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Increase of Chemical Laser Efficiency by
Gasdynamical Pumping

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ABSTRACT

The exhaust of chemical lasers could be used as a source of working fluid and energy for a gasdynamical expansion laser. Molecules such as HF may yield partial vibrational inversions of $\Delta N/N \sim 10^{-3}$ for nozzles with small throat area and large divergence angle. The maximum inversions are calculated and plotted for the P branch lines with rotational quantum numbers $J = (1) - (10)$ of the molecules HF, CH, OH, OD, HCl, CN, CO, NO as function of the vibrational and rotational temperature. The application of these calculations to the flow through Laval nozzles is illustrated with examples. Additional benefit of this scheme is drawn from the fact that the waste molecules of the chemical laser may have an elevated vibrational temperature, so that the inversion in the flow may be produced and improved by combined chemical and gasdynamical pumping.

1. INTRODUCTION

Molecular lasers operating on vibrational rotational transitions require either a complete or a partial vibrational inversion.¹ In the first case the number of particles in the upper vibrational state $n_v(u)$ is larger than the number $n_v(l)$ in the lower vibrational state. In the second case inversion is only present for certain transitions, so that $n_{v,J}(u) > n_{v,J}(l)$ while there is no inversion for other lines of the same and other bands, and in particular $n_v(u) \leq n_v(l)$. Such partial population inversion is found in molecular gases with high vibrational temperature T_v and low rotational temperature T_r . The principle is easily understood in the extreme case $T_r \rightarrow 0$ and $T_v > 0$. In this case the molecules in all vibrational states have the rotational quantum number $J=0$ so that the lower state for the P(1) lines (with $J=0 \rightarrow J=1$) is completely empty.

A difference in vibrational and rotational temperatures is established during the passage of a molecular gas through a supersonic (Laval) nozzle. In such a flow the translational temperature is known to decay, lowering the rotational temperature due to the good coupling between the translational and rotational degrees of freedom. The vibrational temperature, however, stays nearly constant. This selective cooling of the rotational temperature can in principle be used either to create a vibrational rotational population inversion starting from hot gases in thermal equilibrium or to improve inversions that had been produced by other means, for instance by chemical reactions.

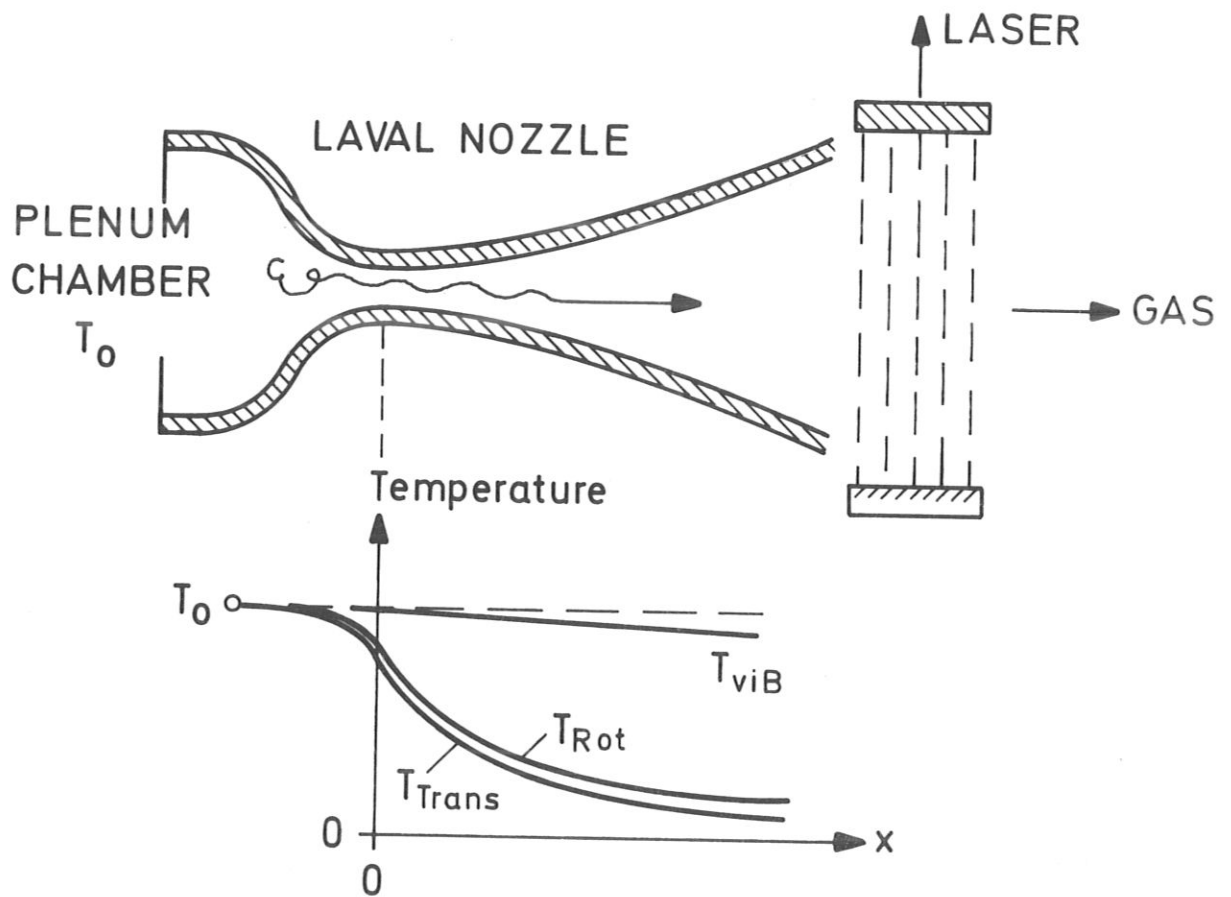


Fig.1 Temperature profiles in Laval nozzle

Chemical CW lasers have been operated so far with efficiencies of up to 15 %² converting the chemical energy into laser radiation. The rest of the reaction energy heats the molecules so that an intense flow of hot waste material - more or less equilibrated by the laser emission and collisions - issues continuously from such lasers.

The question therefore arises whether one could recover an additional fraction of the initially invested energy from a laser pumped by selective cooling in a Laval nozzle which is fed from the exhaust of a chemical laser. One could envisage to construct a chemical-gasdynamical laser as indicated in Fig. 1. However, before embarking on such a project one must know the magnitude of the gasdynamical pumping effect for molecules formed in chemical lasers. For that reason we have calculated the inversions and amplifications for P-branch transitions of diatomic molecules which are already used or are likely candidates for chemical lasers. The results are interpreted for a model nozzle.³ They are, however, given in such a general form that they can be applied to any other molecular system with different rotational and vibrational temperature.

2. MODEL ASSUMPTIONS

A molecular gas can store energy in the form of random translational (kinetic) motion, rotation, vibration, electronic excitation, dissociation, and ionization. Each of these modes or degrees of freedom may be characterized by

a temperature T_t, T_r, T_v, \dots , which all agree if the gas is in local thermal equilibrium. If the system is temporarily disturbed, by extracting some energy out of any one of these modes, it will take some time and require a number of Z gas-kinetic collisions until a new equilibrium is attained.

Equilibrium is reached quickly within rotation and translation by themselves, since $Z_r \sim Z_t = 1 - 10$.⁴ Energy exchange between these two degrees of freedom is also very rapid, with $Z_{t-r} = 10 - 100$ collisions.⁴ Equilibration between translation and vibration, however, takes much longer. Numbers of $Z_{t-v} = 10^2 - 10^7$ are quoted.⁴ Thus vibrational energy can be isolated from rotation and translation for some time. If, for instance, a molecular gas is expanded in a Laval nozzle, the translational and rotational temperature are rapidly lowered while the vibration maintains the high initial temperature of the inlet for quite some time. This behaviour is illustrated in Fig. 2, which shows the translational temperature calculated with standard nozzle theory for the throat area $A^* = 1 \text{ cm}^2$ and the opening angle $\delta = 15^\circ$. Since the temperature reduction depends sensitively on the adiabatic exponent, two curves for $\gamma = 1.2$ and 1.4 are given.

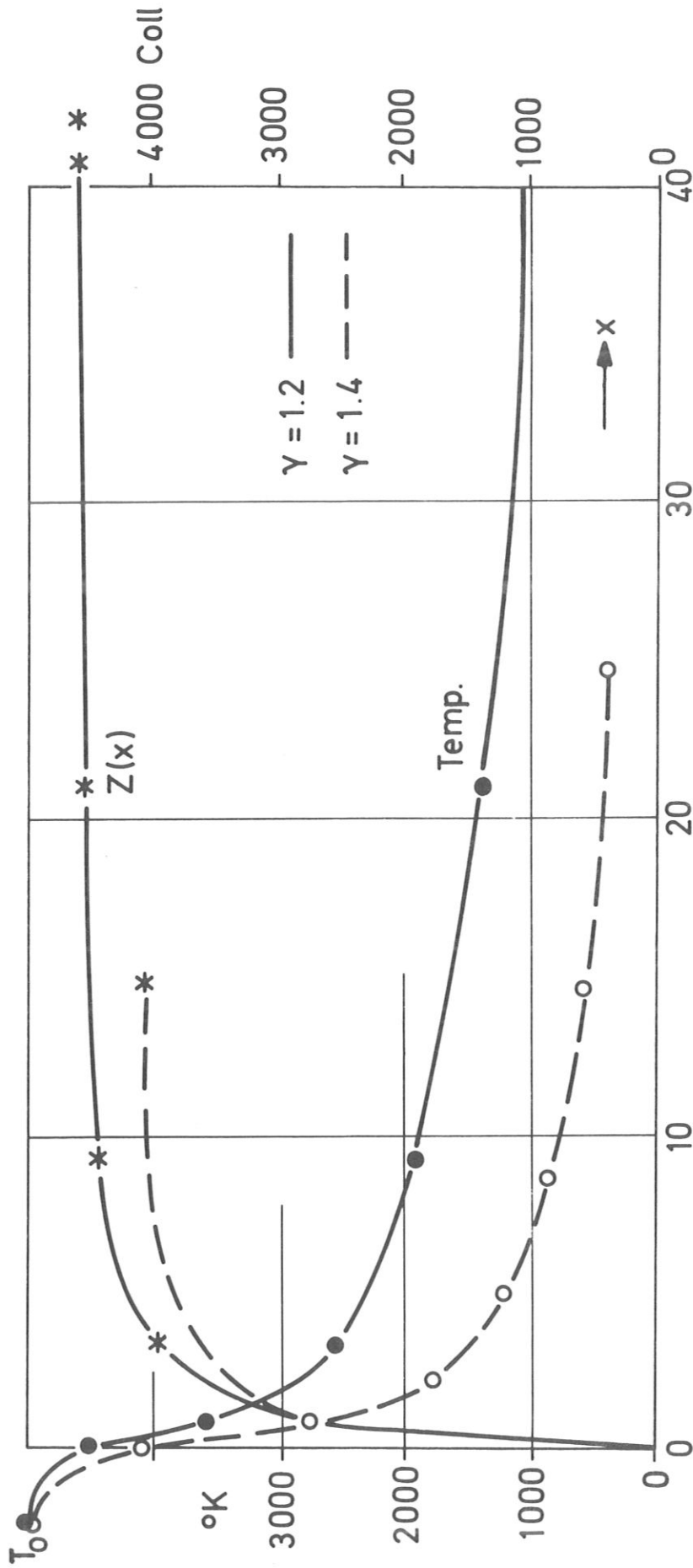


Fig. 2 Temperature drop in Laval nozzle of 15° opening angle. $Z(x)$ is the number of collisions suffered by a particle travelling from $x = 0$ to a position x .

3. EXCITATION AND POPULATION INVERSION

The magnitude of the inversion which may be found in such a flow can be calculated as function of T_v and T_r . For simplicity we assume $T_r = T_t = f(x)$ where x is the distance from the throat (Fig. 2), and further $T_v = T_o = \text{const.}$

The population of the J -th rotational level (rotational energy $F(J)$) within the v -th vibrational state (vibrational energy $G(v)$) is given by (1).⁵

$$N_{vJ} = N \frac{g_J}{Q_v Q_J} \exp \left[- \frac{hc}{k} \left(\frac{G(v)}{T_v} - \frac{F(J)}{T_J} \right) \right] \quad (1)$$

N is the total number of molecules, Q_v and Q_J are the vibrational and rotational partition functions and $g_J = 2J+1$ is the statistical weight of the level. The partition functions are approximated as usual.

$$\begin{aligned} Q_v &= 1 + \sum_{v=1}^{\infty} \exp - \frac{hc}{k} G(v) \\ Q_J &= \frac{k T_r}{hc B_e} \end{aligned} \quad (2)$$

The vibrational and rotational energies can be given as

$$\begin{aligned} G(v) &= (\omega_e v - x_e \omega_e v^2) \approx \omega_e v \\ F(J) &= B_e J(J+1) \end{aligned} \quad (3)$$

where B_e, ω_e, x_e are spectroscopic constants.⁵ We assume that the temperatures T_v and T_r are defined independently and are not equal. Minimum requirement for laser emission is generally that a vibrational rotational population inversion exists.

$$\left(\frac{N_{vJ}}{g_J} - \frac{N_{v'J'}}{g_{J'}} \right) B_{v'J'}^{vJ} = \Delta N_{vJ} B_{vJ} > 0 \quad (4)$$

The prime refers to the lower state, thus for P-branch transitions ($\Delta J = +1$ in emission) $v'=v-1$, $J'=J+1$, $B_{v'J'}^{vJ}$ is the Einstein coefficient for induced emission. Entering expression (1) into (4) the relative inversion for P-branch lines is obtained.

$$\frac{\Delta N_{vJ}}{N} = \frac{1}{Q_v Q_J} \left[\exp - \frac{1}{k} (G(v) + F(J)) - \exp - \frac{1}{k} (G(v-1) + F(J+1)) \right] \quad (5)$$

We assume now that the potential laser emission occurs at the line center and the line is Doppler broadened. The optical gain at the line center is formed by multiplying ΔN with the line shape function $S(\nu)$, the average photon energy $h\nu$ and the time $1/c$ a photon travels through the active laser medium. The gain coefficient α is thus

$$\alpha = \Delta N_{vJ} B_{vJ} S(\nu) h\nu \frac{1}{c} . \quad (6)$$

A positive inversion requires that the bracket in (5) is positive which means that

$$\tau = \frac{T_r}{T_v} < \frac{\Delta F(J)}{\Delta G(v)} \approx 2(J+1) \frac{B_e}{\omega_e} \quad (7)$$

This relation was first stated by J.C. Polanyi.⁶

For a given molecule B_e/ω_e is a constant, so that the temperature reduction τ necessary to reach the threshold of inversion depends linearly on the rotational quantum number J . Inversion is positive below the threshold line $\tau_t = 2(J+1)B_e/\omega_e$, given in Fig. 3 for several molecules. Of course only the ordinates of integer numbers J have physical meaning.

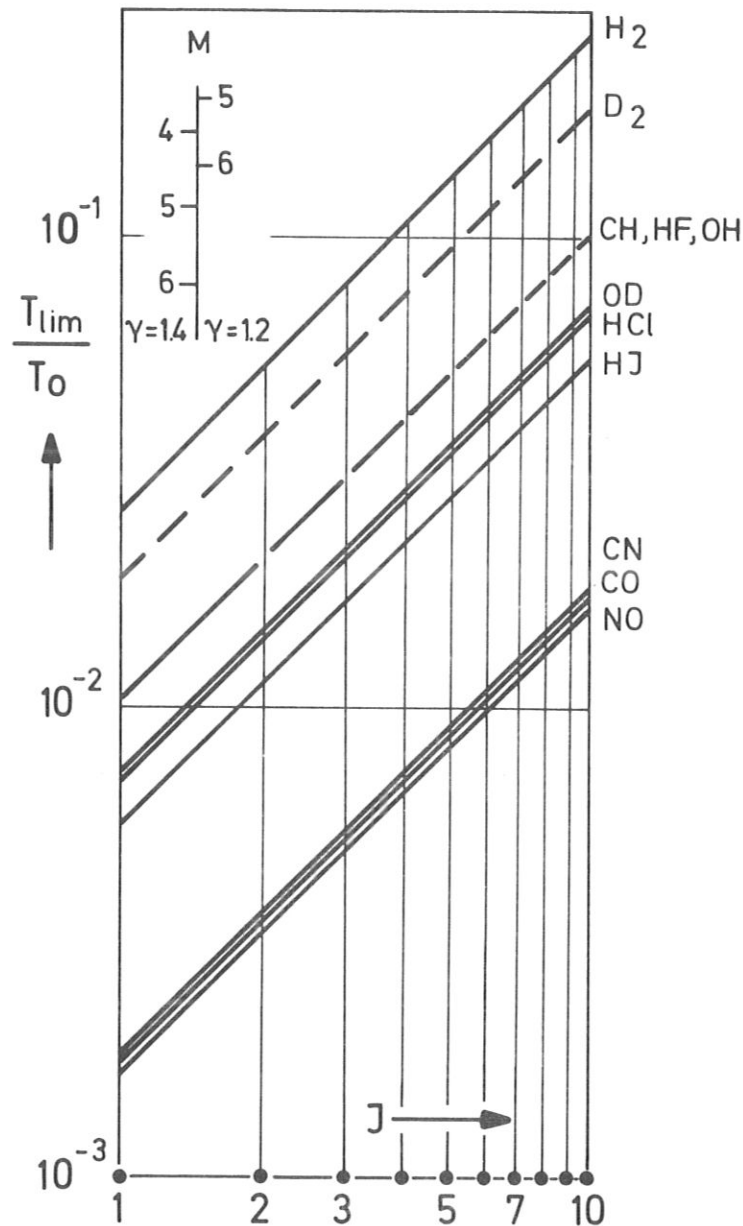


Fig. 3 Temperature ratios below which partial population inversion for P-branch transitions is possible. T_0 = vibrational temperature. T_{lim} = maximal rotational temperature. The abscissa gives the rotational quantum number of the lower level. For instance: Population inversion of the $P(10)$ line of HF is obtained if $T_{rot}/T_{vib} \leq 0.1$. This is obtained in a Laval nozzle at a position where the Mach number has reached $M = 5.3$ (with $\gamma = 1.4$).

The second ordinate scale x of Fig. 3 relates the temperature reduction τ with the distance in the model nozzle. However, the temperature decrease in any supersonic nozzle is unequivocally related to the local Mach number, independently of the particular shape of the nozzle.⁷ This general relation between temperature reduction and Mach number is indicated by the third ordinate scale. For instance, a Mach number of $M = 5.3$ (at $\gamma = 1.4$) is required to obtain inversion for the P(10) transition of CH, HF or OH.

4. INVERSION AND AMPLIFICATION

The population inversions were calculated with equations (5) and (6) using the IBM 360/91 of this Institute for a number of molecules. Some details of the results are discussed for the HF molecule as an example.

Figure 4a gives the relative inversion $\Delta N/N$ defined by equation (10) as function of the rotational temperature T_{rot} for several lines of the P-branch. The vibrational quantum number of the upper state is 1 and an initial temperature of $T_0 = 5000$ °K is used. The corresponding amplification at the line center according to (11) is given in Fig. 4b. Higher vibrational quantum numbers do not yield significantly higher amplification. This can be seen from Fig. 4c, which gives α for $v = 1, 2, 3$ and different initial temperatures, for the P(2) lines.

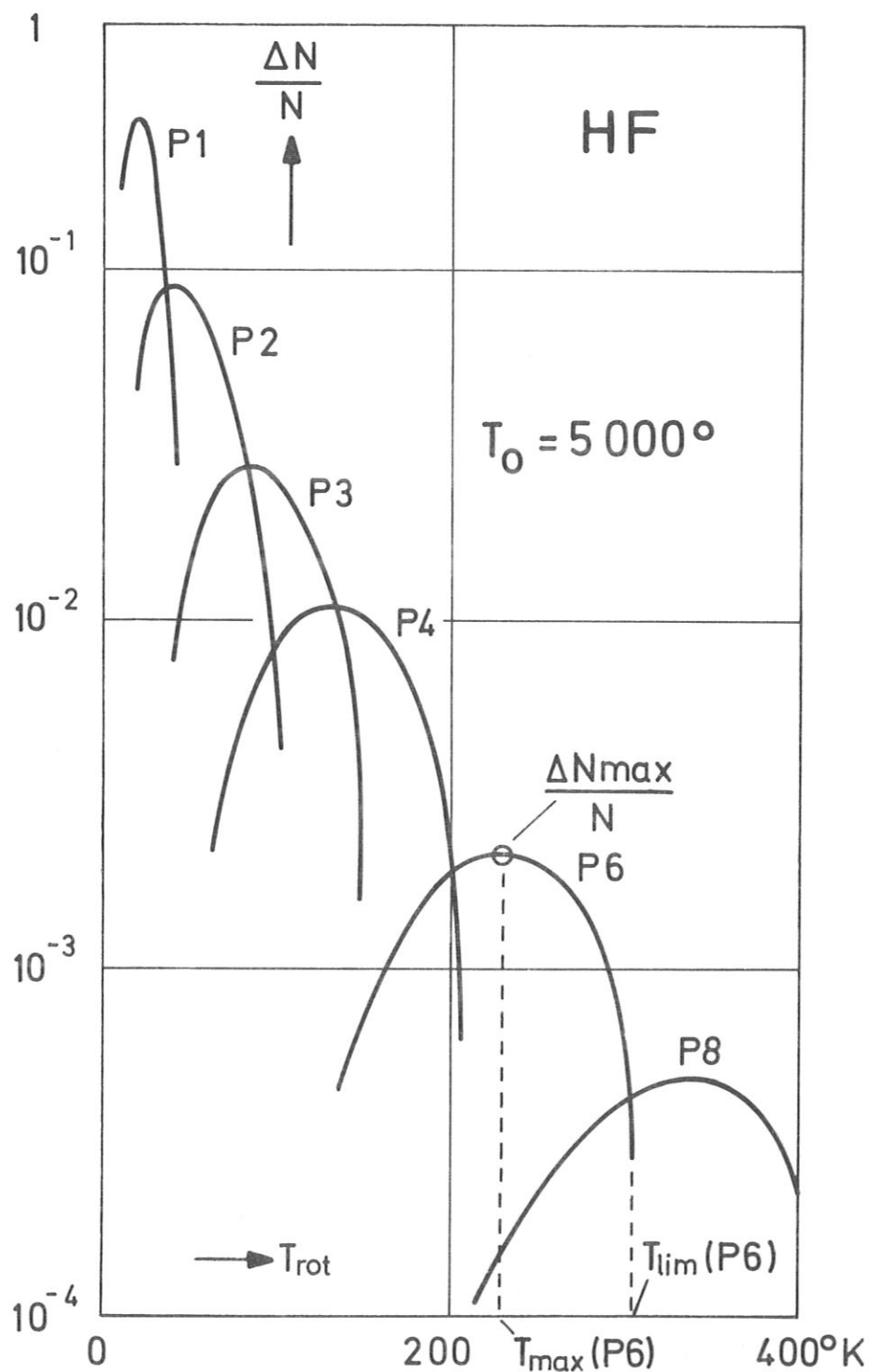


Fig. 4a Relative population inversion of P-branch lines (vibrational quantum number of the upper state $v = 1$) as function of the rotational temperature T_r , T_0 = vibrational temperature, P = rotational quantum number of the lower state.

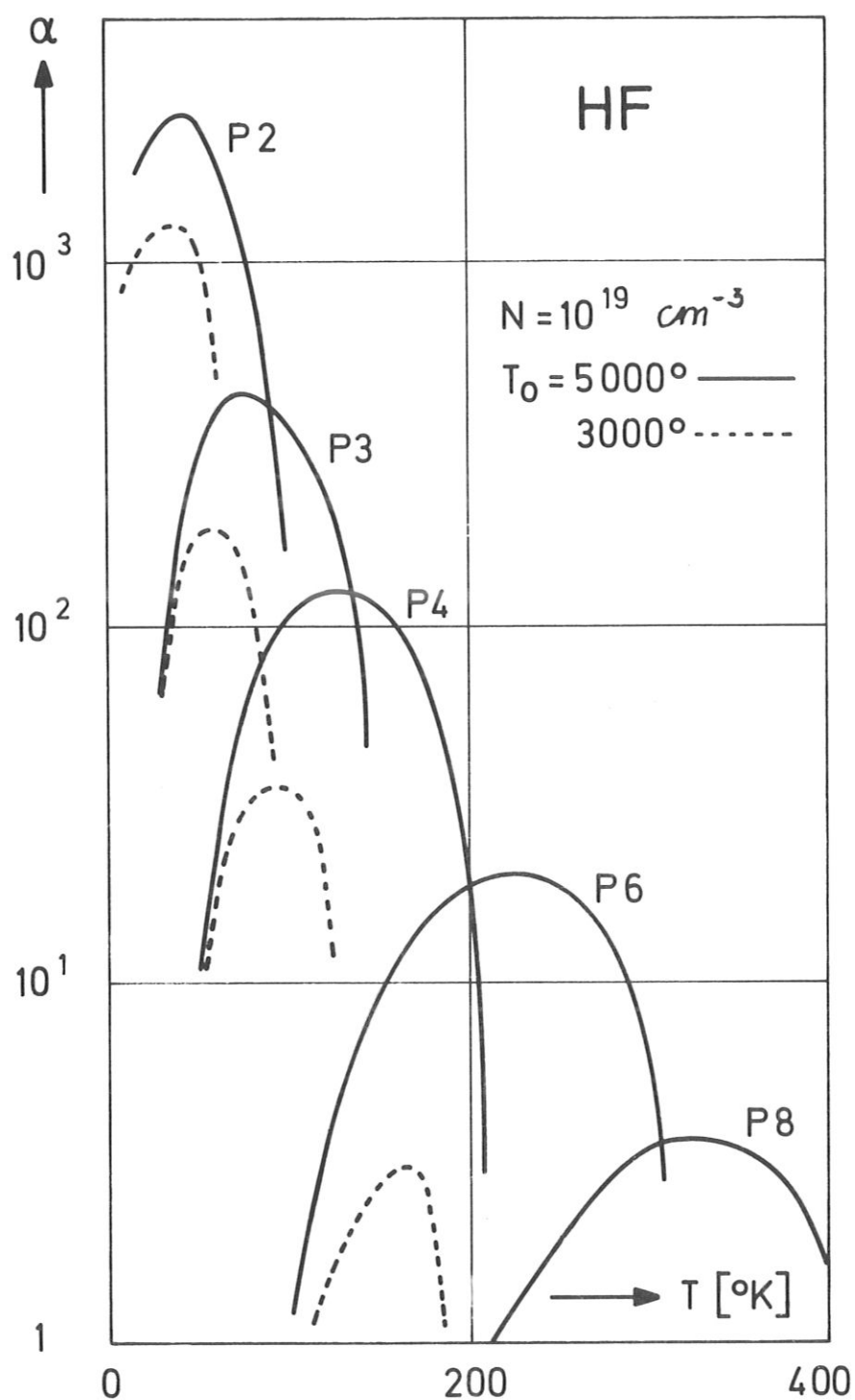


Fig. 4b Amplification at the line center of Doppler-broadened lines as function of rotational (T_r) and vibrational (T_0) temperature.

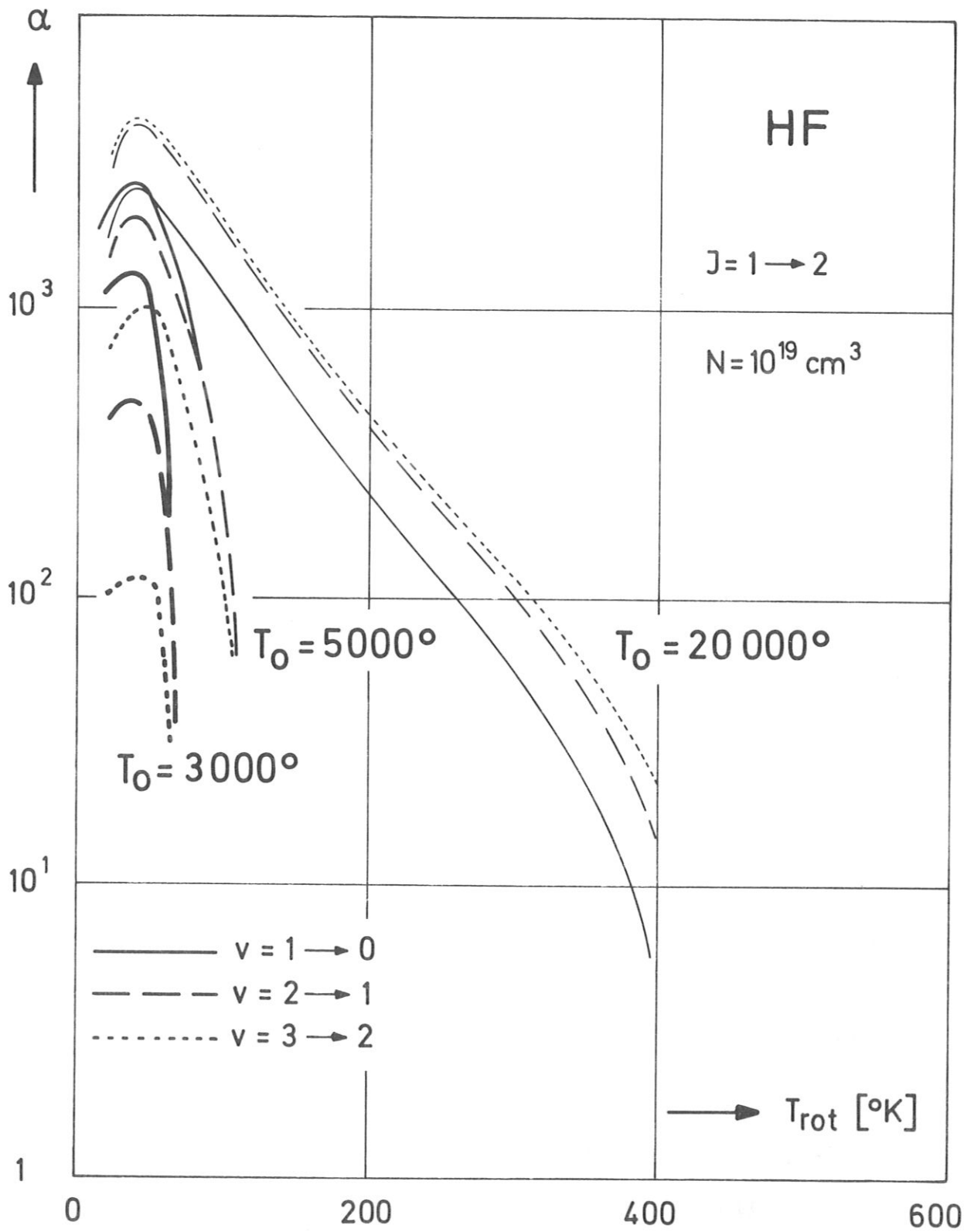


Fig.4c Amplification of P(2) lines as function of rotational temperature for different vibrational temperatures T_0 and vibrational excitation.

The inversion is largest for small J values, but requires very low rotational temperatures to be effective (Fig. 4a). For each line the inversion reaches a maximum $(\Delta N/N)_{\max}$ at a temperature T_{\max} , which is generally close to the limiting temperature T_{\lim} at which the inversion vanishes.

With knowledge of the general structure of the inversion curves as displayed in Figs. 4, a quick survey of the partial inversion of a molecule is possible, if the maximum inversion $(\Delta N/N)_{\max}$, the corresponding temperature T_{\max} and the limiting temperature T_{\lim} are known for each line. One only needs to distinguish different rotational quantum numbers since different vibrational levels have all a similar run (Fig. 4c). The important information about the inversion can therefore be given in a diagram which shows $(\Delta N/N)_{\max}$ as function of T_{\max} with T_0 and the rotational quantum numbers J as parameters, Fig. 4d. The additional information about T_{\lim} is already contained in Fig. 3. Again, in both these diagrams only the abscisses belonging to integer J values have a physical meaning. Figure 4d shows, that the maximum inversion can reach a high value of $(\Delta N/N)_{\max} > 0.1$ at low temperatures T . It drops quickly with increasing J and T .

The highest inversion would be established by this mechanism in H_2 and D_2 , since these molecules have the largest value of B_e/ω_e . Thus H_2 is considered here to show the limitations of the principle although it naturally does not give vibrational rotational emission. Figure 5 is a cross

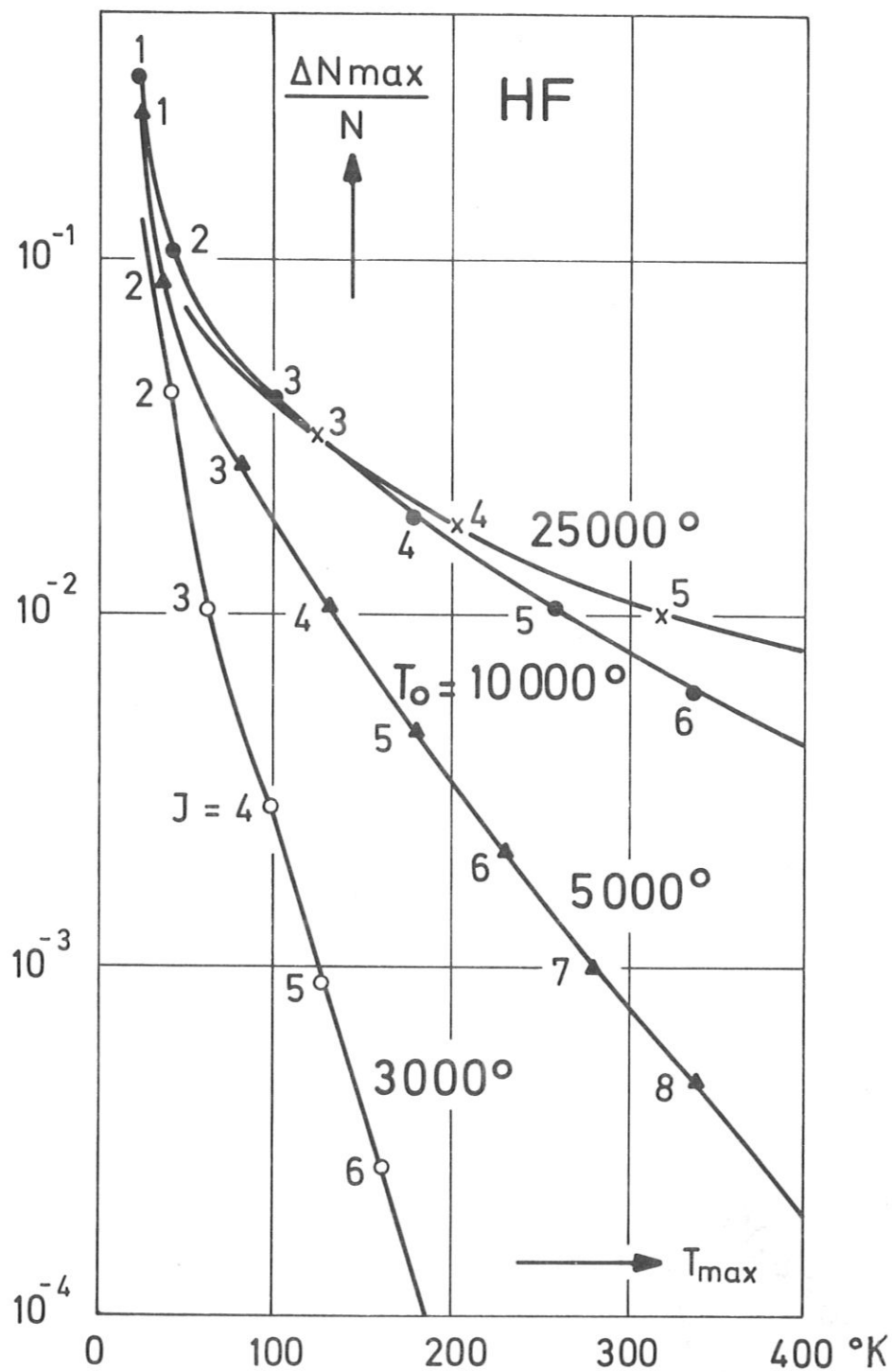


Fig. 4d Maximum inversion as function of the rotational (T_{\max}) and the vibrational temperature T_0 for P-branch lines of HF. Parameter is the rotational quantum number of the lower state.

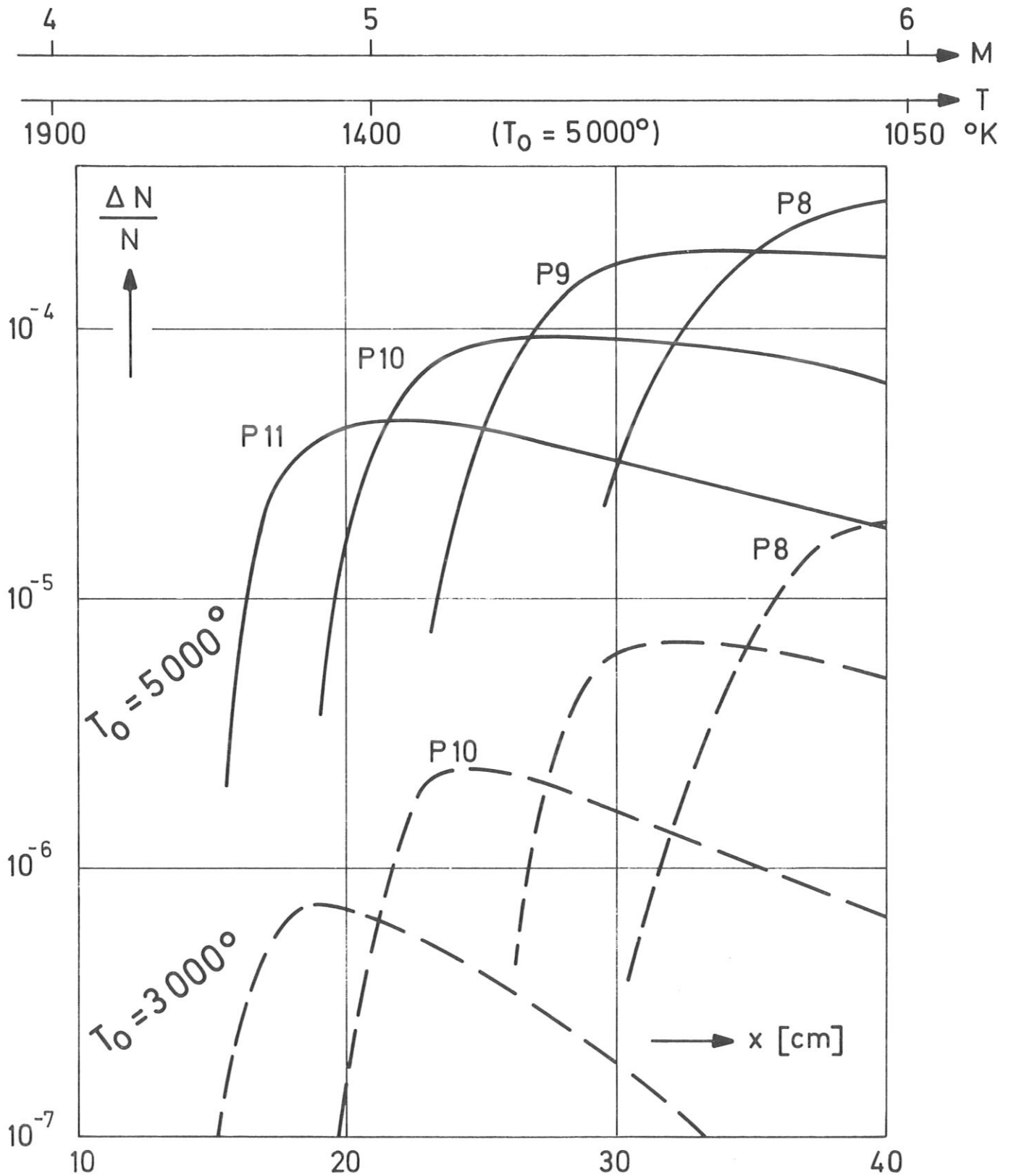


Fig. 5 Population inversion among vibrational rotational states ($v \rightarrow v-1, J-1 \rightarrow J$) in hydrogen.

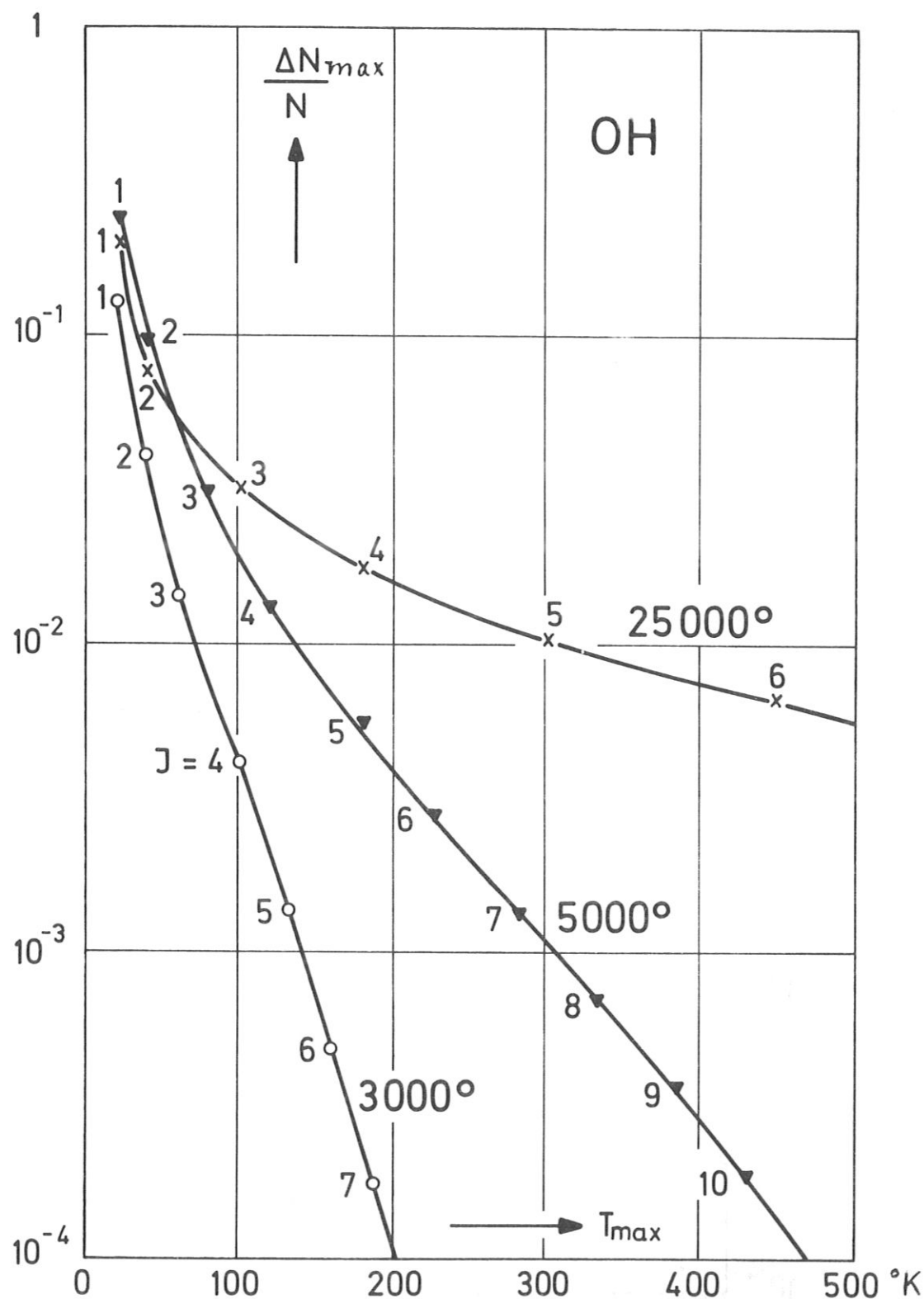


Fig. 6 Maximum inversion as function of the rotational (T_{\max}) and the vibrational temperature T_0 for P-branch lines of OH. Parameter is the rotational quantum number of the lower state.

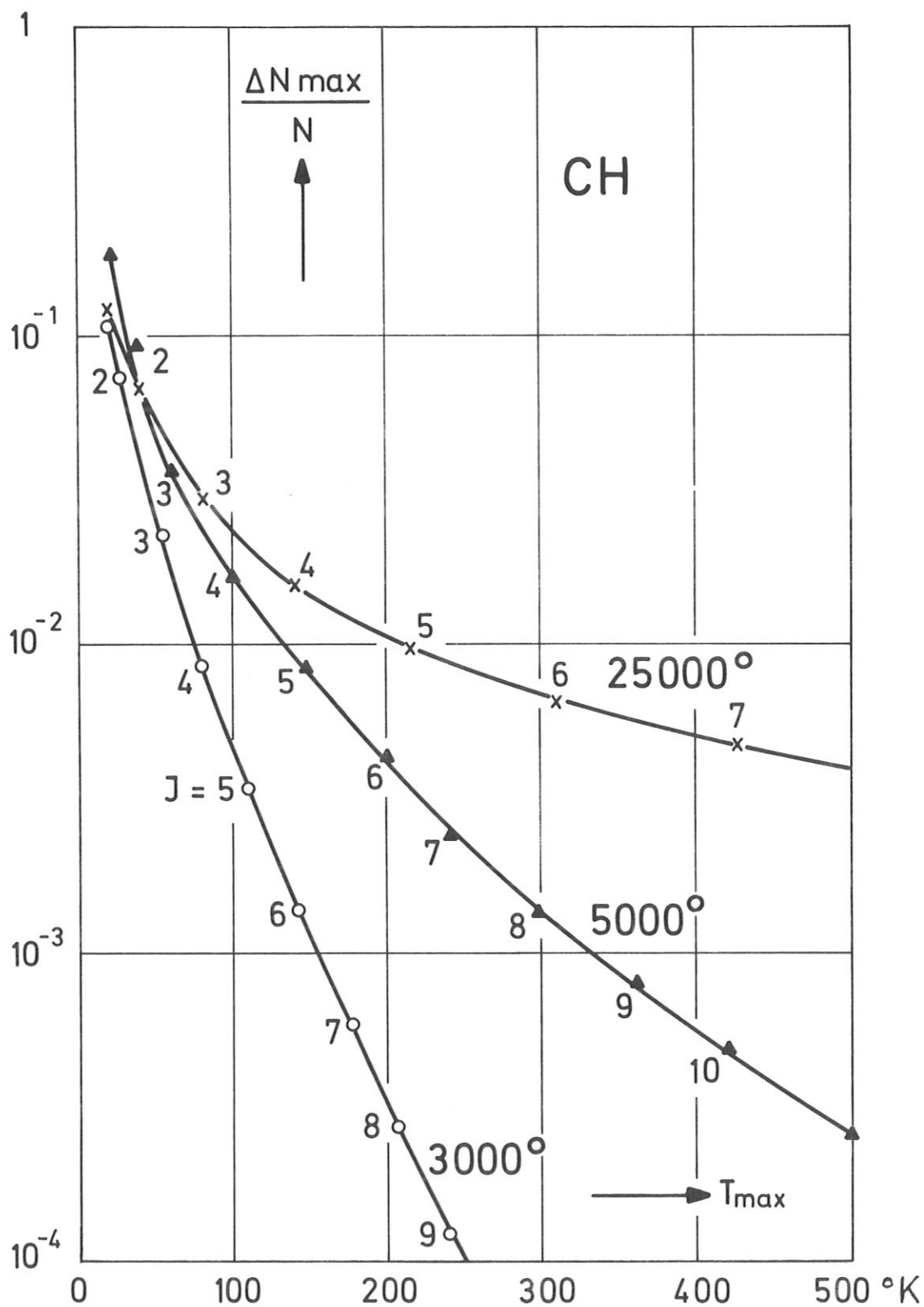


Fig. 7 Maximum inversion as function of the rotational (T_{\max}) and the vibrational temperature T_0 for P-branch lines of CH. Parameter is the rotational quantum number of the lower state.

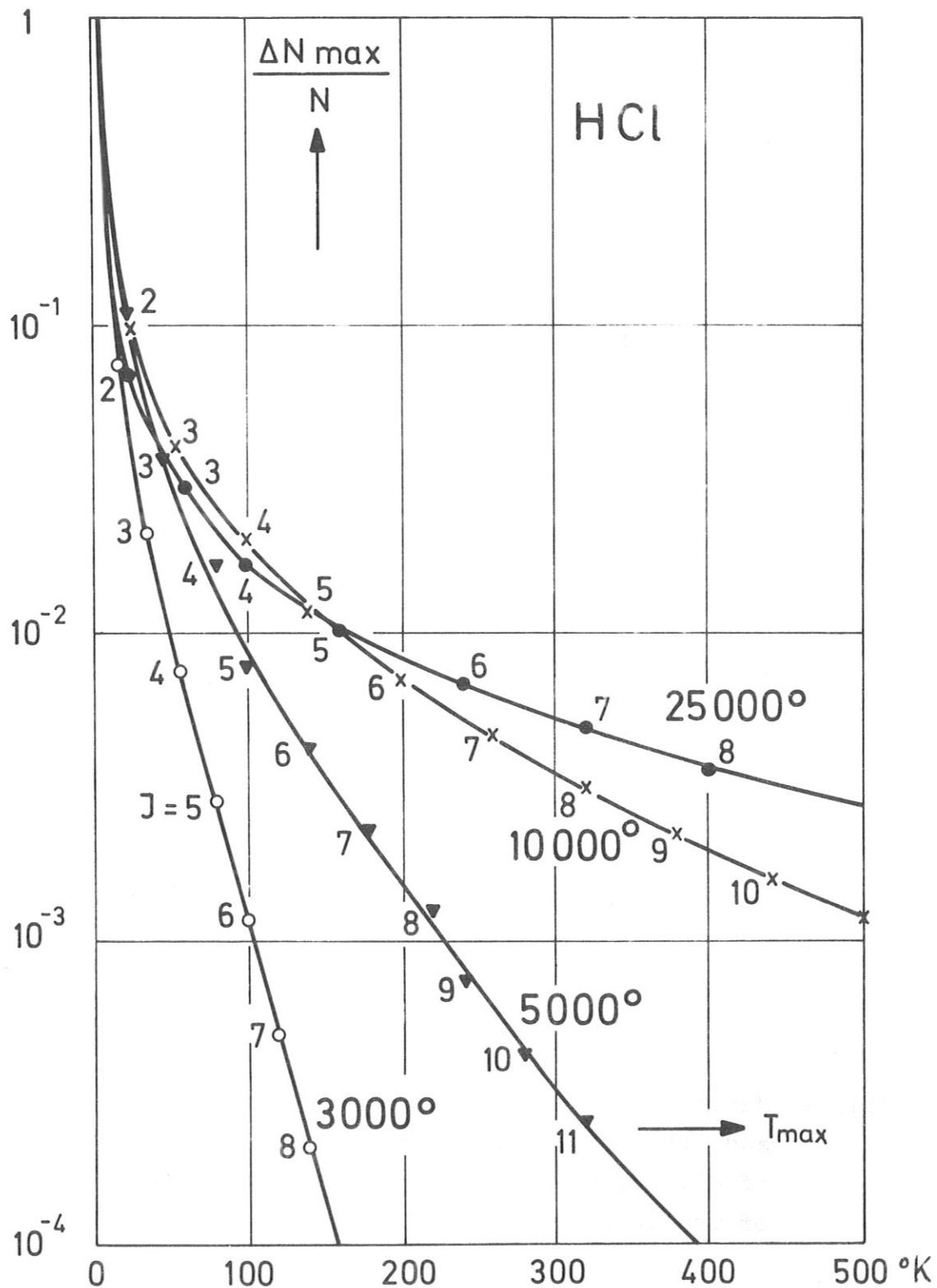


Fig. 8 Maximum inversion as function of the rotational (T_{\max}) and vibrational temperature T_0 for P-branch lines of HCl. Parameter is the rotational quantum number of the lower state.

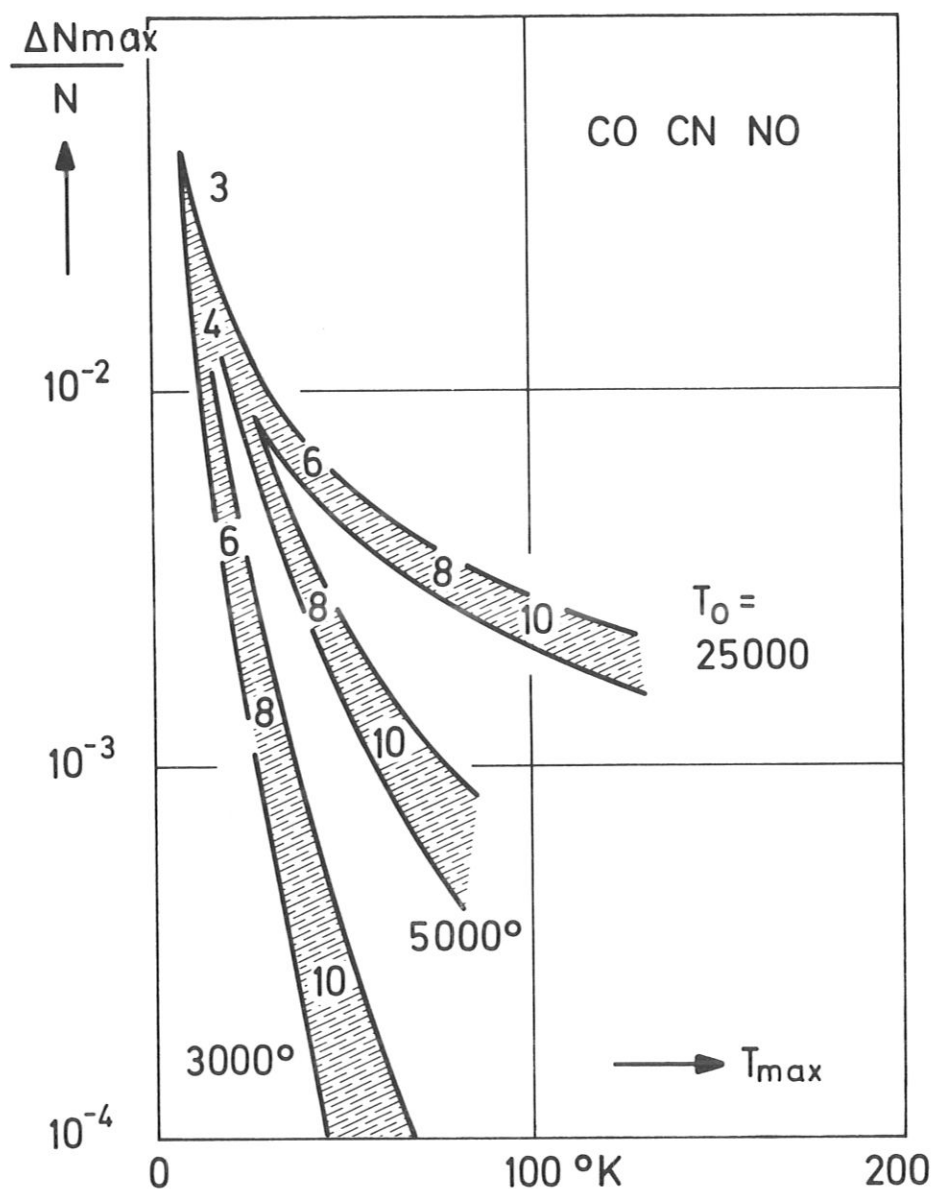


Fig. 9 Maximum inversion as function of the rotational (T_{\max}) and the vibrational temperature T_0 for P-branch lines of CO, CN, NO. Parameter is the rotational quantum number of the lower state.

plot of an inversion diagram $\Delta N/N$ for hydrogen (similar to Fig. 4a) with the temperature profile of Fig. 2 using the unfavourable $\gamma = 1.2$ curve. For different initial temperatures T_0 the inversion becomes positive at the same position in the nozzle, but the maximum inversion is of course higher for the larger starting temperature.

Figures 6, 7, and 8 give the maximum inversions for OH, CH and HCl, which have relatively high inversions due to large values of the ratio B_e/ω_e . Figure 9 summarizes the same data for the molecules CO, CN and NO, these three have all similarly small ratios B_e/ω_e and the maximum inversions fall all within the crosshatched regions. Partial population inversion in these molecules is only obtained if the rotational temperature is kept very low.

5. REACTION PRODUCTS

We have assumed until now, that the starting stagnation temperature is identical for rotation and vibration $T_0 = T_{vo} = T_{ro}$, however this may not necessarily be so. In many chemical reactions a large fraction of the heat of reaction goes into vibrational excitation of the products. Even in cases where a total vibrational inversion exists immediately after the reaction, fast energy transfer processes may lead quickly to equilibrium of the vibrational energy distribution. This situation of partial relaxation then implies a rather high vibrational temperature. For example, Foster and Kimbel found $T_v = 25\,000^\circ\text{K}$ for CO molecules⁸ generated in the reaction of oxygen and carbon disulfide and Cool and Stevens did a whole series of hydrogen halide chemical laser experiments

with chemically formed partial inversions.⁹ Under such conditions rotational cooling in an expansion nozzle can either improve the existing partial inversion or create the inversion if T_r is too high initially to permit lasing. Of course, a similar improvement is obtained by adding cold nonreacting gases to the reaction mixture or by increasing the inversion by selective energy transfer to other gases. The latter principle has been applied in CO¹⁰ and CO₂¹¹. For the above mentioned example of carbon monoxide the inversion as function of T_r is displayed in Fig. 10. We assumed $T_v = 25000$ °K and an inlet rotational temperature of $T_{r0} = 500$ °K. With such a working fluid partial inversion can be reached after only a few cm of travel in the standard nozzle.

6. NOZZLE DIMENSIONS

The detailed calculations of the population inversion have shown that rather drastic temperature reductions or high Mach numbers are required to reach significant inversions. The Mach number increases if the area ratio A/A^* in the nozzle grows. At a fixed distance this ratio may be raised by enlarging the angle δ or by reducing the throat area.

In the limit $\delta \rightarrow 90^\circ$ the gas expands into a half space. The related temperature drop may now be obtained from the adiabatic relation $T \cdot V^{\gamma-1} = \text{const}$, where V is a half sphere volume centered on the axis of the exit cross section. If the gas expands freely into the half space, the temperature will decay as

$$T/T_0 = (r/r_0)^{3(\gamma-1)}.$$

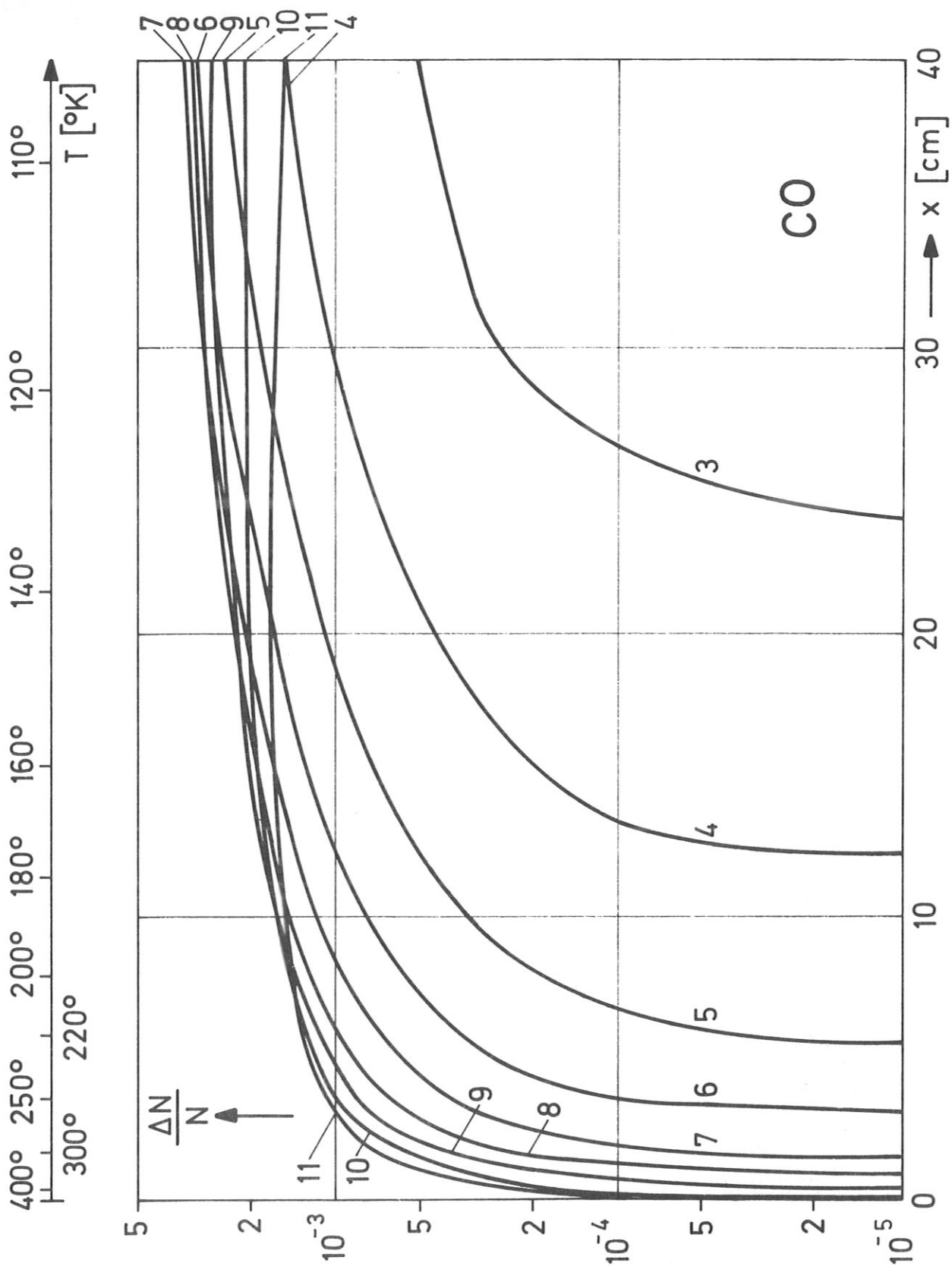


Fig. 10 Population inversion for vibrational rotational transitions ($v \rightarrow v-1$, $J-1 \rightarrow J$) in CO in a 15° Laval nozzle as function of distance x .

Suppose $A^* = \pi r_0^2 = 1 \text{ cm}^2$ the temperature has dropped below $\tau = 5.10^{-2}$ at a distance of $r = 7 \text{ cm}$ (using $\gamma = 1.4$) or $r = 70 \text{ cm}$ for $\gamma = 1.2$. This temperature reduction suffices to reach the inversion threshold of the P(5) line of the HF molecule.

In order to decrease the temperature even faster, one can reduce the cross section A^* and compensate the loss in area by the use of many holes. Suppose the reaction area exit is split up into 100 small holes of 0.01 cm^2 each (instead of one hole of 1 cm^2), then the temperature drop of $\tau = T/T_0 = 5.10^{-2}$ would be obtained at $r = 0.7 \text{ cm}$ or 7.0 cm for $\gamma = 1.4$ or 1.2 respectively. The many small holes can further be arranged in a row (Fig. 11), so that the laser cavity can have a small cross section. In order to prevent ablation of the wall material, the small holes would have to be cooled externally. Such cooling would have a convenient side effect, since it would help to reduce the translational temperature and thereby increase the partial population inversion above the gasdynamically expected value. For the example considered above, with the temperature reduction to the value $\tau = 0.05$, the P(6) transition of the HF molecule would have an inversion of $\Delta N/N = 2.10^{-3}$ for a starting temperature $T_{v0} = 5000 \text{ }^\circ\text{K}$ and $\Delta N/N = 5.10^{-4}$ for $T_{v0} = 3000 \text{ }^\circ\text{K}$.

7. EFFICIENCY

The energy emitted per second at one laser frequency has the upper limit

$$P_m = \frac{1}{2} \Delta N h \nu \dot{N}$$

where \dot{N} is the particle flow rate through the laser cavity, assumed to include the whole cross section of the flow. If the working gas is heated by an external energy source, the power

$$P_e = \dot{N} m c_p T_0$$

has to be supplied continuously. The efficiency of the laser at this single wavelength is then

$$\eta_e = (\Delta N/N) h\nu / m c_p T_0$$

where c_p is the specific heat. Typical numbers for the HF laser are $\Delta N/N = 10^{-3}$, $h\nu \approx 0.5$ eV, $m = 3.2 \cdot 10^{-23}$ g, $c_p = 3.6 \cdot 10^6$ erg/g $^\circ$ and $T_0 = 5000$ $^\circ$ K. Hence the efficiency for the emission of one quantum per excited molecule is $\eta_{th} = 7 \cdot 10^{-4}$.

If the working gas is heated by a chemical reaction, as proposed, the chemical efficiency would be

$$\eta_{ch} = \frac{1}{2} (\Delta N/N) h\nu / m q$$

where q is the heat of reaction. Taking again the HF molecule with 34 Kcal/mole¹² as formed in the reaction $F+H_2$, a chemical efficiency of $\eta_{ch} = 3 \cdot 10^{-4}$ could be expected. η_e and η_{ch} are the efficiencies for the emission of one single quantum $h\nu$ per excited molecule. Considering that inversion is obtained simultaneously for many transitions and that further cascading through different vibrational levels may occur, multi-line efficiencies in the range 0.1 to 1 % may be obtained.

In conclusion we believe that additional gasdynamical pumping is possible with the exhaust of chemical lasers, and that the laser power recovered from the otherwise useless waste may even be a substantial fraction of the total laser power in such a compound chemical-gasdynamical laser. It hence seems worth trying to construct a tandem laser as suggested in Fig. 1.

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