermalised throughout the lasing. Thus,

$$P(v, J) = P(v)\,(2J + 1)\exp[-\beta BJ(J + 1)]/Q_{rot}(\beta)\,, \tag{1}$$

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[1] Dipole selection rules limit the allowed transitions. In lasers using diatomic molecules the important transitions occur on the P-branch lines connecting the vibrotational levels, $(v, J - 1)$ to $(v - 1, J)$. Here v and J are the vibrational and the angular quantum number respectively.

[2] It is important to note that lasing occurs on the strongest ('Highest gain' [1, 2]) line. During the lasing process, this line gradually shifts towards higher J's, see below.

where $T = (R\beta)^{-1}$ is equal to the translational temperature. For simplicity we have used here the rigid rotor level scheme and B is the rotational constant. The necessary lasing condition, i. e. population inversion,[3]

$$P(v, J-1)/(2J-1) > P(v-1, J)/(2J+1)\,, \tag{2}$$

now reads

$$J > (2\beta B)^{-1}\, \ell n[P(v-1)/P(v)]\,. \tag{3}$$

Lasing starts on the line with the highest inversion (more precisely highest gain) corresponding to the initial population P(v). Generally this is one of the low lying J's. The fast rotational relaxation transfers molecules into v, J − 1 and from v − 1, J while preserving the Boltzmann shape of the rotational distributions and preventing "hole burning". The upper vibrational population is thus homogeneously drained (funnelled [1]) into the lower one through the highest gain transition. As P(v − 1)/P(v) increases in this process the lasing is gradually shifted to higher J's as implied by (3). Since J is unlimited, lasing can still go on even when $P(v-1)/P(v) \ll 1$. In practice, lasing terminates at some high J determined by the requirement for threshold inversion [2, 4]. Yet the draining of the upper level due to the cooperation (strong coupling) between the rotational levels is very efficient.

In the low pressure region collisional relaxation is negligible and the population P(v, J) is affected only by the stimulated emission. Thus, molecules can be exchanged only between (v, J − 1) and (v − 1, J) and the different lines form distinct groups. Here the lasing terminates when every line reaches, individually, an equality in (2) so that lasing terminates when $P(v)/P(v-1) \sim 1$; as opposed to the strong coupling case. The passage to the strong coupling limit is formally achieved by removing the constraints on population exchange between the different rotational states of the same vibrational manifold.

1. Work

Discussion of work processes for systems in disequilibrium is conveniently formulated using the maximal entropy formalism [5, 6, 12]. Our first purpose is to relate this point of view to the "energy picture" [8], which is more common in equilibrium thermodynamics. In doing so we shall also introduce our notation and invoke the distinction between the allowed and excluded regions in the mean or internal energy E-entropy S plane which is fundamental to our subsequent discussion.

Our primary concern is with systems in internal molecular disequilibrium where upon spontaneous removal of the constraints the relaxation towards equilibrium is predominately collisional. We shall thus assume that the system is spatially homogenous, dilute and that the time scale of interest is sufficiently coarse that collisions

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[3] P(v, J − 1) is the population in the 2(J − 1) + 1 = 2J − 1 fold degenerate (v, J − 1) vibrotational level. The population per quantum state is P(v, J − 1)/(2J − 1). Population inversion requires inversion between quantum states, [2].

are instantaneous. A complete microscopic characterisation of the system is then provided by the number of molecules in each of the different internal energy states. One can thus consider a distribution function P(n, t) specifying the fraction of all molecules in the internal energy level n (of degeneracy g_n) at the time t.

A macroscopic characterisation of the state of the system is provided by specifying the value of m "constraints"

$$\langle A_r \rangle = \sum_n A_r(n)\, P(n, t)\,, \qquad r = 1, \ldots, m\,, \tag{4}$$

which together with the normalisation

$$1 = \langle A_0 \rangle = \sum_n P(n, t)\,, \tag{5}$$

suffice to determine P(n, t). In (4), $A_r(n)$ is the magnitude of the property A_r in the n'th level. Unless n is comparable to the number of levels which are significantly populated, the m + 1 constraints, (4) and (5) do not suffice, in themselves, to specify a unique distribution function P(n, t). It is here that one invokes the principle of maximum entropy [6] by selecting P(n, t) as that distribution which satisfies the m + 1 constraints and whose entropy[4]

$$S[n] = -R \sum_n P(n, t)\, \ell n[P(n, t)/g_n] \tag{6}$$

is maximal. Provided that the (m + 1) constraints are linearly independent and that their values are consistent (i. e. there is at least one distribution which satisfies (4) and (5)) the maximum problem has a unique solution [14]. Another important feature of the solution is that the addition of constraints can never cause the entropy to increase. Intuitively this is obvious. Adding constraints can only further restrict the range of contending distributions and hence the entopy will at most not change[5] and otherwise will decline. Finally, one notes that the entropy is a convex function of the constraints [14], i. e. for any P(n, t) that satisfies the m + 1 constraint conditions we have

$$\partial^2 S[n]/\partial \langle A_r \rangle^2 < 0\,, \tag{7}$$

where the inequality is strict when the constraints are linearly independent.

The three properties of the maximum entropy procedure are summarised graphically in the top row of Figure 1 where E is the mean energy (per mole) of the system

$$E = \sum_n E_n\, P(n, t)\,. \tag{8}$$

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[4] Equation (6) is the entropy for one mole. Since, by assumption, the gas is dilute and the collisions are uncorrelated, the single molecule distribution function sufficies to describe the system. However, the system consists of N molecules rather than of a single one.

[5] This happens when the additional constraint is "non-informative" [6, 15], i. e. when it does not help to specify the macroscopic state.

Given the value of E, there is a unique maximal value of S shown as the solid line. Moreover, the solid line is convex (cp. (7)). Finally, if additional constraints are present then, for a given value of E, the value of S can only go down. In the S-E plane, the solid line is the boundary between the allowed and excluded states of the system. A given (S, E) point can only be on or below the solid line. It is not possible to find a macroscopic state which is subject to the constraints whose entropy exceeds the boundary line. The physical significance of this boundary is made clear by equilibrium thermodynamics. The normalised distribution of maximal entropy subject only to a given value of the energy is, of course, the equilibrium ('canonical') thermal distribution. The slope of the S-E curve is then a measure of the temperature[6]

$$\partial S/\partial E = 1/T = R\beta\,, \tag{9}$$

and the condition that the distribution be normalised determines the partition function

$$Q = \sum_n g_n \exp(-\beta E_n)\,. \tag{10}$$

The sum over levels in (10) may converge even if β is negative (e. g. if there are only a finite number of levels), in which case the S-E curve can have a maximum (upper left case in Fig. 1). If the sum (10) converges only for positive β (e. g. if the spectrum is unbounded from above) then the S-E curve is monotonic (upper right case in Fig. 1).

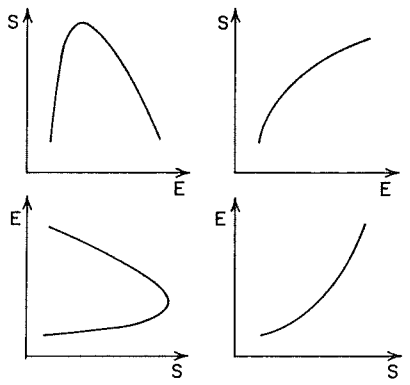

Fig. 1: Maximal entropy curves in the entropy S (upper row) and mean or internal energy E (bottom row) representations for systems with bounded (left column) and unbounded (right column) spectrum. In the S representation every E, S point on the solid curve is obtained by maximizing S subject to the value of E while in the E representation every E, S point on the curve corresponds to the extremal E for a given S (where for the negative temperature region, $R\beta = \partial S/\partial E < 0$, of systems with bounded spectrum, the extremum is a maximum). The allowed region of nonequilibrium E, S points lies on the concave side of the solid curves.

[6] We use the term temperature in a generalized sense as the (inverse) magnitude of the Lagrange parameter (cp. (11)) conjugate to the energy. The letter k denotes Boltzmann's constant.

An alternative macroscopic description and one that is well suited towards the discussion of work processes in an isolated system regards the energy E as a function of the entropy S and other macroscopic variables. This is sometimes known as "the energy picture" [8]. We now show that the tranformation from the entropy to the energy picture is not limited to systems in thermal equilibrium but can be carried out in general.

Assume the energy to be taken as the first (i. e. r = 1) constraint. The problem of seeking an extremum of the entropy subject to m + 1 constraints can be formulated as seeking the unconstrained extremum of the Lagrangian

$$L = S[n] - (\lambda_0 - 1)\langle 1\rangle - R\beta E - \sum_{r=2}^{m} \lambda_r \langle A_r\rangle . \tag{11}$$

Here the m + 1 coefficients (λ_0, β, λ_r; r = 2, . . ., m) are parameters whose values are to be determined by the condition that at the extremum the distribution is consistent with the values of the constraints. One can show that the procedure leads not only to an extremum but indeed to a maximum for the entropy [6, 14]. Say now that L is divided by $R\beta$. The result (cp. (11)) is just a Lagrangian for seeking an extremum of the energy subject to the given value of the entropy and the other m constraints (normalisation and $\langle A_r\rangle$, r = 2, . . ., m). This is the characterisation of the macroscopic state in the energy picture. The only difference is that the extremum is not necessarily a minimum. It will be a *minimum* if (as is typically the case for macroscopic systems) $\beta > 0$. It is a *maximum* if $\beta < 0$.

The formal equivalence between the entropy and the energy pictures is also shown in Fig. 1. The E-S plots in the bottom row are obtained by simple rotation from those in the top row. As in the entropy picture, the line is the boundary between the allowed and excluded macroscopic states. When $\beta > 0$, the equilibrium E-S line is concave.

Work processes in an isolated system are shown schematically in Figure 2. As in Figure 1 the solid E-S curve corresponds to the situation where no other constraints (apart from normalisation) are present. If additional constraints do apply, the system is characterised by some point (e. g. E_i, S_i) within the allowed region. If now some of these additional constraints are removed, part of the energy of the macroscopic state can be extracted as work. If the entropy is unchanged, then say E_j, S_i is a possible final macroscopic state. Removing additional constraints (at constant entropy) enables the energy to drop even further untill, when all constraints are removed, it reaches E_f. For the given value of S_i, $E_i - E_f$ is the maximal work that can be extracted from the system. If the entropy does increase, less work is available.

By regarding every allowed macroscopic state of the system as a state of maximal entropy subject to constraints one obtains a statistical mechanical description of work processes also for systems not in thermal equilibrium. (The corresponding thermodynamic description is well known [9, 10, 16]). Within such a formulation, equilibrium is the state where the constraints are the (additive) time-independent constants of the motion. There are however time-dependent constants of the

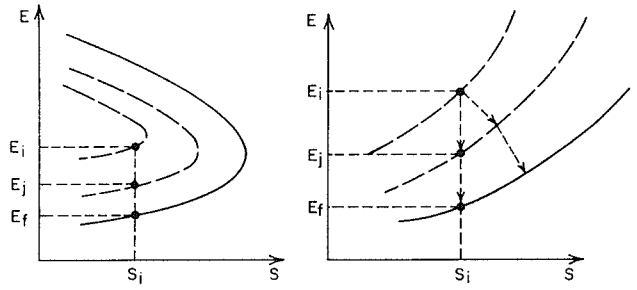

Fig. 2: Work processes in an isolated system of molecules with bounded (left) and unbounded (right) spectrum. The solid lines represent the equilibrium mean or internal energy E-entropy S locus. The broken lines are maximal entropy curves in the presence of additional constraints; the larger the number of constraints the lower is the value of S for a given E. Removal of constraints enables the system to convert part of its energy into work. In the regions of positive temperature, $\partial S/\partial E > 0$, the maximal work, e. g. $E_i - E_j$ is obtained in an isentropic process, $S_i = S_j$. Less work is available in an irreversible process $S_j > S_i$.

motion.[7] By maximizing the entropy subject to such constraints one obtains exact solutions of the Liouville equation which describe non-equilibrium situations. An explicit construction principle for such observables has been described, [17].

The graphical considerations of Fig. 2 can be cast in quantitative terms by recognizing that every point in the allowed region is determined as the solution of an extremum problem. Assume we vary the energy but keep all the other $\langle A_r \rangle$'s constant. For each energy we determine the maximal entropy. The locus of E-S pairs determined in this fashion is shown as a broken line in Fig. 2. (The solid line is, of course, a particular example of a broken line.) Now, let one or more constraints be dropped and the procedure repeated. This generates another broken line which is everywhere exterior to the previous broken line, (imagine Fig. 2 in the entropy picture). The solid line is exterior to all the broken lines.

Let $P_i(n)$ be the distribution of maximal entropy subject to the value E_i of the energy and to additional constraints. The distribution $P_j(n)$ (cp. Fig. 2) differs from $P_i(n)$ in that its energy is lower and some among the constraints on $P_i(n)$ are no longer operative for $P_j(n)$. However, by construction, all of the constraints on $P_j(n)$ are also valid for $P_i(n)$. In other words in going from i to j we have only removed[8] (but have not added) constraints.

As a distribution of maximal entropy $P_j(n)$ is necessarily of the functional form

$$P_j(n) = g_n \exp[-E(n)/RT^j - \sum_{r=2}^{m} \lambda_r^j A_r(n)]/Q_j \,, \tag{12}$$

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[7] These are observables which depend explicitly on time but whose average values are time-independent.

[8] It is important to note that the quantitative argument (eq. (13)) below requires that those constraints which remain do not change their value.

where only the constraints on the state j are present explicitly in the exponent in (12). Consider now the following transformations of the entropy deficiency [6, 12], $DS[P_i|P_j]$, where (12) is used in the final stage[9]

$$\begin{aligned} DS[P_i|P_j] &= R \sum_n P_i(n) \ell n[P_i(n)/P_j(n)] \\ &= R \sum_n P_i(n) \ell n[P_i(n)/g_n] \\ &\quad - R \sum_n P_j(n) \ell n[P_j(n)/g_n] \\ &\quad - R \sum_n [P_i(n) - P_j(n)] \ell n[P_j(n)/g_n] \\ &= S_j[n] - S_i[n] \\ &\quad + R \sum_n [P_i(n) - P_j(n)] [\beta^j E(n) + \sum_r \lambda_r^j A_r(n) - \ell n Q_j] \\ &= S_j[n] - S_i[n] - R\beta^j \sum_n E(n) [P_j(n) - P_i(n)] \\ &= \Delta S - \Delta E/T^j . \end{aligned} \tag{13}$$

Only those constraints on $P_j(n)$ whose values for $P_j(n)$ and $P_i(n)$ are different appear in the final answer. Of course, this result follows from our initial stipulation that apart from the energy and the entropy, all other constraints on $P_j(n)$ are equally valid for $P_i(n)$. If, in addition $S_i[n] = S_j[n]$, we get

$$DS[P_i|P_j] = -\Delta E/T^j . \tag{14}$$

Since $-\Delta E$ is the maximal work available (Fig. 2) it follows that $T^j DS[P_i|P_j]$ is the maximal work even if the system is isolated and not coupled to a heat bath. Moreover, for the conditions in Fig. 2 we have

$$\begin{aligned} E_i - E_f &= (E_i - E_j) + (E_j - E_f) \\ &= T^f DS[P_i|P_f] \\ &= T^j DS[P_i|P_j] + T^f DS[P_j|P_f] . \end{aligned} \tag{15}$$

2. Lasing

In this section we explicitly introduce the constraints which are removed by collisional relaxation and consider the additional work made available by their removal. To simplify the algebra we shall assume that lasing occurs only on P-branch

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[9] Since $DS \geqslant 0$, [6, 12], it follows that for a positive T, the maximal work is obtained when $\Delta S = 0$.

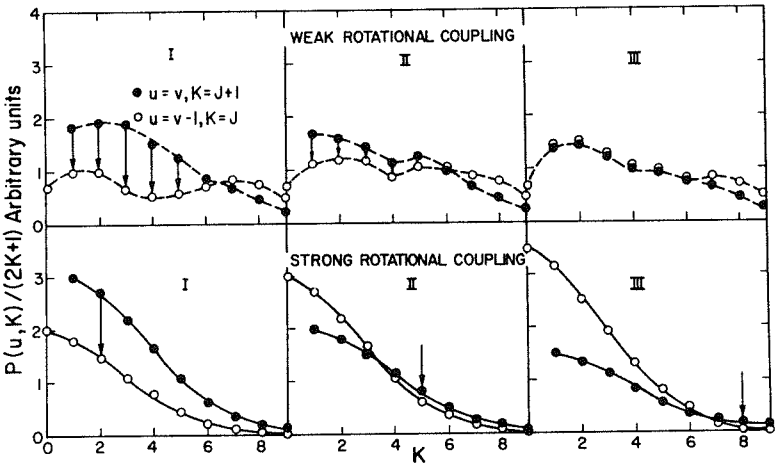

Fig. 3: Stages in the time evolution of the vib-rotational distribution function during the lasing process in the limits of slow (upper pannel) and fast (lower pannel) rotational relaxation. (I . . . just after threshold, II . . . during lasing, III . . . at the end of the pulse). In the limit of fast rotational relaxation the lasing line is an isolated subsystem; lasing occurs independently on each line and terminates upon equalization of the upper and lower populations. In the limit of fast rotational relaxation lasing occurs only on the highest gain line. The effective rotational energy transfer enables the system to lase on high J-lines thereby allowing a very efficient draining of the upper vibrational manifold and consequently high laser efficiency.

lines and that only two vibrational manifolds take part, as is shown in Fig. 3. (This is the case for example in the Cl + HBr → Br + HCl chemical laser [3]). Under such conditions one can easily establish a unique correspondence between the internal energy labels (v and J) of diatomic molecules and the possible lines in the P-branch (v, J − 1 → v − 1, J). Since the lasing is between only two vibrational manifolds, specifying the final rotational state J uniquely assigns the line. Specifying the vibrational quantum number v uniquely assigns the upper or lower state of the transition. Thus, while one often resolves the internal state distribution P(v, J) as

$$P(v, J) = P(J|v)\, P(v)\,, \tag{16}$$

i. e. a distribution of J states within a given vibrational manifold times the vibrational distribution, here we prefer the equivalent but complementary resolution

$$P(u, K) = P(u|K)\, P(K)\,. \tag{17}$$

In (17) we use the same convention as in Fig. 3,

$$P(K) = P(u, K-1) + P(u-1, K) \tag{18}$$

and

$$P(u|K) = \begin{cases} P(v, K-1)/P(K) & u = v \\ P(v-1, K)/P(K) & u = v-1. \end{cases} \tag{19}$$

P(K) is thus the sum of the population in both the upper and lower states of the given P-branch line and hence is the quantity that is constrained in the low pressure limit. P(K) can clearly (cp. (18)) be expressed as an average over the internal state distribution

$$P(K) = \langle A_K \rangle = \sum_v \sum_J A_K(v, J)\, P(v, J)\,, \tag{20}$$

$$A_K(v, J) = \delta(v - u)\,\delta(J - K - 1) + \delta(v - 1 - u)\,\delta(J - K)\,. \tag{21}$$

The low pressure constraint is thus that the magnitude $\langle A_K \rangle$, K = 1, 2, . . . is specified to be equal to that value of P(K) which is characteristic of the nascent (i. e. strictly unrelaxed) products of the chemical reaction.

In Section 1 we have argued that removal of a constraint enables the system to perform work. The proof was based on the unique (and maximum) solution of the extremum entropy problem. Here one can identify explicitly the origin of the increase in the entropy due to the removal of the constraint. The reason is that the expression of the constraints $\langle A_K \rangle$ in the form (20) enables us to state that in the low pressure regime (and over the time interval of interest) the distribution P(K) is unchanging.

Corresponding to the resolution (17) one has a similar form for the degeneracy

$$g(u, K) \equiv g(v, J) = 2J + 1 = g(u|K)\, g(K)\,, \tag{22}$$

where g(K) = [2(J − 1) + 1] + [2J + 1] = 4J, so that

$$g(u|K) = \begin{cases} (2J - 1)/4J & u = v \\ (2J + 1)/4J & u = v - 1\,. \end{cases} \tag{23}$$

The entropy of the internal state distribution P(v, J) can thus be written as

$$\begin{aligned} S[v, J] &= -R \sum_{v,J} P(v, J)\, \ell n[P(v, J)/(2J + 1)] \\ &= -R \sum_{K,u} P(u, K)\, \ell n[P(u, K)/g(u, K)] \\ &= -R \sum_K P(K)\, \ell n[P(K)/g(K)] \\ &\quad - R \sum_K P(K) \sum_u P(u|K)\, \ell n[P(u|K)/g(u|K)] \\ &= S[K] + S[u|K] = S[u, K]\,. \end{aligned} \tag{24}$$

The first term in (24) is not allowed to vary in the low pressure regime. The procedure of seeking the distribution P(v, J) for which S[v, J] is maximal (subject to

energy and other, if any, constraints) is equivalent to seeking the distribution P(u, K) for which S[u, K] is maximal (subject to the same constraints). In the low pressure regime P(K) = const. is a constraint, for all K's. As the pressure is increased, this constraint is removed (by collision induced population transfer). For a given E, the maximal value of S may be higher in the higher pressure regime since both P(u|K) and P(K) are allowed to vary. Conversely, for a given S, the minimal value of E will be lower (cp. Fig. 2) and more work is available.

Additional insight into the role of rotational energy transfer is provided by regarding the entire (isolated) system as a sum of two parts: the internal degrees of freedom of the lasing molecules and a heat bath provided by the translational motion. Coupling between the two is provided by binary collisions and hence is absent in the low pressure regime. In the limit of effective rotational relaxation the coupling is strong enough to ensure that at all times the rotational states are in thermal equilibrium at the temperature of the heat bath [18].

The coupling of the lasing system and heat bath implies that the entropy of the lasing system may decrease during lasing provided that there is a corresponding increase in the entropy of the bath [11, 19], Fig. 4. As is evident from the figure, the more the entropy of the lasing system can decrease the more work is available. A quantitative entropy balance for a chemical laser in the strong rotational coupling regime can be obtained as follows [19]: The rotational state population is maintained unchanged by the collision. The only change is thus in the vibrational state population P(v). Now in a $v \to v - 1$ transition the relations hold:

$$\delta E = hc\omega\delta P\,, \tag{25}$$

$$\delta S = -R\ell n[P(v)/P(v-1)]\,\delta P\,. \tag{26}$$

Here δP is the decrease in P(v) (and the increase in $P(v-1)$) and ω is the vibration frequency. Consider now the P-branch transition $v, J-1 \to v-1, J$. The laser light

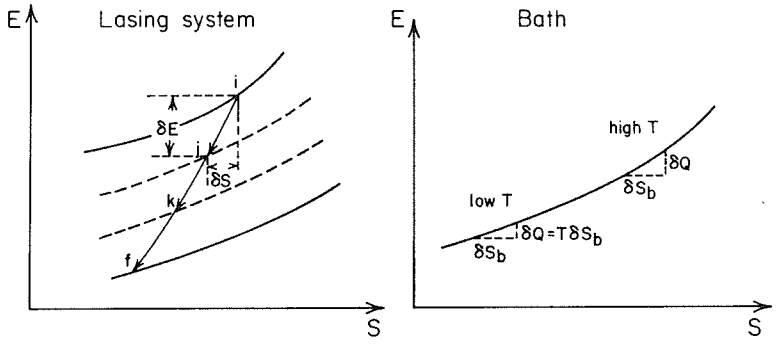

Fig. 4: Changes in the energy and entropy of the lasing system and the heat bath during lasing in the limit of strong rotational coupling. The entropy decrease of the system associated with lasing under partial vibrational inversion, $(P(v)/P(v-1) < 1)$, e. g. δS in the transition $i \to j$, is compensated for by a corresponding entropy increase of the bath $\delta S_b = \delta Q/T \geqslant -\delta S$. The difference $\delta W = -\delta E - \delta Q$ appears as laser radiation.

has a frequency $h\nu_L = h\omega - 2BJ$. The balance of the energy $(\delta E - h\nu_L)$ appears as heat in the bath. For this we have

$$\delta S_b = (2BJ/T)\,\delta P \tag{27}$$

where T is the temperature of the heat bath (Fig. 4). The condition

$$\delta S + \delta S_b \geqslant 0$$

or

$$2BJ/T + R\ell n[P(v)/P(v-1)] \geqslant 0 \tag{28}$$

is the familiar condition for chemical lasing [19], cp. (3).

Two additional insights are provided by (28). First note that even for $P(v)/P(v-1)$ quite below unity, lasing is still possible for a sufficiently high J. This is the reason for the gradual shift of the lasing line towards higher J's [1–3]. (Ultimately, lasing terminates due to the absolute concentrations falling below the loss level [4].) Second, the loss of chemical energy as heat is 2BJ. As the heat bath temperature increases, lasing occurs at a higher J (cp. (28)) and hence less energy is extracted as laser light. The efficiency improves upon cooling of the laser [1, 2].

3. Concluding remarks

The maximal work which can be obtained from a nonequilibrium molecular system has been discussed in terms of the number and character of the constraints on the molecular level populations. The constraints reflect the relative time scales of the relaxation and work producing processes governing the time evolution of the system. In chemical lasers based on vib-rotational transitions the major factor influencing the amount of work (laser light) which can be extracted from the system is the ratio between the rates of rotational relaxation and stimulated emission. When this ratio is large a constraint on the molecular distribution function is removed and the laser operates more efficiently.

It is important to note that all the considerations of this paper refer to the maximal and not the actual work obtained from nonequilibrium systems. The latter depends not only on the constraints but also on the rates of the loss processes which compete with the work producing mechanism. Thus, in chemical lasers vibrational relaxation and cavity losses compete with the stimulated emission and lead to irreversible entropy and heat production. However, time-dependent kinetic and thermodynamic analyses [20, 21] indicate that the major factors influencing the laser efficiency are the constraints implied by the kinetic scheme. Finally, it should be noted that the classification of rate processes as useful (e. g. rotational relaxation) and useless or dissipative (e. g. vibrational relaxation) depends on the form of thermodynamic work generated by the system. For example, while rotational relaxation enhances the stimulated emission in lasers operating on vibrational transitions it is, clearly, a process which should be avoided in lasers operating on pure rotational transitions.

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