

ON PRODUCT ROTATIONAL DISTRIBUTIONS, RELAXATION RATES AND CHEMICAL LASER THRESHOLD TIMES

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A detailed analysis of chemical laser experiments reveals that threshold times of grating selected lines provide a sensitive criterion for rotational nonequilibrium effects. A computer simulation model of the $F + H_2 \rightarrow HF + H$ chemical laser is used to demonstrate that threshold time measurements can yield accurate quantitative information on product rotational state distributions and rotational relaxation patterns. To obtain this information threshold times have to be measured as a function of the cavity loss factor or the initial gas mixture.

1. Introduction

Chemical laser experiments have provided detailed information on vibrational energy partitioning among reaction products and thus complemented other approaches such as infrared chemiluminescence experiments and classical trajectory calculations. The equal gain, zero gain, grating selection and other chemical laser techniques involve, one form or another, of threshold measurements (for reviews, see refs. [1-3]). All these methods rely on the assumption that rotational relaxation is completed before the attainment of the lasing threshold: a buffer gas is usually added to the lasing mixture in order to ensure the validity of this assumption. Consequently, no information about the nascent rotational populations and their subsequent relaxation rates can be extracted from these chemical laser experiments. The major objective of this paper is to demonstrate that by extending the measurement of threshold times to the rotational nonequilibrium regime, chemical laser experiments can yield detailed quantitative information on the rotational distribution of nascent reaction products as well as on rotational relaxation rates. With the aid of "computer experiments" we shall show that the same

amount and quality of kinetic information which has been obtained from arrested relaxation chemiluminescence experiments (see, e.g. refs. [4, 5]) can be extracted from threshold time measurements.

2. Threshold times and rotational populations

As a guiding example in the discussion we consider the



chemical laser. If a grating is used to select specific vib-rotational (v, J) lines this laser can oscillate on both P-branch $(v, J - 1 \rightarrow v - 1, J)$ and R-branch, $(v, J + 1 \rightarrow v - 1, J)$ transitions [2, 6]. In a free running system only P-branch lines are observed, except under extreme conditions of rotational nonequilibrium. In this paper only grating selected experiments and hence both P- and R-branch transitions will be discussed. For the sake of notational brevity the mathematical presentation will be limited to P-branch transitions. Thus, for example, we shall use the notation $\gamma(v, J)$ for the gain coefficient of the P-branch transition $v, J - 1 \rightarrow v - 1, J$ and $\sigma(v, J)$ for the corresponding cross section for stimulated emission.

For lasing on the $v, J - 1 \rightarrow v - 1, J$ line to be possible, the gain coefficient should exceed the rate of cavity (output and dissipative) losses, $1/\tau_p$ [1, 2],

$$\begin{aligned} \gamma(v, J) &= c\sigma(v, J) [N(v, J - 1) \\ &- (g_{J-1}/g_J)N(v - 1, J)] \geq 1/\tau_p, \end{aligned} \quad (2)$$

where τ_p is the photon lifetime in the cavity, c is the speed of light, $g_J = 2J + 1$ is the rotational degeneracy and $N(v, J)$ is the v, J -level population (number density: molecules/cm³). $N(v, J)$ or in full notation $N(v, J; t)$, is a time dependent quantity which can be expressed as

$$N(v, J; t) = N(t)P(v, J; t) = N(t)P(v; t)P(J|v; t), \quad (3)$$

where $N(t) = \sum_{v, J} N(v, J; t)$ is the total concentration of lasing molecules at time t (in our case $N(t) = [\text{HF}(t)]$), $P(v, J; t)$, $P(v; t) = \sum_J P(v, J; t)$ and $P(J|v; t) = P(v, J; t)/P(v; t)$ are, respectively, the normalized vib-rotational, vibrational and rotational (within v) distributions at time t . $N(t)$ is determined only by the overall rate of the pumping reaction (1). The time evolution of $P(v, J; t)$ (at pre-threshold times) is governed by the interplay between the pumping process which generates molecules with the nascent distribution $P(v, J; 0)$ and the relaxation processes which tend to modify this distribution.

The lasing threshold is reached at the moment $t = t_{v, J}$ that the population difference grows large enough to overcome the losses, that is, when the equality in (2) is fulfilled: $\gamma(v, J; t_{v, J}) = 1/\tau_p$. If, as is usually assumed [2, 6] $\tau_{R-T} \ll t_{v, J} \ll \tau_{v-T}$, where τ_{R-T} and τ_{v-T} are the rotational and vibrational relaxation times, respectively, then

$$P(v, J; t_{v, J}) = P(v; 0)P(J|v; \infty) \equiv P_0(v)P_B(J|v), \quad (4)$$

where $P_0(v)$ is the nascent vibrational distribution and

$$P_B(J|v) = g_J \exp[-E_J(v)/kT]/Q_R(v) \quad (5)$$

is the Boltzmann rotational distribution within the vibrational manifold v . $E_J(v) = B_v J(J + 1)$ and $Q_R(v)$ are the rotational energy and partition function of molecules in level v , respectively. T is the rotational-translational ("heat bath") temperature. Combining (2), (3) and (4) we find that the threshold condition reads

$$\gamma(v, J; t_{v, J}) = N(t_{v, J})\alpha_B(v, J) = 1/\tau_p, \quad (6)$$

where

$$\begin{aligned} \alpha_B(v, J) &\equiv c\sigma(v, J) [P_0(v)P_B(J - 1|v) \\ &- (g_{J-1}/g_J)P_0(v - 1)P_B(J|v - 1)] \end{aligned} \quad (7)$$

is defined as the reduced (or relative) gain coefficient for rotationally relaxed populations.

In Berry's detailed chemical laser study [6] of vibrational energy distribution in the $F + H_2(\text{HD}, D_2)$ reactions, an inert gas was added in excess to the lasing mixture to ensure rotational equilibrium. In order to test to what extent this condition has, indeed, been achieved, but primarily in order to demonstrate the sensitivity of threshold times to the fine details of the rotational populations, we turn now to examine the applicability of (4) and (6) to the experimental results of ref. [6]. The functional form of $N(t)$ in this system [6] is determined by three (major) kinetic processes; the production of F atoms by flash photolysis of CF_3I , the pumping reaction (1) and the fast secondary reaction $F + \text{CF}_3\text{I} \rightarrow \text{FI} + \text{CF}_3$. The time profile of $N(t)$ has been calculated in the framework of a modelling study [7] (see also ref.

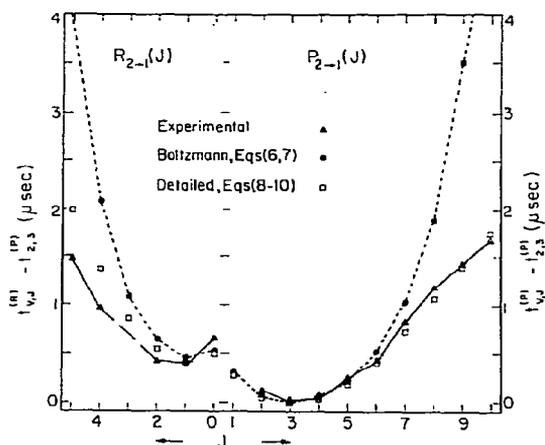


Fig. 1. Threshold times of the $v = 2 \rightarrow 1$ band of the HF laser for the initial mixture $\text{CF}_3\text{I} : \text{H}_2 : \text{Ar} = 1 : 1 : 50$ Torr. $t_{v,J}^{(R)}$ and $t_{v,J}^{(P)}$ denote the threshold times of the R-branch, $v = 2, J + 1 \rightarrow v = 1, J$ and P-branch $v = 2, J - 1 \rightarrow v - 1, J$ transitions, respectively. The origin of the experimental time scale is $t_{2,3}^{(P)} = 3.07 \mu\text{s}$ [6]. \blacktriangle - experimental [6]; \bullet - computed assuming rotational equilibrium, eqs. (6) and (7); \square - computed without assuming rotational equilibrium, using eqs. (8), (9) and (10). (The estimated experimental error is larger for the R-branch [6].)

[8]), of the free running experiments reported in ref. [6]. We have used this $N(t)$ in eq. (6) to determine the threshold times of the various (P- and R-branch) transitions. Both pressure and Doppler broadening were taken into account in the computation of $\sigma(v, J)$. The results, fig. 1, reveal that the difference between the experimental threshold times and the ones computed via (6) is negligible for the low lying J 's but grows very rapidly in the high J region. The most reasonable explanation for this behaviour is that the rotational equilibrium assumption, eq. (4), and consequently (6) are not fully justified for the high lying rotational states, despite the high buffer gas pressure. (The reliability of $N(t)$ is supported by the very good agreement between the experimental and numerical results for the free running system [7]. Besides, variations in the parameters influencing $N(t)$ have not improved the agreement between (6) and the grating experiments.) This explanation is in line with the experimental [4, 9] and theoretical [5, 10] evidence for the relatively slow relaxation of highly excited rotational levels, see (11) below.

If the lasing threshold is reached before the completion of rotational equilibration (but prior to any vibrational relaxation, see section 4 below), the threshold condition (6) should be replaced by

$$N(t_{n,J}) \alpha(v, J; t_{n,J}) = \dot{1}/\tau_p \quad (8)$$

where

$$\alpha(v, J; t) = c\sigma(v, J) [P_0(v)P(J-1|v; t) - (g_{J-1}/g_J)P_0(v-1)P(J|v-1; t)] \quad (9)$$

The time dependence of $P(J|v; t)$ in the time interval $0 \leq t \leq t_{n,J}$ is governed by the master equation

$$\begin{aligned} dP(J|v; t)/dt = R(t)P_0(J|v) - \rho \sum_{J'} [k(J \rightarrow J'|v)P(J|v; t) \\ - k(J' \rightarrow J|v)P(J'|v; t)], \end{aligned} \quad (10)$$

where $R(t) = k[F][H_2] = dN(t)/dt$ is the total pumping rate; k is the overall rate constant of (1) (the reverse process can be neglected), $P_0(J|v) = P(J|v; 0)$ is the nascent rotational distribution within v . The second term in (10) represents the effects of rotational relaxation. For simplicity it is assumed that the R-T rate constants $k(J \rightarrow J'|v)$ are the same for all collision partners and ρ is the total gas density. (This assumption will be discussed in

section 4.) We have solved (10) using exponential gap type rate constants [5, 7-10]

$$\begin{aligned} k(J \rightarrow J'|v) = A \exp \{ -C[E_J(v) - E_{J'}(v)] \} \\ (J > J'), \end{aligned} \quad (11)$$

where A and C are known empirical coefficients (see ref. [7]); $|\Delta J| \leq 3$ transitions were taken into account. $k(J' \rightarrow J < J'|v)$ are given by detailed balancing.

The threshold times evaluated from (8) after solving (10) for $P(J; v, t)$ are shown in fig. 1. The very good agreement between the threshold times computed in this way and the experimental ones confirms our previous notion about the incomplete relaxation of the high lying J levels.

Before concluding this section a remark should be made regarding an empirical relation between the experimental threshold time, $t_{n,J}$, and the Boltzmann gain coefficient (7). It has been shown by Berry [6] that for most $P_{2-1}(J)$ and $R_{2-1}(J)$ transitions $\alpha_B(v, J)$ and the experimental $t_{n,J}$ can be related to a good approximation by the expression $\alpha_B(v, J) \propto \exp(-\kappa t_{n,J})$, where κ is an empirical constant. If the rotational equilibrium assumption was fully justified then this relation, together with (6), implies that $N(t) \propto \exp(\kappa t)$. Clearly, this expression for $N(t)$ cannot be accurate since it does not satisfy the boundary conditions $N(0) = 0$ and $N(\infty) = \bar{N}$, where \bar{N} is the finite final concentration (determined by the initial reactant mixture). Moreover, as mentioned above, $N(t)$ is a rather complex function [7, 8] which cannot be properly approximated by a simple exponential. We thus arrive at two conclusions: First, the rotational equilibrium assumption or, equivalently, (6) is not accurate; in agreement with the above analyses. Second, the empirical relation found in (6) is, most likely, due to a rather incidental combination of the initial conditions determining $N(t)$ and $P(J|v; t)$.

3. Determination of $P(J|v; t)$

The threshold condition (8), combined with (9) and (10), indicates that the threshold times of a given chemical laser system can be controlled by varying the cavity loss factor τ_p , the total gas density ρ or

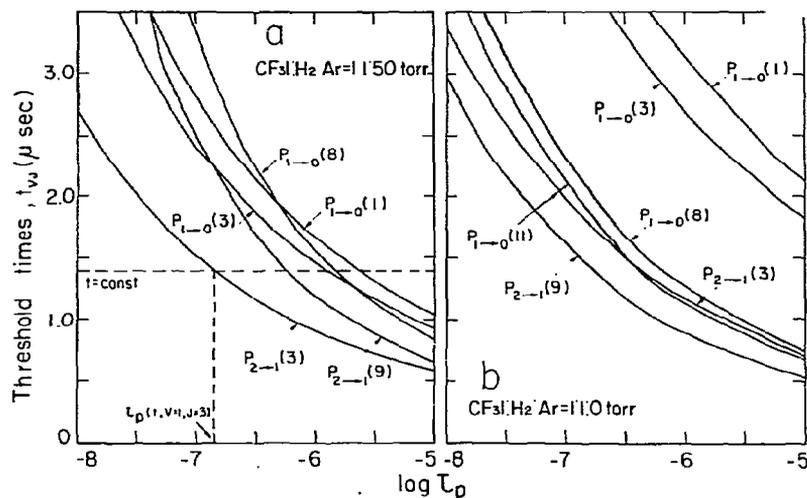


Fig. 2. Threshold times of representative transitions as a function of the cavity loss factor τ_p (or, equivalently as a function of the combined parameter L , see text). The early stages of the relaxation are better resolved in the low pressure case (b).

the initial reactant mixture which determines $N(t)$ or, equivalently, $N(t \rightarrow \infty) = N(\infty)$. (Other parameters, such as the translational temperature T , are of less interest in the case of rotational nonequilibrium.) The two factors, τ_p and $N(\infty)$ can be combined into a single parameter $L = 1/N(\infty)\tau_p$ by introducing the reduced concentration variable $f(t) = N(t)/N(\infty)$, [$f(0) = 0$, $f(\infty) = 1$]. The threshold condition (8) can thus be rewritten as

$$f(t_{vJ}) \alpha(v, J; t_{vJ}) = 1/N(\infty)\tau_p = L. \quad (12)$$

In the previous section we have used (8), (9) and (10) to evaluate t_{vJ} . Here we suggest adopting an opposite procedure in order to derive $P(J|v; t)$ from threshold time measurements. Practically this can be achieved by measuring the various t_{vJ} 's as a function of τ_p , $N(\infty)$ or, equivalently, L . To demonstrate the procedure we have applied it to a "noiseless" system realized by a computer simulation model [7] of the flash-initiated HF laser described briefly above [6]. The "experimental" threshold times provided by the computer model for a range of τ_p values (equivalently $N(\infty)$ or L) are plotted in fig. 2, for two extreme buffer gas pressures, corresponding to the initial mixtures $\text{CH}_3\text{I} : \text{H}_2 : \text{Ar} = 1 : 1 : 50$ Torr and $1 : 1 : 0$ Torr. The early stages, when relaxation has hardly begun, are resolved in more detail by the low pressure results.

The data in fig. 2 suffice to determine the time evolution of $P(J|v; t)$. The crossing point of the horizontal, $t = \text{constant}$, line with a t_{vJ} versus $1/\tau_p$ curve defines the equation

$$\begin{aligned} f(t) \sigma(v, J) [P_0(v)P(J-1|v; t) \\ - (g_{J-1}/g_J)P_0(v-1)P(J|v-1; t)] \\ = 1/N(\infty)\tau_p(t; v, J), \end{aligned} \quad (13)$$

where $\tau_p(t; v, J)$ [or $L(t; v, J) \equiv 1/N(\infty)\tau_p(t; v, J)$], is the value of τ_p , (L), for which the transition $v, J-1 \rightarrow v-1, J$ reaches threshold at time t . Similar equations apply to R-branch lines. We thus obtain a set of linear equations for the unknowns $P(J|v; t)$. The number of P- and R-branch equations together with the normalization conditions $\sum_J P(J|v, t) = 1$ is generally larger than the number of (significantly populated) levels and thus suffice for determining (and cross checking) all the relevant $P(J|v; t)$'s. Note also that a knowledge of $f(t)$, or equivalently $N(t) = f(t)N(\infty)$ (which can be determined by macroscopic reaction kinetics) is not really necessary since it appears as a common factor in all the equations and therefore can easily be eliminated. The nascent vibrational populations, $P_0(v)$, are usually known, e.g. from the grating selection technique [6] which at high buffer gas

pressures corresponds to the rotational equilibrium limit, $P(J|v; t) = P_B(J|v)$, of the present procedure. [Alternatively, $P_0(v)$ can be determined from the set of equations (13) which contain more information than is necessary for $P(J|v; t)$.] To demonstrate the procedure, consider the evaluation of $P(J|v = 1; t)$. In this case (13) is very simple since $P_0(v = 0) \ll P_0(v = 1)$ [4, 6]. Setting $P_0(v = 0) = 0$, we find

$$P(J - 1|v; t) \propto [\sigma(v = 1, J)\tau_p(t; v, J)]^{-1}. \quad (14)$$

The proportionality factor, $[P_0(1)f(t)N(\infty)]^{-1}$, is known but not necessary since the absolute values of $P(J|v; t)$ can be determined by the normalization condition. The results derived from (14) on the basis of the data shown (partially) in fig. 2a, are displayed in fig. 3.

The rotational relaxation curves of fig. 3 closely resemble the results provided by infrared chemiluminescence measurements [4, 5]. In particular we

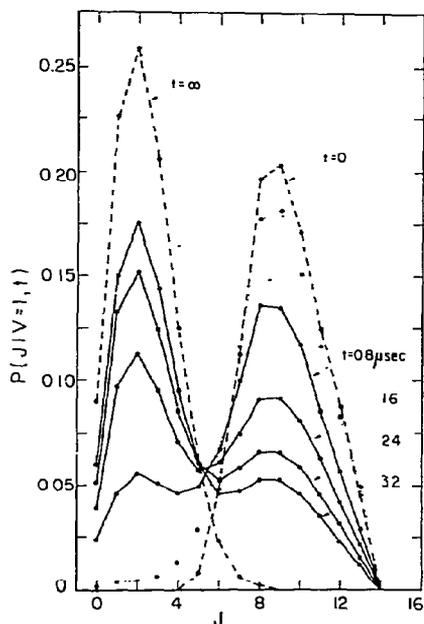


Fig. 3. Rotational distribution functions of HF ($v = 1$) molecules for various times. Full lines - data obtained by solving (13), [or (14)], for the initial gas mixture $\text{CF}_3\text{I} : \text{H}_2 : \text{Ar} = 1 : 1 : 50$ Torr, cf. fig. 2a. For comparison, also shown are the nascent ($t = 0$) and Boltzmann ($t = \infty$) distributions. The dotted line which closely approximates the nascent distribution is obtained from the low pressure data, $\text{CF}_3\text{I} : \text{H}_2 : \text{Ar} = 1 : 1 : 0$ (at $t = 2.2 \mu\text{s}$), cf. fig. 2b.

observe that the nascent rotational distribution is adequately approximated by the $t \rightarrow 0$ limit of $P(J|v; t)$. The double-peak structure of the intermediately relaxed populations reflects the rapid decrease in the rotational relaxation rate as J increases [4, 5, 7-10].

The rotational relaxation patterns shown in fig. 3 can serve as a basis for determining the detailed rate constants $k(J \rightarrow J'|v)$. The common procedure is to assume a functional form like (11), and then evaluate the parameters (A and C) by solving (10) and optimizing the agreement with the experimental data [5, 10]. Another, more fundamental, but practically more complicated approach, consists in direct inversion. Namely, if the experimental data on $P(J|v; t)$ [and $R(t)$] are sufficiently detailed so that $P(J|v; t)$, $dP(J|v; t)/dt$ and $R(t)P_0(J|v)$ are known for many instants of time t , then (10) yields a system of linear equations from which the (time independent) unknown $k(J \rightarrow J'; v)$ can be evaluated.

4. Discussion and summary

The aim of the analysis presented in the previous sections was to demonstrate that the time required to reach threshold in chemical lasers may not suffice for complete rotational relaxation in the high J regime, even at high buffer gas pressures. Similar conclusions were reached in other studies [7, 11]. Based on these notions, it was argued that the extent of rotational relaxation may be further diminished by reducing the buffer gas pressure and/or by varying the parameter L , cf. (12), thereby revealing different stages in the time evolution of $P(J|v, t)$, fig. 3. The procedure proposed for evaluating $P(J|v, t)$ utilizes the fact that chemical laser threshold times are sensitive to the fine details of the vibrational populations, fig. 1. The method suggested may complement other techniques like infrared laser fluorescence [9d] and double resonance [9a, b]. For example, threshold time measurements for the high J region can complement the detailed (and species selected) rotational relaxation data obtained in double resonance studies for the low J region.

Our analysis involved several simplifying assumptions. The two most important ones were: (a) The assumption that the vibrational distribution,

$P(v)$, is practically identical to the nascent distribution, $P_0(v)$, at pre-threshold times, cf. (9). (b) The effects of various species on the rotational relaxation of a given J level were represented by a single rate constant $k(J \rightarrow J'|v, T)$. Hence, this effective rate constant may vary from one reaction mixture to another.

The rate constants for vibrational energy transfer are sometimes larger than those for rotational energy transfer, especially in the high J regime. For example, the cross sections for V-V and V-R, T transfer in HF-HF collisions [12] are known to be very large and may exceed $k(J \rightarrow J'|v)$ for high J levels. However, detailed kinetic analyses [7, 13] of the F + H₂ system reveal that the effects of V-V and V-R, T processes on $P(v)$ are negligible during the short time interval between the beginning of the pumping process and the attainment of the lasing threshold. The reason for that is the very low HF concentration at this time interval. Thus although the V-V, R, T rate constants are large, the absolute rates are small. On the other hand, V-R, T and V-V processes may play a major role in other chemical laser systems, e.g., the ClF₂/H₂ [13] and the CH₂CHF photo-elimination [14] lasers. Clearly, in such cases the procedure suggested above for determining $P(J|v, t)$ is inadequate. (In principle, one may extend (10) to include the variations of $P(v)$ but then the procedure becomes cumbersome.)

Every term in the sum in (12) can be decomposed as

$$k(J \rightarrow J'|v) = \sum_i k_i(J \rightarrow J'|v)x_i$$

where $x_i = \rho_i/\rho$ is the molar fraction of species i . A given reaction mixture $\{x_i\}$ thus determines an average rate constant $k(J \rightarrow J'|v)$. Hence, the k_i 's can be evaluated by determining k for several reaction mixtures, as was done for example in double-resonance studies [9a]. In practice the situation may be less complicated. For instance, in the F + H₂ system which was used as a model in our analysis the HF concentration at pre-threshold times is negligible; $[HF] \approx 10^{-2}[H_2] \approx 2 \times 10^{-4}[Ar]$ for the high buffer gas pressure case [6, 7]. At low buffer gas pressures both HF-H₂ and HF-HF collisions must be taken into account.

Based on the observation that the vib-rotational threshold times are sensitive to the detailed structure

of the rotational distribution, we have proposed to extend the application of chemical laser methods to the rotational nonequilibrium regime. Computer experiments have been carried out in order to demonstrate the scope and the accuracy of the proposed method. Of course, only real experiments can reveal the feasibility of our proposals.

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References

- [1] K.L. Kompa, in: Topics in current chemistry, Vol. 37 (Springer, Berlin, 1973).
- [2] M.J. Berry, in: Molecular energy transfer, eds. R.D. Levine and J. Jortner (Wiley, New York, 1976).
- [3] R.W.F. Gross and J.F. Bott, eds., Handbook of chemical lasers (Wiley, New York, 1976).
- [4] J.C. Polanyi and K.B. Woodall, J. Chem. Phys. 57 (1972) 574.
- [5] J.C. Polanyi and K.B. Woodall, J. Chem. Phys. 56 (1972) 1563.
- [6] M.J. Berry, J. Chem. Phys. 59 (1973) 6229.
- [7] A. Ben-Shaul, S. Feliks and O. Kafri, Chem. Phys. 36 (1979) 291.
- [8] A. Ben-Shaul, K.L. Kompa and U. Schmailzl, J. Chem. Phys. 65 (1976) 1711.
- [9] (a) J.J. Hinchin and R.H. Hobbs, J. Chem. Phys. 65 (1976) 2732.
(b) J.J. Hinchin, Appl. Phys. Letters 27 (1975) 672.
(c) A.M.G. Ding and J.C. Polanyi, Chem. Phys. 10 (1975) 39.
(d) N.C. Lang, J.C. Polanyi and J. Wanner, Chem. Phys. 24 (1977) 219.
- [10] (a) I. Procaccia, Y. Shimoni and R.D. Levine, J. Chem. Phys. 63 (1975) 3181.
(b) R.B. Bernstein, J. Chem. Phys. 62 (1975) 4570.
(c) L.H. Sentmann, J. Chem. Phys. 67 (1977) 966.
- [11] O.D. Krogh, D.K. Stone and G.C. Pimentel, J. Chem. Phys. 66 (1977) 368.
- [12] N. Cohen and J.F. Bott, in: Handbook of chemical lasers, eds. R.W.F. Gross and J.F. Bott (Wiley, New York, 1976) ch. 2.
- [13] O.D. Krogh and G.C. Pimentel, J. Chem. Phys. 67 (1977) 2993.
- [14] E. Sirkin, unpublished.