A THEORETICAL STUDY OF THE PULSED Cl₂ + HI CHEMICAL LASER INCLUDING NONEQUILIBRIUM EFFECTS

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In this study a new approach for handling the time evolution of the rotational distribution in a pulsed chemical laser is discussed. The suggested procedure assumes that the rotational distribution in each vibrational state during the lasing period can be described in any instant of time as a linear combination of known functions with time dependent coefficients. The evolution in time of these coefficients (three for each vibrational level) is given in terms of rate equations which are smoothly incorporated in the ordinary frame of the kinetic master equations. The method has been applied to the Cl₂ + HI pulsed chemical laser for which it is shown that the results obtained are similar to those we would expect from a treatment where each vibrational state is treated separately. In the preliminary study of the Cl₂ + HI system it is found that in the experimental setup used by Airey the photon yield is about 1.0 photons per HCl molecule.

I. Introduction

The success of simple models to simulate the kinetic behaviour of gas lasers has aroused a lot of interest in the numerical and theoretical study of such systems. About a decade ago Moore et al. [1] were able to predict by a simple steady state analysis most of the electric discharge CO₂ laser. This kind of a study was later extended by several other authors [2,3] but was still based on the steady state assumptions. Deviations from this approach are found in the first extensive theoretical studies in chemical lasers as performed by Cohen et al. [4] for the H₂/Cl₂ laser, by Airey [5] for the Cl₂/HBr laser and later by Kerber et al., Suchard et al. and Skifstad [6] for the H₂/F₂ laser. The main approximation incorporated in these studies is concerned with the rotational distribution. In order to avoid the need to follow the evolution in time of each rotational state separately it was assumed that, at each instant of time, the molecules are distributed in the rotational levels according to the Boltzmann distribution with the translational temperature. This assumption has been recently tested by several authors [7-10] and was found to be in many cases unjustified. These studies are based on solving the master equations in which the evolution of time of each vib-rotational state is followed separately. In a treatment like that the number of equations to be solved becomes very large; for instance, in the Cl₂/HI system (of five vibrational levels) this number may become three to four hundred.

In the present work we are discussing an intermediate case in which the rotational distribution is not taken to be Boltzmann but, on the other hand also avoids the need of treating each vib-rotational state separately. This is achieved, as will be described later in greater detail, by representing the total rotational distribution as a linear combination of three functions of a given shape with coefficients that are time dependent. The evolution in time of the coeffi-
coefficients (three for each vibrational level) is governed by rate equations which are smoothly incorporated in the ordinary frame of the kinetic master equations.

In this work we apply the model to the pulsed Cl₂/HI chemical laser. In contrast to other laser systems the experimental results for this flash initiated system are rather scarce. Except for short publications by Airey [11] and Chen et al. [12] very little has been published on this system. Airey reported on the oscillations of the lines he observed (these are listed in table 2). The most attractive feature found there is the relative small number of lines that are related to each vibrational transition — 2, 3 and 5 for the 3 → 2, 2 → 1 and 1 → 0 transitions respectively — as compared to the large number that were observed, for instance, in the Cl₂/HBr system [5] — 10 for the 1 → 0 transition (a relative small number of lines has also been observed in the F/H₂ system [13] and the F₂/H₂ system [14]). This fact hints on a possibility that a rotational Boltzmann distribution has not been reached during the lasing period, and consequently a treatment that attributes a Boltzmann distribution for the rotations is expected to yield oscillations of inadequate lines.

In section 2 the structure of the master equations is described; most of the details are deleted since they can be found in the literature [4–10,11] and the emphasis is only on the new concepts introduced in the present work. In section 3 a standard case is defined which yields results that are close to the ones found in Airey's experiments. The results are also compared with these obtained for the case of a pure rotational Boltzmann distribution. In section 4 the sensitivity of the results is tested against variations in the assumed parameters; in section 5 some preliminary results related to the Cl₂/HI system are discussed and a summary is given in section 6.

2. The master equations

2.1. The vibrational rate equations

Since the vibrational rate equations were frequently discussed in the literature [5] we shall only refer to the main points.

If \( N(v) \) is the number of HCl molecules in the vibrational state \( v \), then the differential equation that governs its development in time is written as:

\[
\frac{dN(v)}{dt} = P_v + \sum_{v'} N(v')k_{vv'} - N(v)\sum_{v'} k_{v'v}L_{v+1v} - L_{v-1v},
\]

(2.1)

where \( P_v \) is the pumping rate of this level, \( k_{vv'} \) is the decay rate of level \( v' \) to the \( v \) level due to collisional processes and \( L_{v+1v} \) is the rate of production of the \( v \) level due to lasing processes from the \( v + 1 \) level. The various rate constants are discussed in appendix A.

2.2. The rotational distribution

The rotational distribution \( N(v, J) \) is assumed to be represented as a linear combination of three distributions:

\[
N(v, J) = \sum_{i=1}^{3} N_i(v) f_i^R(J),
\]

where \( f_i^R(J) \), \( i = 1, 2, 3 \) are normalized functions of a given shape which depend on the vibrational state and the coefficients \( N_i(v) \), \( i = 1, 2, 3 \) are assumed to be time dependent. We shall distinguish between the following distributions: (i) an initial distribution, (ii) an intermediate distribution and (iii) a final distribution.

2.2.1. The initial distribution

Maylotte et al. [16] suggested that the initial rotational distribution, due to the chemical reaction process only (ignoring all other collisional as well as radiative processes) can be well represented in terms of the Gauss (normal) distribution function, i.e.:

\[
f_G(J) = C_G(2J+1) \times \exp\left\{-[B(J(J+1) - J_G(J_G+1))]^2/2\sigma^2\right\},
\]

(2.2)

where \( B \) is the rotational constant, \( J_G \) is the \( J \) value which corresponds to the most populated rotational level, \( \sigma \) is half the width of the distribution and \( C_G \) is a normalization factor. The values of \( B, J_G \) and \( \sigma \) for each vibrational level are given in table 1.

2.2.2. The final distribution

The final distribution (for \( t \to \infty \)) is taken to be the Boltzmann distribution defined in terms of a rotational temperature \( T_R \):

\[
f_B(J) = C_B(2J+1) \exp\left\{-BJ(J+1)/kT_R\right\},
\]

(2.3)
Table 1
List of parameters as used in the standard case

| $v$ | $B_G$ | $
u_G$ | $J_G$ | $p_{MG}$ | $J_M$ | $p_{BM}$ |
<table>
<thead>
<tr>
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<tr>
<td>0</td>
<td>10.4</td>
<td>0.29</td>
<td>22</td>
<td>$1.26 \times 10^{-2}$</td>
<td>12</td>
<td>$0.15 \times 10^{-2}$</td>
</tr>
<tr>
<td>1</td>
<td>10.1</td>
<td>0.18</td>
<td>20</td>
<td>$1.40 \times 10^{-2}$</td>
<td>11</td>
<td>$0.19 \times 10^{-2}$</td>
</tr>
<tr>
<td>2</td>
<td>9.8</td>
<td>0.11</td>
<td>16</td>
<td>$2.5 \times 10^{-2}$</td>
<td>6</td>
<td>$0.44 \times 10^{-2}$</td>
</tr>
<tr>
<td>3</td>
<td>9.5</td>
<td>0.10</td>
<td>12</td>
<td>$4.7 \times 10^{-2}$</td>
<td>4</td>
<td>$0.66 \times 10^{-2}$</td>
</tr>
<tr>
<td>4</td>
<td>9.2</td>
<td>0.027</td>
<td>5</td>
<td>$9.4 \times 10^{-2}$</td>
<td>4</td>
<td>$2.12 \times 10^{-2}$</td>
</tr>
</tbody>
</table>

$^a$ Ref. [21]; numbers in cm$^{-1}$.

$^b$ Numbers in eV (estimated from fig. 6 of ref. [16]).

$^c$ Ref. [16].

where $k$ is the Boltzmann constant, and $C_R$ is a normalization factor. In what follows we assume $T_R$ to be identical to the translational temperature $T$ which is assumed to change in time.

2.2.3. The intermediate distribution

Except for $u = 4$ and $u = 3$ the two previous distributions hardly overlap because they are defined in different regions along the $J$ axis. Since during the relaxation process there is a continuous flow from the initial Gauss distribution towards the final Boltzmann distribution we found it necessary to introduce a third distribution to fill the gap between the two.

In general we expect this distribution to decrease for high values of $J$ as well as for low values of $J$ which means that it has to reach a maximum at some value $J_M$. It decreases towards the high $J$ values because it is fed either by the initial Gauss distribution which is distributed along a finite $J$ interval or from higher vibrational states which are also of a limited range. It also decreases towards the lower values of $J$ due to the fact that relaxation processes are faster the lower is the $J$ value [16].

A distribution that can be defined in terms of one parameter only (excluding the normalization factor) and that has these features is the Boltzmann function that will be written as:

$$f_M(J) = C_M(2J + 1) \exp[-2J(J + 1)(2J_M + 1)^2],$$

where $J_M$ is the value of $J$ for which $f_M(J)$ is maximum. In contrast to the known parameters in terms of which $f_G(J)$ and $f_B(J)$ are expressed the present parameter $J_M$ is not a priori known. We have determined these parameters (one for each vibrational state) so to fit Airey's experimental results [11]. However, we shall discuss the sensitivity of the results towards variations of these parameters.

2.2.4. The total rotational distribution

If $N_G(u), N_B(u)$ and $N_M(u)$ are the number of HCl molecules being distributed in a given vibrational state $u$ according to the Gauss (G) Boltzmann (B) and the intermediate (M) distributions then the total number of HCl molecules in a given vib-rotational state is

$$N(v, J) = N_G(v) f_M^G(J) + N_M(v) f_M^M(J) + N_B(v) f_B^M(J).$$

Since each $f$-function is normalized it can be easily seen that $N(v) = \text{the total number of HCl molecules in a certain vibrational state is given in the form}


The value of $N(v)$ is determined from the rate equations as described in section 2.1 and therefore we need two out of the three $N_j(u)$ to determine $N(v, J)$.

2.2.5. The intra-vibrational distribution

The populations $N_G(u), N_M(u)$ and $N_B(u)$ were assumed to be coupled with each other in the sense that relaxation processes cause transition from one distribution to the other.

The $G$ distribution is assumed to be formed only through the direct pumping process and may relax either due to $v \rightarrow v' (u \neq u')$ collisional and radiative processes or due to $(v, J) \rightarrow (v, J')$ collisional processes which necessarily means a transition from this distribution to the M distribution. If $k_{MG}^{u'}$ is the rate constant that couples the G and the M distributions in the $u$th vibrational level, then the rate equation for $N_G(u)$ takes the form:
\[ \frac{dN_G(u)}{dt} = P_v - k_{MG}^u N_G(u) - N_G(u) \sum_{v'} k_{v'u} - L_{u-1u}^G, \]  

(2.7)

where \( P_v \) and \( k_{v'u} \) were defined earlier and \( L_{u-1u}^G \) is the rate of molecules leaving this distribution due to lasing processes.

The B distribution can be formed only through direct \((v, J) \rightarrow (v', J')\) processes from the M distribution and may relax either through \(v \rightarrow v'\) collisional or radiative processes:

\[ \frac{dN_B(u)}{dt} = k_{BM}^u N_M(u) - N_B(u) \sum_{v'} k_{v'u} - L_{u-1u}^B, \]  

(2.8)

where \( k_{BM}^u \) is the rate constant for the collisional relaxation process that shifts an HCl molecule from the M to the B distribution and \( L_{u-1u}^B \) is the rate of molecules leaving the distribution due to lasing processes.

A discussion on the physical interpretation and the numerical values of \( k_{BM}^u \) and \( k_{MG}^u \) will be given later.

Once \( N_G(u) \) and \( N_B(u) \) are known and since \( N(u) \) is also known \( N_M(u) \) will be derived using eq. (2.9), namely:

\[ N_M(u) = N(u) - N_G(u) - N_B(u). \]  

(2.6')

Although not explicitly shown, the M distribution is the “sink” for any molecule that leaves the G distribution by R–T collisions and for any molecule that leaves the G, M or the B distributions by collisional or radiative processes of the type \((v, J) \rightarrow (v', J')\) where \( v \neq v' \).

2.3. Treatment of the radiation and the lasing

In order to find the evolution in time of the radiation from each vibrational level, each vib-rotational state is treated separately. If \( \rho_v(J) \) is the photon density due to emission \((v, J) \rightarrow (v-1, J+1)\) (we consider \( P \) transitions only) then its equation is given in the form:

\[ d \rho_v(J)/dt = \Delta \rho_v(J) N_G(u, J) - B_f(u) \rho_v(J), \]  

(2.9)

where

\[ \Delta \rho_v(J) = [N(v, J)/(2J+1)] \]  

\[ - N(v-1, J+1)/(2J+3)] (J+1). \]  

(2.10)

\( \Delta N_0(v, J) \) is the threshold inverted population needed to overcome the radiation losses in the system (see appendix B), \( B_f(u) \) is the Einstein coefficient for stimulated emission (see appendix B) and \( A_f(J) \) is the Einstein coefficient for spontaneous emission. Knowing \( \rho_v(J) \) we can immediately calculate \( L_{u-1u}^G, L_{u-1u}^B \) and \( L_{u-1u}^B \) needed for the vibrational and the intra-vibrational rate equations:

\[ L_{u-1u}^v = \sum f \rho_v(J) \Delta N_G(u, J) B_f(J), \]  

(2.11)

where \( \Delta N_G(u, J) \) is given by eq. (2.10) and

\[ L_{u-1u}^B = \sum f \rho_v(J) \Delta N_B(u, J) B_f(J), \]  

(2.12)

where

\[ \Delta N_G(u, J) = [N_G(v, J)/(2J+1)] - N_G(v-1, J+1)/(2J+3)] (J+1). \]  

(2.13)

Similar expressions are given for \( L_{u-1u}^B \) and \( \Delta N_B(v, J) \) respectively.

2.4. The pumping rate

The pumping rate \( P_v \) is given in the form

\[ P_v = k_v N_{Cl} N_{HI}, \]  

(2.14)

where \( N_{Cl} \) is the number of Cl atoms per cm\(^3\), \( N_{HI} \) is the number of HI molecules per cm\(^3\) and \( k_v \) is the rate constant for the reaction

\[ Cl + HI \rightarrow HCl(v) + I; \quad v = 0, ..., 4. \]  

The values of \( k_v \) are discussed in appendix A.

The rate equation for \( N_{Cl} \) is given in the form

\[ dN_{Cl}/dt = K(T) N_{Cl} - \sum_{v'} P_{v'}. \]  

(2.15)

The first term corresponds to the rate of production of chlorine atoms by photolysis, \( N_{Cl} \) is the number of Cl\(_2\) molecules per cm\(^3\) and \( K(T) \) is the rate constant for the dissociation of Cl\(_2\) molecules which is discussed in appendix A.

The equation for \( N_{HI} \) takes the form

\[ N_{HI} = N_{HI}^0 - \sum_{v'} N_{HI}' \]  

(2.16)

where \( N_{HI}^0 \) is the initial number of HI molecules per cm\(^3\); the equation for \( N_{Cl} \) is of a similar form:
The changes in the temperature as a function of time are caused by the heat that is fed into the gaseous medium due to three processes:

(i) The average energy causing the dissociation is always greater than the dissociation energy of a Cl₂ molecule (85.7 kcal/mole versus 57.1 kcal/mole [5]). The difference ΔQ is equal to 14.3 kcal/mole per Cl atom.

(ii) Reaction processes. Although most of the exothermicity of the reaction is channeled into the vibrational states still part of it − hₚ − is directly converted into heat (hₚ = 0.17 [16]).

(iii) Vib-rotational relaxation processes.

The equation for the temperature T is given in the form:

\[
\frac{dT}{dt} = \frac{1}{C_v} \left[ K(t)N_{Cl_2} \Delta H^0 + \left( \sum_v P_v \right) h_t \Delta H^0 \right.
\]

\[+ \sum_u \sum_v N(u') k_{uu'} \Delta q_{uv'} + \sum_v k_{BM}^v N_M(v) \Delta q_{BM}^v \left. \right] + \sum_u k_{BM}^u \frac{N_M(u)}{2} \Delta q_{BM}^u , \tag{2.18}
\]

where ΔH^0 is the exothermicity of the reaction (ΔH^0 = 32.5 kcal/mole) and the different Δq's stand for the various heat quantities released in each respective relaxation process. The magnitude C_v is the heat capacity which takes the form:

\[
C_v = \frac{3}{2} N_d k + \frac{3}{2} N_m k , \tag{2.19}
\]

where N_d is the number of diatomic molecules, N_m is the number of monoatomic molecules and k is the Boltzmann constant.

3. The study of the model

In formulating the model we have introduced three sets of parameters, k_{BM}^v, k_{MG}^v and J_M(v) that have to be determined. We shall discuss a procedure that relates k_{BM}^v and k_{MG}^v to the detailed rotational rate constants as formulated by Polanyi and Woodall [17] and later modified by Ding and Polanyi [18]. In contrast to k_{BM}^v and k_{MG}^v, the values of J_M(v) are not known a priori and have to be determined by "trial and error".

3.1. Determination of k_{BM}^v

In order to calculate k_{BM}^v we shall consider the evolution in time of a given initial rotational distribution governed by the equation [17,19,20]

\[
dN_J/dt = - \left( \sum_{J'} k_{J'}^J \right) N_J + \sum_{J''} k_{J''}^J N_{J''} , \tag{3.1}
\]

where k_{J'}^J is the rate for a transition from J to J'. Following Ding and Polanyi [18] we assume k_{J'}^J(J > J') to take the form

\[
k_{J'}^J = Z_e C(2J'+1) \exp[-\beta(E_J - E_{J'})] , \tag{3.2}
\]

where Z_e is the gas kinetic collision frequency, E_J is the rotational energy associated with J

\[
E_J = BJ(J+1) , \tag{3.3}
\]

and C and β are two adjustable parameters. Eq. (3.2) stands for the case of downward transitions. The corresponding rate constant for the upward transition J' → J is determined by the detailed balance relation

\[
k_{J'}^J = [(2J+1)/(2J'+1)] k_{J'}^J \exp[-(E_J - E_{J'})/kT] . \tag{3.4}
\]

Fig. 1. The collision probability P_J^J' (|J - J'| = 1) for downward (---) and upward (-----) transitions as a function of the initial rotational state J.
In fig. 1 are shown $P_{j-1}^i$ and $P_{j}^{i-1}$ (where $P_{j}^i = k_{j}^i/Z_{j}$) for $\beta = 0.011$ cm and $C = 0.020$.

The system of eq. (3.1) can be written in a matrix notation as:

$$\frac{dN}{dt} = kN,$$  \hspace{1cm} (3.5)

where the elements of the $k$ matrix are the corresponding $k_{j}^i$. In the present treatment we allowed the transitions to be of the type $\Delta J = \pm 1$ only and consequently $k$ becomes a tridiagonal matrix.

The solution of this equation is given in the form

$$N(t) = A \exp A^{-1}N(0),$$  \hspace{1cm} (3.6)

where $A$ is the transformation matrix of $k$ and $E$ is a diagonal matrix of the form

$$E_{ii} = \exp(q_i t) \delta_{ii},$$  \hspace{1cm} (3.7)

where the $q_i$s are the eigenvalues of $k$ and $\delta_{ii}$ is the Kronecker $\delta$ function. In appendix C is shown that all $q_i$, $i = 0, \ldots$ are non-positive (at least one has to be zero to ensure the conservation of the total number of molecules). The vector $N(0)$ stands for the initial distribution and is taken to be the $M$ distribution in a given vibrational state

$$N(0) = f_M^v.$$  \hspace{1cm} (3.8)

Due to the assumed detailed balance relation the final distribution is guaranteed to be a Boltzmann distribution:

$$N(t \to \infty) = f_B^v.$$  \hspace{1cm} (3.9)

Thus, eq. (3.5) with the initial distribution given in eq. (3.8) describes the transition from the $M$ to the $B$ distribution. Let us assume that $N(t)$ for any $t$ can be written as a linear combination of $f_M^v$ and $f_B^v$:

$$N(t) = n_B^v(t)f_B^v + N_M^v(t)f_M^v,$$  \hspace{1cm} (3.10)

where

$$n_B^v(t) + N_M^v(t) = 1.$$  \hspace{1cm} (3.11)

The values of $N_B^v(t)$ and $N_M^v(t)$ are determined by the least squares method for each value of $t$. In fig. 2 the dependence of $N_M^v(t)$ on $t$ is shown for four different initial $f_M^v$ distributions (each characterized by a different $J_M$ value). As can be seen $N_M^v(t)$ is approximately an exponential function of $t$

$$N_M^v(t) = \exp(-\lambda_v t).$$  \hspace{1cm} (3.12)

The meaning of $\lambda_v$ is the rate constant for the transition from the $M$ to the $B$ distribution and therefore:

$$k_{BM}^v = \lambda_v.$$  \hspace{1cm} (3.13)

If $k_{BM}^v$ is written in the form

$$k_{BM}^v = Z_e P_{BM}^v,$$  \hspace{1cm} (3.14)

then $(P_{BM}^v)^{-1}$ is the average number of collisions needed to shift a molecule from $M$ to $B$. The values of $P_{BM}^v$ found in this way depend on the values of $C$ and $\beta$ [cf. eq. (3.2)]. Since only transitions with $\Delta J = \pm 1$ are included we assumed, following Polanyi and Woodall [17] and Ding and Polanyi [18], $\beta$ to be 0.011 cm. Very little has been said in these publications on the value of $C$. We assumed this value to be 0.020 which yields a value of 0.06 for $(P_{BM}^v)_{\max}$. In table 1 are given the values of $P_{BM}^v$ as a function of $J_M$ and in fig. 3 is shown the dependence of $P_{BM}^v$ on $J_M$ which is approximately an exponential, namely:

$$P_{BM} = A \exp(-\alpha J_M),$$  \hspace{1cm} (3.15)

where $\alpha = 0.167$ and $A = 0.0124$.

3.2 Determination of $k_{MG}^v$

In principle $k_{MG}^v$ can be determined in the same way as $k_{BM}^v$ except that eq. (3.10) should be replaced by

$$N(t) = n_B^v(t)f_B^v + n_M^v(t)f_M^v + n_G^v(t)f_G^v.$$  \hspace{1cm} (3.16)
However, this procedure does not always yield reliable results and therefore we used a different procedure which yields only the upper values for the $k^v_{MG}$'s that still were good enough for our purposes. If $P_{MG}(J)$ is defined as the collision probability for a G-molecule in a $J$ state to be shifted to the M distribution then $k^v_{MG}$ can be defined as:

$$k^v_{MG} = Z_g \sum_J f^v_G(J) P_{MG}(J), \quad (3.17)$$

where the summation yields the average probability.

In the model $P_{MG}(J)$ is assumed to be given by

$$P_{MG}(J) = \sum_{J' \neq J} P^J_{J'}, \quad (3.18)$$

which physically means that any collision that is accompanied by a change of the rotational state of the G-molecule necessarily shifts it to the M distribution. This procedure yields an upper limit for the "real" $k^v_{MG}$'s but as will be shown later, are still good enough to reproduce the experimental results.

Again, the $P^J_{J'}$'s (or $K^J_{J'}$'s) were calculated using eqs. (3.2) and (3.4) with the same values of $C$ and $\beta$ as were taken for the calculations of $k^v_{BM}$'s. The values of $P^v_{MG} = k^v_{MG}/Z_g$ are given in table 1.

### 3.3. Determination of $J_M(\nu)$

The reason for adding the M distribution was to fill the gap between the two well-defined distributions G and B. As was shown earlier the M distribution is defined in terms of a single parameter $J_M$ which mainly defines its position along the $J$ axis. We do not have any rigorous way of determining a priori the values of $J_M(\nu)$. Since the M distribution has to be between the G and B distributions we took as a first guess for $J_M(\nu)$ the value

$$J_M(\nu) = \frac{[J_G(\nu) + J_B]}{2}, \quad (3.19)$$

where $J_B$ is taken to be equal to three. The final values of $J_M(\nu)$ as listed in table 1 were derived after refinements to obtain the experimental results.

### 3.4. The standard case

#### 3.4.1. Experimental results

Airey [11] has measured the output of a flash initiated Cl$_2$+HI laser. He reported only the found vib-rotational lines and therefore the experimental setup was assumed to be the same as in a later publication on Cl$_2$+HBr [5]. The partial pressures were taken as 20 and 5 torr for Cl$_2$ and HI, respectively.

#### 3.4.2. A comparison of the "standard" case and the "Boltzmann" case

In what follows we refer to the "standard" case as the one for which the probabilities $P_J^J$ are calculated with the parameters, $C = 0.020$, $\beta = 0.011$ cm$^{-1}$ and the values of $J_M(\nu)$ are as listed in table 1. The "Boltzmann" case is the case where the rotational distribution function is assumed to be Boltzmann throughout the laser pulse. This is achieved by assuming $P^v_{MG} = 1$ and $P^v_{BM} = 1$ for any $\nu$; it is found that the final results are entirely independent of $J_M(\nu)$.

In fig. 4 the lasing profiles of each vibrational transition for the standard and the Boltzmann cases are shown and in fig. 5 the total intensities of each vib-rotational transition for the two cases are compared. The lasing transitions as obtained in the two cases are given in table 2 and compared with those found in the experiment; the intensities for each vibrational transition are compared in table 3. The agreement between the experimental results and those obtained in the standard case is very good whereas the agreement with those derived in the Boltzmann case is rather poor. This fact strongly indicates that the rotational distribution in Airey's experiment is far from...
being Boltzmann. The results in figs. 4 and 5 and in tables 2 and 3 show clearly that both the number of lines as well as the output intensity for each vibrational transition is much larger in the Boltzmann case.
Table 2
The experimental and theoretical transitions

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<th>Vibrational transition</th>
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<th>Theoretical transitions standard b)</th>
<th>Theoretical transitions Boltzmann b)</th>
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</thead>
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<tr>
<td>3 → 2</td>
<td>$P_3(4), P_3(5)$</td>
<td>$P_3(4), P_3(5)$</td>
<td>$P_3(7) - P_3(13)$</td>
<td>4</td>
</tr>
<tr>
<td>2 → 1</td>
<td>$P_2(5) - P_2(7)$</td>
<td>$P_2(5) - P_2(7)$</td>
<td>$P_2(8) - P_2(14)$</td>
<td>5</td>
</tr>
<tr>
<td>1 → 0</td>
<td>$P_1(9) - P_1(13)$</td>
<td>$P_1(9) - P_1(14)$</td>
<td>$P_1(8) - P_1(16)$</td>
<td>10</td>
</tr>
</tbody>
</table>

b) Here are listed all the transitions for which the integrated (on time) intensities are larger than 0.2 $I$ ($J_{\text{max}}$).
c) $J_{\text{max}}$ is the rotational state $J$ for which the integrated intensity is the largest.

Table 3
Partial output intensities. A comparison between standard and Boltzmann cases

<table>
<thead>
<tr>
<th>Transition</th>
<th>Output intensity at $J_{\text{max}}$</th>
<th>Total output intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>standard</td>
<td>Boltzmann</td>
</tr>
<tr>
<td></td>
<td>standard</td>
<td>Boltzmann</td>
</tr>
</tbody>
</table>

| 3 → 2      | 1.02 a)                               | 1.33                   | 1.92                    | 6.58            | 9           | 20          |
| 2 → 1      | 4.66                                  | 2.56                   | 9.00                    | 14.04           | 43          | 40          |
| 1 → 0      | 2.43                                  | 2.21                   | 10.23                   | 13.93           | 48          | 40          |

a) Numbers in $10^3$ $J$ cm$^{-2}$.

Thus the fact that the rotational distribution has not become Boltzmann prevents the system from employing its full potential for the radiation.

The differences between the two cases are also represented in fig. 6 in which the vibrational population for each case is compared. As can be seen the populations in the standard case are larger from the Boltzmann one for $u = 1, 2, 3$ whereas for $u = 0$ the population is larger for the Boltzmann case. This result is expected since the high vibrational states relax faster the stronger is the lasing. Comparing figs. 4 and 6 it is seen that the lasing process takes place as long as the rate of increase in the population of the corresponding upper level is fast enough. The lasing from $u = 3$ in the standard case terminates about 4 $\mu$s before the increase in the population stops and about 2 $\mu$s for $u = 2$. The situation in the Boltzmann case is much better as the lasing terminates, for both transitions, only about 1 $\mu$s before the increase in population stops. It is also noticed that the populations in the various vibrational levels start to decrease after a while, except $u = 0$. The reason for this is mainly the increasing number of chlorine atoms in the system which deactivate the high vibrational levels.

3.4.3. The time evolution of the vib-rotational states $N(u, J)$

The time evolution of the rotational states distribution are presented in fig. 7. To each figure we also added a Boltzmann distribution calculated at $t = 7.04$ $\mu$s (the corresponding temperature is 330 K). The shapes of the curves are of the same type as those given by Polanyi and Wodall [17] and Keren et al. [10]. As is seen the $u = 3$ moves rather fast towards the low $J$ values without passing through the double hump shape. On the other hand the $u = 2$ which is centered initially at a higher $J$ value (see table 1) assumes the double hump form as is the case in the more detailed calculations where each vib-rotational state is treated separately. Again, however, the peak of the distribution moves relatively fast towards the low $J$ values so that at $t = 1.0$ $\mu$s the shape is not too far from being Boltzmann.

A different behaviour is found for $u = 0, 1$. There
the motion of the peaks is slowed down and only after 2 μs an appreciable shift in their positions can be noticed. The double hump shape is completely washed out due to the relative low pumping rates which compete with the fast relaxations from the higher vibrations. It is obvious that the overall shape of rotational distribution in each vibration depends heavily on the location of $J_M(v)$. In order to obtain the correct pattern of the lasing we had to place $J_M(v)$ in an increasing order as $v$ decreases and in this way avoided the distribution to become a Boltzmann type too fast. The location of $J_M(v)$ has a strong impact on the shape of the total distribution not only because it fixes the location of the intermediate distribution (which is assumed to be constant in time) but also because it affects directly the rate of the transition from the M to the B distributions. Since $P_{BM}$ is smaller the larger $J_M(v)$ (see fig. 3) the molecules will stay longer in the intermediate distribution the higher $J_M(v)$. This explains how in the proposed model the Boltzmann distribution is achieved faster the higher is the vibrational state.

4. Parametric study of the model

In this section the sensitivity of the final results will be tested against variations of the new parameters introduced in the previous sections. In fact only one set of parameters namely $J_M(v)$ $v = 0–4$ has been
introduced but since no rigorous way of determining $P_{MG}$ is given (the procedure suggested here yields only an upper bound for that value) we shall also discuss them to some extent.

4.1. Sensitivity study of $J_M(v)$

Almost as a rule it can be stated that the final results are only slightly dependent on $J_M(v)$ as long as they are chosen in a "reasonable" way. By a reasonable choice, is meant the following criteria:

(i) The $J_M(v)$ have always to be located in between $J_G(v)$ (which is known) and the location of the Boltzmann peak which is determined by the temperature (for $T = 300$ K the location of the peak is between $J = 2$ and $J = 3$).

(ii) They have to be arranged in a decreasing order as $v$ increases.

The second requirement is not self-evident but it was realized that interchanging their relative locations results in a non-systematic way of lasing from the different rotational states; in other words it causes to discontinuous jumps from one lasing state to another.

In fig. 8 are presented the oscillations of the vibrotational transitions as a function of time for four different sets of $J_M(v)$ all chosen according to the
Fig. 8. The lasing profile for each vib-rotational state for different sets of $J_M(u)$; the lower figure is for $1 \rightarrow 0$ transition, the upper left is for $2 \rightarrow 1$ and the upper right is for $3 \rightarrow 2$ transition. Each column stands for the indicated $J$ value: (A) The standard case, $J_M(u) = (12, 11, 6, 4, 4)$; (B) $J_M(u) = (13, 12, 8, 5, 4)$; (C) $J_M(u) = (14, 13, 9, 6, 4)$; (D) $J_M(u) = (11, 10, 7, 5, 4)$.

Fig. 9. The lasing profile for each vib-rotational state for various values of $\alpha$; the lower figure is for $1 \rightarrow 0$ transition, the upper left is for $2 \rightarrow 1$ and the upper right for the $3 \rightarrow 2$ transition. Each column stands for the indicated $J$ value: (A) The standard case ($\alpha = 1$); (B) $\alpha = 0.8$; (C) $\alpha = 0.6$; (D) $\alpha = 0.4$; (E) $\alpha = 0.2$. 
"rules". It can be seen that although the various sets of $J_M(v)$ differ quite a lot from each other no principal changes are recorded. The most that happens is a shift in one rotational state. This result is quite encouraging and very significant because usually the $J_M(v)$ are not given a priori and have to be determined by "trial and error". However since the dependence of the final results on $J_M(v)$ is rather weak a first guess will not distort the results too much.

4.2. Sensitivity study of $P_{MG}^v$

In order to test the dependence of the final results on $P_{MG}^v$ a few calculations were performed in which $P_{MG}^v$ assumed their original values multiplied by $\alpha$ where $\alpha = 0.8, 0.6, 0.4, 0.2$. The results are shown in fig. 9 where again are presented the lasing profiles for each vib-rotational state. By varying $\alpha$ from 1.0 to 0.2 no significant changes are recorded in any of the transitions which again is quite encouraging since also these values like the $J_M(v)$ values are not known a priori and can only be estimated.

5. Preliminary study of the Cl2/HI laser

In tables 3 and 4 are presented some preliminary results that are related to the output intensities and efficiencies of the Cl2/HI laser. In table 3 the intensities for each vibrational transition, once for the standard case and once for the Boltzmann case, are presented. The main differences are:

(1) The intensity in each vibrational transition is larger in the Boltzmann case. For the $2 \rightarrow 1$ and $1 \rightarrow 0$ transitions the intensity in the Boltzmann case is about 50% larger than for the standard case and for the $3 \rightarrow 2$ transition the intensity is about 3 times larger.

(2) The intensity in the standard case is in general due to a much smaller number of rotational states than in the Boltzmann case. In the $3 \rightarrow 2$ and the $2 \rightarrow 1$ transitions more than 50% of the intensity is due to a single line.

In table 4 the total intensities and efficiencies for the two cases are compared. As is noticed, both, the total intensity and efficiency of the laser are almost twice as much in the Boltzmann case. These results confirm what was already known before, namely that fast R-T processes increase the intensity of the laser. One way of stimulating R-T processes is by adding inert (He, etc.). Therefore if we assume that adding inert gases has only a minor effect on other properties or processes in the laser cavity, the intensity as obtained in the Boltzmann case can be considered as the upper bound for these magnitudes in a given operating conditions (partial pressures, radiation losses, etc.).

Fig. 10 shows the output intensity and the photon yield as a function of the pressure for the two cases. Two main points are to be noticed:

(a) The output intensity increases rather fast as a function of the pressure in the low pressure region whereas for higher pressures an increase in pressure either does not change the intensity at all or cause it to decrease (all calculations are performed for the same partial pressures ratio, Cl2:Hl = 4:1).

(b) The photon yield decreases as a function of the pressure along the whole range which means that the increase in the pressure is accompanied by a larger rate of production of HCl molecules as compared to the rate of photon production.

Table 4
Total output intensities and efficiencies. A comparison between standard and Boltzmann cases

<table>
<thead>
<tr>
<th></th>
<th>Standard</th>
<th>Boltzmann</th>
</tr>
</thead>
<tbody>
<tr>
<td>total output intensity</td>
<td>0.021</td>
<td>0.035</td>
</tr>
<tr>
<td>(J/cm²)</td>
<td>1.93 $\times$ 10$^{18}$</td>
<td>3.21 $\times$ 10$^{18}$</td>
</tr>
<tr>
<td>total number of photons</td>
<td>2.1 $\times$ 10$^{18}$</td>
<td>2.6 $\times$ 10$^{18}$</td>
</tr>
<tr>
<td>produced/cm² a)</td>
<td>0.83</td>
<td>1.11</td>
</tr>
<tr>
<td>total number of HCl</td>
<td></td>
<td></td>
</tr>
<tr>
<td>molecules/cm² b)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>efficiency (photons/molecule)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a) The numbers given stand for the total number of photons produced, namely the useful as well as the useless part.
b) The number of HCl molecules was calculated at time $t$ which corresponds to the time when 90% of the lasing action has been performed.
c) In calculating the total number of HCl molecules a value of 60 cm has been assumed for $l$. 
6. Summary

In this study is presented a model by which the time evolution of a pulsed chemical laser can be followed and the laser output intensity and efficiency can be derived. The main difference between the model discussed here and the ones found in the literature is in handling the rotational distribution. In the earlier studies the rotational states were assumed to be distributed according to the Boltzmann function (with a translational temperature) throughout the lasing period. In the more recent studies, this assumption was found to be unjustified and therefore to each vib-rotational state a differential equation was attached by which its development in time was followed. There is no doubt that the simulation as performed in the second way is much more reliable but the effort needed to perform such a calculation can easily grow beyond the capabilities of present computers (to treat properly a system like F/H\textsubscript{2} will probably require the need of solving around three hundreds coupled differential equations and a system like HD/F\textsubscript{2} probably six hundreds).

In this study we are presenting a model which can be considered as an intermediate case. In its nature it is very similar to the first kind namely the overall rotational distribution is expressed in terms of a linear combination of given functions (in the earlier treatments their number was one whereas we assumed it to be three). However, by making the relative weight of each function (in the linear combination) time dependent it was shown that many features that characterize the second kind of models are found here. This is in particular true for the time evolution of the rotational distributions and the determination of the correct vib-rotational lasing lines.

The model was applied to the Cl\textsubscript{2}/HI system because such a complex system (three lasing vibrations) put it under a severe test. This test would have been probably less definitive if applied to a simpler system like Cl\textsubscript{2}/HBr where lasing is encountered due to one vibrational transition only.

The great advantage of this model is in reducing the computational efforts in performing the simulation without effecting the reliability of the results. Instead of dealing with thirty or more differential equations (one equation for each rotational state) per vibration one has to deal with three only. This can reduce the total number of equations in a model which follows the development in time of radiation from each vib-rotational state separately, by a factor of three.

As a final point we would like to refer to the preliminary study of the Cl\textsubscript{2}/HI laser. Although no detailed study has been performed it is our belief that for pressures below 30 torr the system is capable to produce around one photon per one HCl molecule produced during the lasing period. This number is of the same quality as the one found for the F/H\textsubscript{2} laser [8].

Acknowledgement

We would like to thank Dr. A. Avni in performing part of the programming and Dr. M. Shapiro and Mr. E. Keren for helpful discussions. We would also like to thank Mr. E. Keren and Dr. A. Ben-Shaul for showing us preprints of their studies prior to publication.

Appendix A: Rate constants

A.1. Cl formation

The rate of formation of chlorine atoms by flash photolysis was calculated by Airey [5], from the spec-
Fig. 11. The rate constant of formation of chlorine atoms as a function of time.

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The distribution of the hydrogen chloride molecules into the different vibrational states was measured by Maylotte et al. [16] and found to be 0.12:0.33:1.00:0.77 for \( v = 1:2:3:4 \), respectively. The formation of the ground state \((v = 0)\) was assumed to be 1% of the total formation of HCl. Due to the high reaction rates the rate constants were assumed to be temperature independent. The formation of HCl(4) is only slightly exothermic (580 cal/mole) and thus we included also the reverse reaction.

A.3. \( V-R,T \) relaxation

(a) HCl(1) + HCl(0) \( \rightarrow \) 2HCl(0)

Zittel and Moore [23] measured the rate constant for this reaction and found that in the temperature range of 300–500 K the probability of the reaction per collision is independent of temperature. Since the number of collisions (in cm\(^{-3}\) molecule\(^{-1}\) s\(^{-1}\)) is proportional to \( T^{1/2} \) it was assumed that \( k_n = \alpha T^{1/2} \)

where the value of \( \alpha \) is taken from Zittel and Moore [23].

(b) HCl(\( n \)) + Cl \( \rightarrow \) HCl(\( n-J \)) + Cl \( J = 1, 2, \ldots n \)

The values of these rate constant for \( n = 1, 2, 3, 6 \) were taken from Wilkins [24] whereas the rate constants for \( n = 4, 5 \) were estimated by interpolation.

(c) HCl(\( n \)) + Cl₂ \( \rightarrow \) HCl(\( n-1 \)) + Cl₂

The rate constant \( k_1 \) for HCI(1) as a function of temperature was taken from Bott and Cohen [25] interpolating their values, on a semi-logarithmic scale, by two lines which intersect at 480 K. The values of the rate constants for \( n > 1 \) were calculated assuming that the SSH theory [26] yields the correct ratio \( k_n/k_1 \) for rate constants at 300 K while the temperature dependence was assumed to be the same as for HCl(1).

A.4. \( V-V \) relaxation

(a) HCl(\( m \)) + HCl(\( n \)) \( \rightarrow \) HCl(\( m-1 \)) + HCl(\( n+1 \))

There exists reliable measurements for the case \( n = m = 1 \) [27] and for \( m = 3, n = 0 \) [28]. We have used the first result and the SSH theory [26] to determine all rate constants at \( T = 300 \) K for the exothermic reactions whereas those for the endothermic ones were derived by using the microscopic reversibility principle. The results of Ambartzumian et al. [28] for the case \( m = 3, n = 0 \) is about 60% smaller than the one derived in the calculations.

As for the temperature dependence it was found that the SSH prediction is wrong. According to this
theory the rate constants should increase as a function of temperature whereas Noter et al. [27] found it for the case $n = m = 1$ to decrease (in the temperature range of interest). This finding is also supported by a recent theoretical approach based on quadrupolar transitions [29]. The experimental results of Noter et al. [27] were approximated by the expression

$$\ln P = \frac{580}{T} - 5.54,$$

which when converted to rate constants takes the form

$$k(T) = k(300 \text{ K})(T/300)^{1/2} \exp(580/T - 580/300).$$

The same temperature dependence was attributed to all rate constants.

(b) HCl$(n)$+HI$(0) \rightarrow$ HCl$(n-1)+HI$(1)

Some studies on V–V transfer reaction show that the rate constants are a linear function on a semi-logarithmic scale of the exothermicity of the reaction, namely

$$\ln k_n = a - \Delta E/RT.$$

Chen and Moore [30] and Hopkins and Chen [31] found that the same equation holds for HCI(1) and HBr(1). Bott and Cohen [32] and Bott [33] obtained the same relation for HF(1) but with a different value of $a$.

We assumed that the same relation holds for the various vibrational level of HCl and thus

$$k_n/k_1 = \exp[(\Delta E_1 - \Delta E_n)/RT],$$

and $k_1$ were taken from the measurement of Chen and Moore [30].

The complete list of rate constants for this system is given in Table 5.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate constant $k$($\text{cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$)</th>
<th>$k(300 \text{ K})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl+HI → HCl(0)+I</td>
<td>1.64 x 10$^{-12}$</td>
<td>1.64 x 10$^{-12}$</td>
</tr>
<tr>
<td>Cl+HI → HCl(1)+I</td>
<td>1.25 x 10$^{-11}$</td>
<td>1.25 x 10$^{-11}$</td>
</tr>
<tr>
<td>Cl+HI → HCl(2)+I</td>
<td>3.00 x 10$^{-11}$</td>
<td>3.00 x 10$^{-11}$</td>
</tr>
<tr>
<td>Cl+HI → HCl(3)+I</td>
<td>6.97 x 10$^{-11}$</td>
<td>6.97 x 10$^{-11}$</td>
</tr>
<tr>
<td>Cl+HI → HCl(4)+I</td>
<td>5.16 x 10$^{-11}$</td>
<td>5.16 x 10$^{-11}$</td>
</tr>
<tr>
<td>I+HCl(4) → HI+Cl</td>
<td>5.16 x 10$^{-11}$ exp$(-290/T)$</td>
<td>5.6 x 10$^{-11}$</td>
</tr>
<tr>
<td>HCl(1)+HCl(0) → 2HCl(0)</td>
<td>1.4087 x 10$^{-15}$ $T^{1/2}$</td>
<td>2.44 x 10$^{-14}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate constant $k$($\text{cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$)</th>
<th>$k(300 \text{ K})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl+HCl(1) → HCl(0)+Cl</td>
<td>10$^{-10.03 + 0.20 \lg T + 181.4/T}$</td>
<td>7.41 x 10$^{-12}$</td>
</tr>
<tr>
<td>Cl+HCl(2) → HCl(1)+Cl</td>
<td>10$^{-9.42 + 0.37 \lg T + 213.3/T}$</td>
<td>8.96 x 10$^{-12}$</td>
</tr>
<tr>
<td>Cl+HCl(3) → HCl(2)+Cl</td>
<td>10$^{-9.04 + 0.50 \lg T + 222/T}$</td>
<td>9.58 x 10$^{-12}$</td>
</tr>
<tr>
<td>Cl+HCl(4) → HCl(3)+Cl</td>
<td>10$^{-9.01 + 0.44 \lg T + 233.4/T}$</td>
<td>1.33 x 10$^{-11}$</td>
</tr>
<tr>
<td>Cl+HCl(5) → HCl(4)+Cl</td>
<td>10$^{-8.97 + 0.38 \lg T + 244.8/T}$</td>
<td>1.94 x 10$^{-11}$</td>
</tr>
<tr>
<td>Cl+HCl(2) → HCl(0)+Cl</td>
<td>10$^{-10.03 + 0.28 \lg T + 220.5/T}$</td>
<td>3.48 x 10$^{-12}$</td>
</tr>
<tr>
<td>Cl+HCl(3) → HCl(1)+Cl</td>
<td>10$^{-9.42 + 0.47 \lg T + 215/T}$</td>
<td>5.02 x 10$^{-12}$</td>
</tr>
<tr>
<td>Cl+HCl(4) → HCl(2)+Cl</td>
<td>10$^{-9.45 + 0.39 \lg T + 218.1/T}$</td>
<td>7.19 x 10$^{-12}$</td>
</tr>
<tr>
<td>Cl+HCl(5) → HCl(3)+Cl</td>
<td>10$^{-9.48 + 0.31 \lg T + 221.2/T}$</td>
<td>1.03 x 10$^{-11}$</td>
</tr>
<tr>
<td>Cl+HCl(3) → HCl(0)+Cl</td>
<td>10$^{-10.03 + 0.41 \lg T + 186.2/T}$</td>
<td>2.16 x 10$^{-12}$</td>
</tr>
<tr>
<td>Cl+HCl(4) → HCl(1)+Cl</td>
<td>10$^{-9.9 + 0.36 \lg T + 200.6/T}$</td>
<td>3.45 x 10$^{-12}$</td>
</tr>
<tr>
<td>Cl+HCl(5) → HCl(2)+Cl</td>
<td>10$^{-9.77 + 0.31 \lg T + 215/T}$</td>
<td>5.57 x 10$^{-12}$</td>
</tr>
<tr>
<td>Cl+HCl(4) → HCl(0)+Cl</td>
<td>10$^{-10.2 + 0.36 \lg T + 200.6/T}$</td>
<td>1.73 x 10$^{-12}$</td>
</tr>
<tr>
<td>Cl+HCl(5) → HCl(1)+Cl</td>
<td>10$^{-10.07 + 0.31 \lg T + 215/T}$</td>
<td>2.78 x 10$^{-12}$</td>
</tr>
<tr>
<td>Cl+HCl(5) → HCl(0)+Cl</td>
<td>10$^{-10.37 + 0.31 \lg T + 215/T}$</td>
<td>1.40 x 10$^{-12}$</td>
</tr>
</tbody>
</table>

*continued on the next page*
<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate constant $k$ (cm$^3$ molecule$^{-1}$ s$^{-1}$)</th>
<th>$k$ (300 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl$_2$ + Cl + HCl$^<em>$ $\rightarrow$ ClH + Cl + HCl$^</em>$</td>
<td>$7.4 \times 10^{-14}$ $f_1(T)$</td>
<td>$7.4 \times 10^{-14}$</td>
</tr>
<tr>
<td>Cl$_2$ + Cl + HCl$^<em>$ $\rightarrow$ ClH + Cl + HCl$^</em>$</td>
<td>$4.14 \times 10^{-13}$ $f_1(T)$</td>
<td>$4.14 \times 10^{-13}$</td>
</tr>
<tr>
<td>Cl$_2$ + Cl + HCl$^<em>$ $\rightarrow$ ClH + Cl + HCl$^</em>$</td>
<td>$1.78 \times 10^{-12}$ $f_1(T)$</td>
<td>$1.78 \times 10^{-12}$</td>
</tr>
<tr>
<td>Cl$_2$ + Cl + HCl$^<em>$ $\rightarrow$ ClH + Cl + HCl$^</em>$</td>
<td>$6.89 \times 10^{-12}$ $f_1(T)$</td>
<td>$6.98 \times 10^{-12}$</td>
</tr>
<tr>
<td>Cl$_2$ + Cl + HCl$^<em>$ $\rightarrow$ ClH + Cl + HCl$^</em>$</td>
<td>$2.54 \times 10^{-11}$ $f_1(T)$</td>
<td>$2.54 \times 10^{-11}$</td>
</tr>
<tr>
<td>+ HCl$^<em>$ $\rightarrow$ ClH + Cl + HCl$^</em>$</td>
<td>$1.6 \times 10^{-14}$ $T^{1/2}$</td>
<td>$2.77 \times 10^{-13}$</td>
</tr>
<tr>
<td>+ HCl$^<em>$ $\rightarrow$ ClH + Cl + HCl$^</em>$</td>
<td>$3.2 \times 10^{-14}$ $T^{1/2}$</td>
<td>$5.54 \times 10^{-13}$</td>
</tr>
<tr>
<td>+ HCl$^<em>$ $\rightarrow$ ClH + Cl + HCl$^</em>$</td>
<td>$4.9 \times 10^{-14}$ $T^{1/2}$</td>
<td>$8.49 \times 10^{-13}$</td>
</tr>
<tr>
<td>HCl$^<em>$ + HCl$^</em>$ $\rightarrow$ ClH + Cl + HCl$^*$</td>
<td>$5.0 \times 10^{-12}$ $f_2(T)$</td>
<td>$5.00 \times 10^{-12}$</td>
</tr>
<tr>
<td>HCl$^<em>$ + HCl$^</em>$ $\rightarrow$ ClH + Cl + HCl$^*$</td>
<td>$8.79 \times 10^{-13}$ $f_2(T)$</td>
<td>$8.79 \times 10^{-13}$</td>
</tr>
<tr>
<td>HCl$^<em>$ + HCl$^</em>$ $\rightarrow$ ClH + Cl + HCl$^*$</td>
<td>$1.72 \times 10^{-12}$ $f_2(T)$</td>
<td>$1.72 \times 10^{-12}$</td>
</tr>
<tr>
<td>HCl$^<em>$ + HCl$^</em>$ $\rightarrow$ ClH + Cl + HCl$^*$</td>
<td>$3.74 \times 10^{-14}$ $f_2(T)$</td>
<td>$3.74 \times 10^{-14}$</td>
</tr>
<tr>
<td>HCl$^<em>$ + HCl$^</em>$ $\rightarrow$ ClH + Cl + HCl$^*$</td>
<td>$8.55 \times 10^{-15}$ $f_2(T)$</td>
<td>$8.55 \times 10^{-15}$</td>
</tr>
<tr>
<td>HCl$^<em>$ + HCl$^</em>$ $\rightarrow$ ClH + Cl + HCl$^*$</td>
<td>$1.64 \times 10^{-11}$ $f_3(T)$</td>
<td>$1.64 \times 10^{-11}$</td>
</tr>
<tr>
<td>HCl$^<em>$ + HCl$^</em>$ $\rightarrow$ ClH + Cl + HCl$^*$</td>
<td>$2.58 \times 10^{-12}$ $f_3(T)$</td>
<td>$2.58 \times 10^{-12}$</td>
</tr>
<tr>
<td>HCl$^<em>$ + HCl$^</em>$ $\rightarrow$ ClH + Cl + HCl$^*$</td>
<td>$4.74 \times 10^{-12}$ $f_3(T)$</td>
<td>$4.74 \times 10^{-12}$</td>
</tr>
<tr>
<td>HCl$^<em>$ + HCl$^</em>$ $\rightarrow$ ClH + Cl + HCl$^*$</td>
<td>$9.55 \times 10^{-14}$ $f_3(T)$</td>
<td>$9.55 \times 10^{-14}$</td>
</tr>
<tr>
<td>HCl$^<em>$ + HCl$^</em>$ $\rightarrow$ ClH + Cl + HCl$^*$</td>
<td>$3.57 \times 10^{-11}$ $f_3(T)$</td>
<td>$3.57 \times 10^{-11}$</td>
</tr>
<tr>
<td>HCl$^<em>$ + HCl$^</em>$ $\rightarrow$ ClH + Cl + HCl$^*$</td>
<td>$5.28 \times 10^{-12}$ $f_3(T)$</td>
<td>$5.28 \times 10^{-12}$</td>
</tr>
<tr>
<td>HCl$^<em>$ + HCl$^</em>$ $\rightarrow$ ClH + Cl + HCl$^*$</td>
<td>$9.0 \times 10^{-13}$ $f_3(T)$</td>
<td>$9.0 \times 10^{-13}$</td>
</tr>
<tr>
<td>HCl$^<em>$ + HCl$^</em>$ $\rightarrow$ ClH + Cl + HCl$^*$</td>
<td>$6.46 \times 10^{-11}$ $f_3(T)$</td>
<td>$6.46 \times 10^{-11}$</td>
</tr>
<tr>
<td>HCl$^<em>$ + HCl$^</em>$ $\rightarrow$ ClH + Cl + HCl$^*$</td>
<td>$8.82 \times 10^{-11}$ $f_3(T)$</td>
<td>$8.82 \times 10^{-11}$</td>
</tr>
<tr>
<td>HCl$^<em>$ + HCl$^</em>$ $\rightarrow$ ClH + Cl + HCl$^*$</td>
<td>$1.01 \times 10^{-10}$ $f_3(T)$</td>
<td>$1.01 \times 10^{-10}$</td>
</tr>
<tr>
<td>HCl$^<em>$ + HCl$^</em>$ $\rightarrow$ ClH + Cl + HCl$^*$</td>
<td>$3.04 \times 10^{-12}$ $f_3(T)$</td>
<td>$3.04 \times 10^{-12}$</td>
</tr>
<tr>
<td>HCl$^<em>$ + HCl$^</em>$ $\rightarrow$ ClH + Cl + HCl$^*$</td>
<td>$9.98 \times 10^{-12}$ $f_3(T)$</td>
<td>$9.98 \times 10^{-12}$</td>
</tr>
<tr>
<td>HCl$^<em>$ + HCl$^</em>$ $\rightarrow$ ClH + Cl + HCl$^*$</td>
<td>$2.18 \times 10^{-11}$ $f_3(T)$</td>
<td>$2.18 \times 10^{-11}$</td>
</tr>
<tr>
<td>HCl$^<em>$ + HCl$^</em>$ $\rightarrow$ ClH + Cl + HCl$^*$</td>
<td>$3.94 \times 10^{-11}$ $f_3(T)$</td>
<td>$3.94 \times 10^{-11}$</td>
</tr>
<tr>
<td>HCl$^<em>$ + HCl$^</em>$ $\rightarrow$ ClH + Cl + HCl$^*$</td>
<td>$3.25 \times 10^{-13}$ $f_4(T)$</td>
<td>$3.25 \times 10^{-13}$</td>
</tr>
<tr>
<td>HCl$^<em>$ + HCl$^</em>$ $\rightarrow$ ClH + Cl + HCl$^*$</td>
<td>$9.59 \times 10^{-13}$ $f_4(T)$</td>
<td>$9.59 \times 10^{-13}$</td>
</tr>
<tr>
<td>HCl$^<em>$ + HCl$^</em>$ $\rightarrow$ ClH + Cl + HCl$^*$</td>
<td>$1.97 \times 10^{-12}$ $f_4(T)$</td>
<td>$1.97 \times 10^{-12}$</td>
</tr>
<tr>
<td>HCl$^<em>$ + HCl$^</em>$ $\rightarrow$ ClH + Cl + HCl$^*$</td>
<td>$3.89 \times 10^{-14}$ $f_5(T)$</td>
<td>$3.89 \times 10^{-14}$</td>
</tr>
<tr>
<td>HCl$^<em>$ + HCl$^</em>$ $\rightarrow$ ClH + Cl + HCl$^*$</td>
<td>$1.08 \times 10^{-13}$ $f_5(T)$</td>
<td>$1.08 \times 10^{-13}$</td>
</tr>
<tr>
<td>HCl$^<em>$ + HCl$^</em>$ $\rightarrow$ ClH + Cl + HCl$^*$</td>
<td>$5.15 \times 10^{-15}$ $f_6(T)$</td>
<td>$5.15 \times 10^{-15}$</td>
</tr>
<tr>
<td>HCl$^<em>$ + HCl$^</em>$ $\rightarrow$ ClH + Cl + HCl$^*$</td>
<td>$1.6 \times 10^{-13}$ $f_6(T)$</td>
<td>$1.6 \times 10^{-13}$</td>
</tr>
<tr>
<td>HCl$^<em>$ + HCl$^</em>$ $\rightarrow$ ClH + Cl + HCl$^*$</td>
<td>$2.62 \times 10^{-13}$ $f_6(T)$</td>
<td>$2.62 \times 10^{-13}$</td>
</tr>
<tr>
<td>HCl$^<em>$ + HCl$^</em>$ $\rightarrow$ ClH + Cl + HCl$^*$</td>
<td>$4.28 \times 10^{-13}$ $f_6(T)$</td>
<td>$4.28 \times 10^{-13}$</td>
</tr>
<tr>
<td>HCl$^<em>$ + HCl$^</em>$ $\rightarrow$ ClH + Cl + HCl$^*$</td>
<td>$7.01 \times 10^{-13}$ $f_6(T)$</td>
<td>$7.01 \times 10^{-13}$</td>
</tr>
<tr>
<td>HCl$^<em>$ + HCl$^</em>$ $\rightarrow$ ClH + Cl + HCl$^*$</td>
<td>$1.15 \times 10^{-12}$ $f_6(T)$</td>
<td>$1.15 \times 10^{-12}$</td>
</tr>
</tbody>
</table>

a) $f_1(T) = 0.81137 \times 10^{3.026 \times 10^{-4} T}$; $T \leq 480$ K,

  $= 0.1742 \times 10^{1.695 \times 10^{-3} T}$; $T > 480$ K.

b) $f_2(T) = (T/300)^{1/3} \exp(380/T - 1.9333)$.

c) $f_3(T) = f_2(T) \exp(0.492 - 147.8/T)$.

d) $f_4(T) = f_3(T) \exp(0.492 - 147.8/T)$.

e) $f_5(T) = f_4(T) \exp(0.492 - 147.8/T)$.

f) $f_6(T) = f_5(T) \exp(0.492 - 147.8/T)$. 
Appendix B: Calculation of the stimulated emission coefficient and the threshold inverted population

In the present treatment $A_J(u)$ and $B_J(u)$—Einstein coefficients for spontaneous and stimulated emission respectively—were assumed to be independent of $J$.

The relation between $B(u)$ and $A(u)$ is given in the form [34]

\[ B(u) = A(u) \lambda_{u-1}^2 c/8\pi \Delta \nu_u, \]  

where $\lambda_{u-1}$ is the wavelength corresponding to the $u \rightarrow u - 1$ transition, $c$ is the light velocity and $\Delta \nu_u$ is the line width given as a sum of the Doppler line width $\Delta \nu_D$ and the pressure broadening line width $\Delta \nu_P$ [35].

The line width due to Doppler effect is of the form

\[ \Delta \nu_D = \frac{2 \lambda_{u-1}}{\nu_{u-1}} \left[ 2kT/Mc^2 \right] \ln 2 \]  

where $T$ is the temperature and $M$ is the mass of the HCl molecule. As for $\Delta \nu_P$ it was shown experimentally [35] that

\[ \Delta \nu_P = \psi P, \]  

where $\psi$ is a constant independent of the pressure and $P$ is the pressure.

In calculating $\Delta \nu_D$ it was assumed to be independent of $u$. From eq. (B.2) we find that at $T = 300 \text{ K}$, $M = 37$, and $\Delta \nu_D = 1.76 \times 10^8 \text{ s}^{-1}$.

In order to calculate $\Delta \nu_P$ we have to know $\psi$. We used for $\psi$ the value $5 \times 10^8 \text{ s}^{-1}$, independent of both $u$ and $J$, which is an estimate taken from Rank et al. [36]. For $P = 25 \text{ torr}$, $\Delta \nu_P$ becomes $1.25 \times 10^8 \text{ s}^{-1}$, a value which is close to $\Delta \nu_D$.

The threshold inverted population $\Delta N_0$ can be written as

\[ \Delta N_0 = [\tau B(u)]^{-1}, \]  

where $B(u)$ was defined earlier and $\tau$ is the average lifetime of the photon in the cavity, given in the form [15]

\[ \tau^{-1} = -(c/2I) \ln [(1 - r)(1 - L_c)]. \]  

Here $I$ is the length of the cavity ($I = 60 \text{ cm}$), $r$ stands for the lost fraction of light and $L_c$ for the output coupling coefficient. We assume $r = 0.08$ and $L_c = 0.02$ so that the total fraction of light that leaves the cavity during a round trip is 10%. The data is summarized in table 6.

Appendix C. The eigenvalues of the k matrix

The elements of the $k$ matrix [19] are given in the form

\[ k_{ij} = -[(k_{i-1}^j + k_{i+1}^j); 
\]

\[ = k_{i-1}^j; \quad j = i - 1, \]

\[ = k_{i+1}^j; \quad j = i + 1, \]

\[ = 0; \quad \text{elsewhere}, \]  

where $i = 0, 1, \ldots, N$, and due to the detailed balance relation we have

\[ k_{i+1}^j = k_{i-1}^j \left[(2i+1)/(2i+3)\right] \exp[-(E_{i+1} - E_i)/kT]. \]  

Let us introduce a diagonal matrix $T$ such that

\[ T_{ij} = (2i+1)^{-1} \exp(-E_i/kT) \delta_{ij}, \]  

then it can be shown that $k$ takes the form

\[ k = -LT, \]  

where $L$ is a symmetric matrix of the form:

\[ L_{ij} = \begin{cases} 
-1 & j = i, \\
1 & j = i + 1, \\
0 & \text{elsewhere}. 
\end{cases} \]  

Our first statement is that $L$ is a positive definite matrix. In order to prove that we have to show that if $X$ is an arbitrary vector then:

\[ XLX^* \geq 0. \]
By simple manipulations of the indices it can be shown that:

$$N \sum_{ij} X_i L_{ij} X_j = \frac{1}{2} N \sum_{i=1}^{N} (X_i - X_{i-1})^2 \geq 0 .$$  \hfill{C.7}

Consequently all the eigenvalues of $L$ are positive (or zero) which means that there exists a symmetric matrix $m$ such that:

$$m^2 = L .$$ \hfill{C.8}

Returning to eq. (C.4) we obtain that $k$ can be written as

$$k = -m^2 T .$$ \hfill{C.9}

Let us now define a matrix $Q$ such that:

$$Q = m^{-1} k m ,$$ \hfill{C.10}

then one obtains from (C.9) that $Q$ is a symmetric matrix with the $q_{ij}$, $i = 0, \ldots, N$, as eigenvalues and $U$ as the orthogonal transformation matrix:

$$Q = U q U^* ,$$ \hfill{C.11}

where

$$q_{ij} = \delta_{ij} q_i .$$ \hfill{C.12}

Consequently we obtain for $k$ that

$$k = (m U) q (m U)^{-1} ,$$ \hfill{C.12}

which means that the eigenvalues of $k$ are all real ($= q_i$) and that the transformation matrix $A$ is $(m U)$. We still have to show that all $q_i$'s are negative. Since the $q_i$ are eigenvalues of $Q$ that means they are eigenvalues of

$$Q = -m T m .$$ \hfill{C.13}

The matrix $m$ is positive definite by the way it was derived, i.e.

$$m = B \lambda B^* ,$$ \hfill{C.14}

where $\lambda$ is a diagonal matrix with elements which are the positive square roots of the eigenvalues of $I$. Combining eqs. (C.14) and (C.13) it is obtained that

$$Q = -B \lambda (B^* T B) \lambda B^* .$$ \hfill{C.15}

Since $T$ is a diagonal matrix with positive elements the matrix $B^* T B$ is a positive definite matrix and it can be easily shown that the same holds for the matrix $D = (\lambda B^* T B \lambda)$. Since $D$ is positive definite the same holds for $BDB^*$ which is equivalent to $D$ and consequently $Q$ is negative definite [cf. eq. (C.15)] which proves our statement.

We still have to show that for any finite order the matrix $k$ has at least one eigenvalue which equals zero. Considering the matrix $k$ it can be easily verified that

$$\sum_{i=1}^{N} k_i^2 = 0 ,$$ \hfill{C.16}

where $k_i$ is $i$th row of the matrix. Condition (C.16) simply means that $k$ is singular and therefore at least one of its eigenvalues is identically zero.

Eq. (C.16) ensures the conservation of the total number of molecules. In order for this to happen the following condition has to be fulfilled:

$$\sum_i dN_i(t)/dt = 0 ,$$ \hfill{C.17}

or from eq. (3.5)

$$\sum_{ij} k_{ij} N_j(t) = 0 .$$ \hfill{C.18}

Eq. (C.18) is fulfilled if eq. (C.16) exists.

References