

Microscopic and macroscopic analysis of non-linear master equations : vibrational relaxation of diatomic molecules

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The thermodynamic and kinetic characteristics of vibrational relaxation of diatomic molecules are studied using HF gas as a model system. The non-linear master equation governing the relaxation is solved numerically using a comprehensive set of exponential gap rate constants. The results indicate a two-stage relaxation mechanism. A very fast V-V dominated stage leading to an intermediate quasi-equilibrium distribution which depends only on the initial mean number of vibrational quanta. During this stage the vibrational distribution can be described as a superposition of the initial and intermediate distributions. A second, very slow, V-T dominated stage ultimately brings the system to complete equilibrium with the heat bath. The relaxation is characterized microscopically by the time evolution of the vibrational distribution and macroscopically by the evolution of the moments. The bridge between the two levels of analysis is provided by the maximal entropy procedure. It is shown that the entropy deficiency is the only convex function which decays monotonically to equilibrium irrespective of the order of the relaxation mechanism. Using the maximal entropy form of the distribution it is shown that two moments, i.e. two macroscopic observables, suffice to describe the distribution during the first stage while only a single moment is required to describe the final approach to equilibrium. During the intermediate stage more than two moments may be required.

1. INTRODUCTION

A relaxation process is characterized at the microscopic level by the time evolution of the population distribution. For a fairly wide class of problems this evolution is governed by linear master equations and in a number of special cases, e.g. harmonic oscillators coupled to a heat bath, it is even possible to obtain closed analytical solutions [1]. More generally though, exact solutions are not possible and one must resort to approximate schemes or numerical methods.

Recently the information theoretic characterization of (Markovian) relaxation processes has been discussed [2] and its use as a practical means of analysing such processes (when governed by a linear master equation) has been demonstrated [3]. The central idea is to use macroscopic properties of the system,

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i.e. bulk averages, provided they correspond to independent ('informative') observables, as constraints in a maximal entropy procedure to determine the relaxing population distribution. There are good reasons to justify the use of this procedure. For example, of the many convex functions that decay monotonically with the approach to equilibrium, and hence could be used to characterize the relaxation process, it is only the 'entropy deficiency' (its rate of decay is called the rate of entropy production) that satisfies essential 'additivity' or 'grouping' conditions [4, 5]. Further, it may be shown that, of all possible distributions consistent with the observed data, the maximal entropy distribution gives a lower bound for this rate [2]. Throughout this paper the term entropy refers exclusively to the information theoretic entropy (see [2-4]).

There are many processes, however, that are governed not by linear master equations but by *non*-linear master equations. These non-linear processes are of particular significance, for example, in molecular lasers. Here, fast vibrational-vibrational (V-V) transfer processes can, due to anharmonicity, cause rapid pumping up to inverted quasi-equilibrium distributions before the slower vibrational-translational (V-T) processes take over [6, 7]. Unfortunately, non-linear master equations are considerably less amenable to analytic investigation than their linear counterparts and can normally only be solved by approximation or numerical techniques. Obviously, then, alternative methods need to be investigated and, in view of its success for linear processes, the maximal entropy procedure is a likely candidate. Once again it is important to demonstrate the validity of such a procedure. In the next section we show that for non-linear master equations (unlike linear ones) the only convex function that has a definite rate of decay is the entropy deficiency. This result demonstrates that the entropy is a suitable, if not the only quantity with which to characterize the relaxation process. (Since the definite rate of entropy production can be interpreted as the generalized second law of thermodynamics, it seems eminently suitable to characterize the process with a quantity that satisfies this condition!)

In § 3 we give a detailed examination, with numerical examples, of the relaxation of a (dilute) gas of HF molecules. First we solve the relevant (non-linear) master equation numerically using a comprehensive set of exponential-gap [8, 9] state-to-state rate constants. These results illustrate general features of the process, e.g. effect of initial distribution, fast pumping to a quasi-equilibrium distribution and subsequent relaxation etc., as well as the time dependence of the moments (bulk observables). In § 4 we then go on to show how entropy provides a convenient characterization of the process and that the maximal entropy distribution, determined with only a small number of constraints, accurately reproduces (albeit phenomenologically at this stage) the evolving population distribution.

2. ENTROPY AND MACROSCOPIC DISEQUILIBRIUM

A linear master equation [1]

$$dP(n, t)/dt = \sum_m A(n, m)P(m, t)$$

specifies the time evolution of the population $P(n, t)$ in state n at time t . For

convenience in later manipulations we rewrite it as a discrete equation over a short time interval Δt ,

$$P(n, t + \Delta t) = \sum_m \Pi(n|m)P(m, t). \quad (2.1)$$

The $\Pi(n|m)$ give the probability that a system in state m will be found after Δt in state n . For Δt sufficiently small [1] $\Pi(n|m) = \delta_{n,m} + A(n, m)\Delta t$ and, in order to conserve probability

$$\sum_n \Pi(n|m) = 1. \quad (2.2)$$

The stationary distribution $P^0(n)$ is unchanged by the passage of time, i.e.

$$P^0(n) = \sum_m \Pi(n|m)P^0(m). \quad (2.3)$$

There are many functions of the form

$$E = \sum_n P^0(n) \phi \left[\frac{P(n, t)}{P^0(n)} \right], \quad (2.4)$$

which, for distributions governed by a linear master equation, satisfy $-dE/dt \geq 0$ provided only that the function $\phi = \phi(x)$ is convex (i.e. $\partial^2 \phi / \partial x^2 \geq 0$). This result is obtained in the form of the inequality [10]

$$\sum_n P^0(n) \phi \left[\frac{P(n, t)}{P^0(n)} \right] \geq \sum_n P^0(n) \phi \left[\frac{P(n, t + \Delta t)}{P^0(n)} \right], \quad (2.5)$$

by using the property that the mean of a convex function is greater than or equal to the function of the mean, i.e.

$$\langle \phi(x) \rangle_{av} \geq \phi(\langle x \rangle_{av}), \quad (2.6)$$

where the averaging is over any set of (normalized) probabilities. If the convex function is taken to be the entropy, i.e. $\phi(x) = x \ln x$, then (2.4) defines the entropy deficiency

$$\Delta S = \sum_n P^0(n) \frac{P(n, t)}{P^0(n)} \ln \left[\frac{P(n, t)}{P^0(n)} \right] = \sum_n P(n, t) \ln \left[\frac{P(n, t)}{P^0(n)} \right] \quad (2.7)$$

and its rate of change, the rate of entropy production, has a definite sign $-d\Delta S/dt \geq 0$. However, purely from this point of view, as mentioned in the introduction, there is nothing to distinguish our choice of the entropy as a means of characterizing the approach to equilibrium, from any other convex function. It is distinguished, though, by its additivity properties which, as we shall see, are of particular significance when we examine the evolution of functions of the form (2.4) for processes governed by *non-linear* master equations.

We write the stochastic equation for non-linear processes in the form

$$P(r, t + \Delta t) = \sum_{s, m, n} \Pi(rs|mn)P(m, t)P(n, t), \quad (2.8)$$

where the transition probabilities satisfy the conservation condition

$$\sum_{rs} \Pi(rs|mn) = 1. \quad (2.9)$$

The stationary distributions are defined in the same way as in equation (2.3), i.e.

$$P^0(r) = \sum_{s, m, n} \Pi(rs|mn) P^0(m) P^0(n). \quad (2.10)$$

Our aim is to see which functions of the form (2.4) still have a definite rate of decay. For this purpose it is convenient to reduce equation (2.8) by summing over one less index. This then gives a non-linear equation of the form

$$P(r, t + \Delta t) P(s, t + \Delta t) = \sum_{m, n} \Pi(rs|mn) P(m, t) P(n, t). \quad (2.11)$$

Notice that we write a product of distributions on both sides of the equation; this is to maintain its stochastic (or Markov) form and is consistent with its stationary form which must be

$$P^0(r) P^0(s) = \sum_{m, n} \Pi(r, s|mn) P^0(m) P^0(n). \quad (2.12)$$

We consider the convex function of the form

$$\phi = \phi \left[\frac{P(m, t) P(n, t)}{P^0(m) P^0(n)} \right] \quad (2.13)$$

and average it over the quantities $\Pi(rs|mn) P^0(m) P^0(n) / P^0(r) P^0(s)$ which, as can be seen from equation (2.12), can be regarded as a set of normalized probabilities, i.e.

$$\sum_{m, n} \Pi(rs|mn) \frac{P^0(m) P^0(n)}{P^0(r) P^0(s)} = 1. \quad (2.14)$$

Using the property of convex functions given in equation (2.6) we have

$$\begin{aligned} \sum_{m, n} \Pi(rs|mn) \frac{P^0(m) P^0(n)}{P^0(r) P^0(s)} \phi \left[\frac{P(m, t) P(n, t)}{P^0(m) P^0(n)} \right] \\ \geq \phi \left[\sum_{m, n} \Pi(rs|mn) \frac{P(m, t) P(n, t)}{P^0(r) P^0(s)} \right], \end{aligned} \quad (2.15)$$

which, by (2.8) becomes

$$\begin{aligned} \sum_{m, n} \Pi(rs|mn) P^0(m) P^0(n) \phi \left[\frac{P(m, t) P(n, t)}{P^0(m) P^0(n)} \right] \\ \geq P^0(r) P^0(s) \phi \left[\frac{P(r, t + \Delta t) P(s, t + \Delta t)}{P^0(r) P^0(s)} \right], \end{aligned} \quad (2.16)$$

summing over r and s and using the conservation condition (2.9) we obtain

$$\begin{aligned} \sum_{m, n} P^0(m) P^0(n) \phi \left[\frac{P(m, t) P(n, t)}{P^0(m) P^0(n)} \right] \\ \geq \sum_{r, s} P^0(r) P^0(s) \phi \left[\frac{P(r, t + \Delta t) P(s, t + \Delta t)}{P^0(r) P^0(s)} \right]. \end{aligned} \quad (2.17)$$

This is our basic result for a general convex function (of the form (2.4)) with distributions governed by a non-linear equation. This result can easily be

generalized to processes of any order (molecularity). Thus for the stochastic equation of order s

$$P(n_1, t + \Delta t) = \sum_{\substack{n_2, \dots, n_s \\ m_1, \dots, m_s}} \Pi(n_1, n_2, \dots, n_s | m_1, m_2, \dots, m_s) \times \prod_{i=1}^s P(m_i, t), \quad (2.18)$$

we obtain the inequality

$$\begin{aligned} \sum_{n_1, \dots, n_s} \prod_{i=1}^s P^0(n_i) \phi \left[\prod_{i=1}^s \frac{P(n_i, t)}{P^0(n_i)} \right] \\ \geq \sum_{m_1, \dots, m_s} \prod_{i=1}^s P^0(m_i) \phi \left[\prod_{i=1}^s \frac{P(m_i, t + \Delta t)}{P^0(m_i)} \right]. \end{aligned} \quad (2.19)$$

As it stands, our result is not very useful since it only relates products of distributions at earlier and later times. We do not obtain the simple result (2.5) that we have for linear processes. However, in the case of the entropy ($\phi(x) = x \ln x$) we can go further. Considering for simplicity the bimolecular process, equation (2.17) becomes

$$\begin{aligned} \sum_{m, n} P(m, t) P(n, t) \ln \left[\frac{P(m, t) P(n, t)}{P^0(m) P^0(n)} \right] \\ \geq \sum_{r, s} P(r, t + \Delta t) P(s, t + \Delta t) \ln \left[\frac{P(r, t + \Delta t) P(s, t + \Delta t)}{P^0(r) P^0(s)} \right] \end{aligned} \quad (2.20)$$

and the unique additivity properties of the logarithmic function can now be exploited. Noting the normalization condition $\sum_m P(m, t) = 1$, equation (2.18) reduces immediately to

$$\sum_m P(m, t) \ln \left[\frac{P(m, t)}{P^0(m)} \right] \geq \sum_m P(m, t + \Delta t) \ln \left[\frac{P(m, t + \Delta t)}{P^0(m)} \right] \quad (2.21)$$

and hence we obtain the rate of entropy production

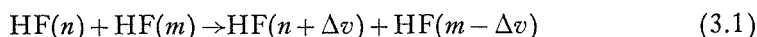
$$-\frac{d\Delta S}{dt} \geq 0. \quad (2.22)$$

Thus we see that the entropy deficiency has a definite rate of decay independent of the molecularity of the process; a result which stems from the unique additivity properties of the entropy. Furthermore, at equilibrium ΔS corresponds to the appropriate thermodynamic potential which, in the case of a closed system coupled to a heat bath, is the Helmholtz free energy. We add that if one merely wished to obtain the rate of entropy production (2.22) without considering convex functions in general, an alternative derivation is possible starting from the master equation corresponding to (2.8). This is shown in the Appendix.

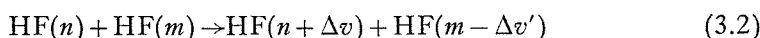
3. VIBRATIONAL RELAXATION

We now investigate the relaxation of HF molecules in the presence of a buffer gas (heat bath) at 300 K. The rotational and translational (R-T) processes are assumed to be sufficiently rapid for these degrees of freedom to be

considered in equilibrium with the heat bath. The remaining processes fall into two main categories. These are the V-V processes by which vibrational quanta are transferred between molecules, i.e.



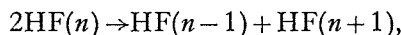
and V-T processes in which vibrational quanta are lost to (or gained from) the heat bath, i.e.



where $\Delta v \neq \Delta v'$. We assume that although the buffer gas (e.g. Ar) is an efficient agent for R-T processes it is inefficient for vibrational relaxation and we therefore neglect V-T processes of the form $\text{HF}(n) + \text{Ar} \rightarrow \text{HF}(m) + \text{Ar}$. The vibrational energy levels of HF are anharmonic and taken to be Morse oscillator levels, i.e.

$$E_n = (n + \frac{1}{2})\hbar\omega - (n + \frac{1}{2})^2 \hbar\omega x_e, \quad (3.3)$$

where for the frequency and anharmonicity we take the values $\omega = 4138.7 \text{ cm}^{-1}$ and $x_e = 0.0218$ respectively [11]. Because of the anharmonicity the V-V processes are 'off resonance' and a small amount of energy, the energy defect, is lost (or gained) to (or from) the heat bath. Thus, unlike V-V processes between harmonic oscillators, the mean vibrational energy is no longer a conserved quantity; only the mean number of quanta is conserved [6, 7]. Furthermore, due to the anharmonicity, the V-V processes that excite quanta, e.g.



are exothermic (this may be easily verified using equation (3.3)) and hence thermodynamically preferred. Thus for V-V processes the trend is towards population inversion in contrast to the V-T processes which favour de-excitation. It is the competition between these two opposing trends that leads to many of the characteristic features of the relaxation process.

3.1. Master equation and rate constants

We study the relaxation process by means of the non-linear master equation

$$\frac{dP(r, t)}{dt} = \sum_{s, m, n} \{k(r, s \leftarrow m, n)P(m, t)P(n, t) - k(m, n \leftarrow r, s)P(r, t)P(s, t)\}. \quad (3.4)$$

The rate constants $k(r, s \leftarrow m, n)$ for which $r + s = m + n$ correspond to V-V processes whereas we define V-T processes as all those for which $r + s \neq m + n$. We also mention that in this master equation the rate constants have been multiplied by the total molecular density N since the populations $P(r, t)$ are defined as $N(r, t)/N$ where $N(r, t)$ is the (time dependent) density of molecules in state r .

In order to solve equation (3.4) we need all the state-to-state rate constants. We use the exponential gap form [12]

$$k(r, s \leftarrow m, n) = Ak^0(r, s \leftarrow m, n) \exp(-\lambda|E_m + E_n - E_r - E_s|/kT) \quad (3.5)$$

where $k^0(r, s \leftarrow m, n)$ is the prior rate constant (computed on the basis that all quantum states are equally accessible) which increases with increasing energy

defect $\Delta E = E_m + E_n - E_r - E_s$, A is a normalization factor and λ a measure of the deviation of k from k^0 . The rate constants k have an obvious temperature dependence but it should also be remembered that A and k^0 are also temperature dependent.

A detailed description of this type of rate constant, and a means of evaluating (synthesizing) the parameters A and λ is given elsewhere [12]. For our study we normalize the rate constants such that $k(0, 0 \leftarrow 1, 0)$ has its experimental value of $1.0 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 300 K and set λ equal to 0.5. Rate constants computed in this way with similar values of λ have been shown to compare quite well with the available experimental results for the first few levels of HF [13, 14]. In all calculations the total HF density was taken as $N = 5.35 \times 10^{-8} \text{ mol cm}^{-3}$ (1 torr, 300 K).

For low quantum numbers the V-V processes have much smaller energy defects and hence larger rate constants than the corresponding V-T processes. However, as the quantum numbers involved become larger the V-V energy defect increases and the V-T energy defect decreases. Eventually a crossing point, which will be temperature dependent, is reached after which it is the V-T rate constants that become dominant. In figure 1 we plot series of V-V and V-T rate constants which clearly illustrate this point.

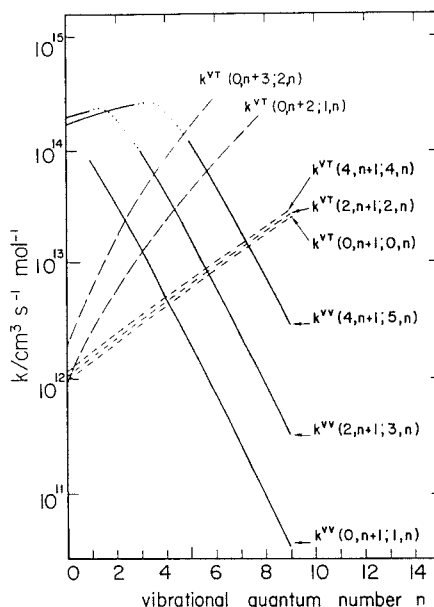


Figure 1. Series of V-V and V-T rate constants at 300 K. The rate constants are computed according to the exponential gap formula (3.5).

In order to keep our computations down to realistic proportions we include only the first 11 vibrational levels ($n = 0$ to 10). We retain all pairs of transitions $n + m \rightleftharpoons r + s$ such that either the forward, $k(n, m \rightarrow r, s)$ or the reverse, $k(r, s \rightarrow n, m)$ rate constants are greater than or equal to $k(1, 0 \rightarrow 0, 0) = 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. This still leaves us with over 300 (pairs of) rate constants including a number

corresponding to multiple ($\Delta n = \pm 2, \pm 3, \pm 4$) quantum transitions, of the types (3.1) and (3.2). The role of the multiple V-V rate constants is discussed in § 3.2. Obviously, with a non-linear master equation, the number of rate constants increases enormously with the number of levels included.

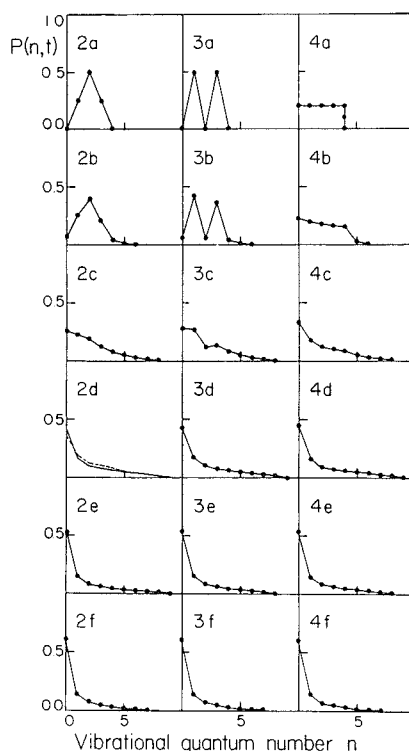
The master equation was solved by direct numerical integration using a modified version of the 6th order Gear Hybrid, predictor-corrector, method.

3.2. Population evolution

We choose the initial distributions (which might have been formed, for example, by a pulse of radiation) to have a specified mean number of vibrational quanta, i.e.

$$\langle n \rangle_0 = \sum_n n P(n, 0). \quad (3.6)$$

In figures 2, 3, 4 we show the relaxation of three different distributions all with $\langle n \rangle_0 = 2$. We immediately see that in a very short time (about $0.3 \mu\text{s}$) relative to the total relaxation time all initial distributions relax to virtually the same intermediate distribution (figures 2 (*d*), 3 (*d*), 4 (*d*)) which then develops more slowly and, quite obviously, independently of the initial distribution. The fact that the initial distributions in figures 3 and 4 are rather unphysical only serves



Figures 2, 3 and 4. Time evolution of the populations for different initial distributions having the same initial mean quantum numbers $\langle n \rangle_0 = 2$. Times are (for all figures): $a = 0.00$, $b = 0.02$, $c = 0.10$, $d = 0.31$, $e = 1.01$, $f = 2.02 \mu\text{s}$. The broken line in figure 2 (*d*) corresponds to a computation including only single quantum jump V-V rate constants.

to emphasize this point. The intermediate distribution, although not displaying strong population inversion shows a distinct smearing out of the distribution. The time scale for the first relaxation stage can be interpreted as follows: the lifetime of a vibrational level due to the V-V processes can be estimated as $\tau \sim 1/kN$ where k is the sum of all rate constants involving the given vibrational quantum numbers. On the average in our calculation each level participates in about 20 V-V processes while $k_{V-V} \sim 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $N \simeq 5 \times 10^{-8} \text{ mol cm}^{-3}$, hence $\tau \sim 10^{-7} \text{ s}$.

In figure 2 (d) we have also marked the distribution that was obtained when including only single quantum jump ($\Delta n = \pm 1$) V-V rate constants in the master equation. To date, most computations have only included these rate constants [15, 16, 17] and we therefore investigated the effect of the multiple jump ones. Our general conclusion was that if only single jump rate constants are included, although all the basic features are still demonstrated, the degree of population inversion tended to be greater. We always included all multiple jump V-V rate constants of significant value in our calculations.

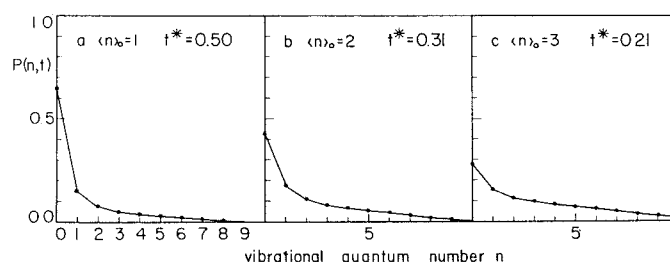


Figure 5. Intermediate quasi-equilibrium distributions observed for population evolution starting with different $\langle n \rangle_0$, t^* is the estimated time of attainment (in μs).

We also performed computations for initial distributions with mean quantum number $\langle n \rangle_0 = 3$ and $\langle n \rangle_0 = 1$. Again the same general phenomena observed for $\langle n \rangle_0 = 2$ were also apparent. We found, however, that the lower the initial number of quanta the longer it took to attain a first common intermediate distribution. In figure 5 we show the intermediate distributions obtained for $\langle n \rangle_0 = 1, 2$ and 3 with the approximate times of attainment. The reason why a distribution with a larger $\langle n \rangle_0$ should relax more quickly may simply be due to the fact that at higher quantum numbers more and more processes with larger rate constants (see figure 1) come into play.

Quite clearly, then, the relaxation process can be divided into two stages; a very fast V-V dominated stage giving rise to a quasi-equilibrium intermediate distribution and then a very much slower, V-T dominated relaxation process. The only important feature of the initial distribution seems to be the (mean) number of quanta, the precise form being apparently unimportant. The markedly different roles of the V-V and V-T processes and their different time scales can be illustrated quite strikingly by solving the master equation with either only V-V rate constants or only V-T rate constants included. This is shown in figure 6 which can be compared directly with figure 2 where all rate constants have been included. An additional feature of interest is that, in the case of V-V rate constants only, a population inversion or up-pumping process [6, 18] is

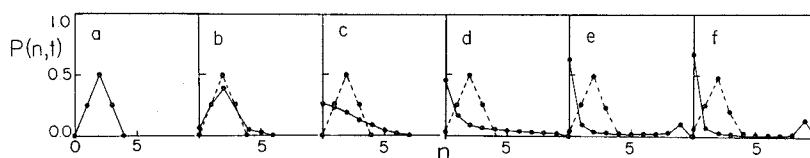


Figure 6. Time evolution of the populations with initial distribution as in figure 2 (a). Full line : V-V rate constants only. Broken line : V-T rate constants only.

starting to develop (figures 6 (e) and 6 (f)) that would in fact ultimately lead to dissociation (see § 4.2). However, it is precisely here that the V-T processes come into play and make this exceedingly inefficient.

In view of the very fast nature of the V-V stage there is the possibility of considerable differences in the observed initial vibrational distribution for a given experiment carried out under different conditions, e.g. measurement of the initial CO distribution in the highly exothermic chemical laser reaction $O + CS \rightarrow CO + S$ [19].

3.3. Superposition

In a number of relaxation processes where the energy defect is small compared with kT it has been found that the evolving population distribution can be represented as a linear superposition of initial and final distributions. For example, in cases of rotational relaxation [20] (which is a *linear* process) the rotational distribution was found to be well fitted by the form

$$P(J, t) = P^0(J) + [P(J, 0) - P^0(J)] \exp(-t/\tau), \quad (3.7)$$

where $P(J, 0)$ is the initial (or nascent) distribution and $P^0(J)$ the final equilibrium distribution. A similar type of superposition was also found to give a good fit to the observed results of the vibrational relaxation of CO [7]. However, for this non-linear process the superposition was of the form

$$P(n, t) = P(n, t^*) + [P(n, 0) - P(n, t^*)] \exp(-t/\tau), \quad (3.8)$$

where $P(n, t^*)$ is not the final equilibrium distribution but the distribution obtained when the V-V (but not the V-T) processes had reached equilibrium, i.e. a quasi-equilibrium intermediate distribution of the type discussed in the previous section.

Accordingly, we tried to fit our numerical results for the first, V-V dominated, stage of the relaxation of HF with a superposition of the form (3.8). We chose $P(n, 0)$ to be of the form shown in figure 2 (a) ($\langle n \rangle_0 = 2$) and hence took $t^* = 0.31 \mu\text{s}$ (see figure 2 (d)). In practice, the computation was performed by taking a fixed value of τ (which gives a measure of the relaxation time of the V-V process) and just fitted the final distribution $P(n, t^*)$. We found that the fitting was not very sensitive to the value of τ and for a wide range of values ($\tau^{-1} = 10.0$ to $20.0 \mu\text{s}^{-1}$) we obtained good results. In figure 7 we compare the exact, master equation results with the superposition (3.8) for $\tau^{-1} = 14.0 \mu\text{s}^{-1}$. For the larger times the agreement is remarkably good.

Superpositions of the type described imply that the system retains a memory of the initial distribution during the relaxation process. Our results have shown

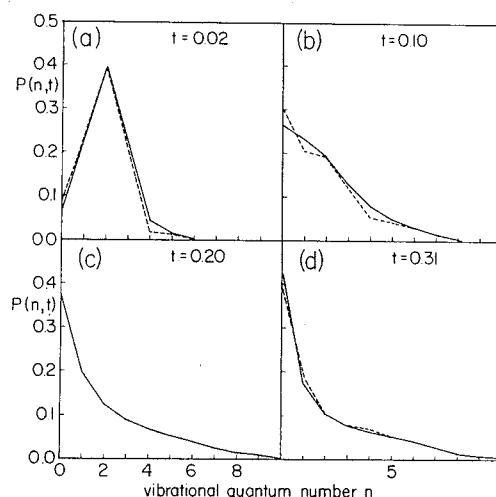


Figure 7. Comparison of exact population evolution (full line) with superposition model, equation (3.8) (broken line) for the first stage of the relaxation process (time in μs). Initial distribution as in figure 2 (a). In figure 7 (c) the two results are graphically indistinguishable (times in μs).

that beyond t^* the system apparently relaxes quite independently of $P(n, 0)$ and hence we cannot expect the superposition to hold beyond this time. This is not too surprising since now the relaxation is dominated by a different mechanism, namely the (large energy defect) V-T processes.

3.4. Evolution of the moments

So far we have only discussed the behaviour of microscopic quantities (the populations) and we now turn to the behaviour of macroscopic quantities, namely the moments. We consider the vibrational energy moments

$$\langle E_n^i(t) \rangle = \sum_n E_n^i P(n, t) \quad (3.9)$$

and the moments of vibrational quanta

$$\langle n^i(t) \rangle = \sum_n n^i P(n, t). \quad (3.10)$$

The first three of both are plotted (logarithmic ordinate for compaction) in figure 8. A number of interesting features are apparent. In the first stage of the process the second and third moments of both the energy and quantum number show a rapid increase. At much longer times they all decay in roughly the same manner. This is also true of the first moments but their early behaviour is very different. The energy actually shows almost pure exponential decay whereas the mean quantum number displays a different behaviour. If the first stage was a *pure* V-V process then $\langle n(t) \rangle$ should be constant; this actually appears to be approximately the case for the first few collisions.

In the last section we saw that the first stage of the relaxation could be fitted by a simple superposition (3.8). Hence all moments ($\langle M(t) \rangle$) can easily be

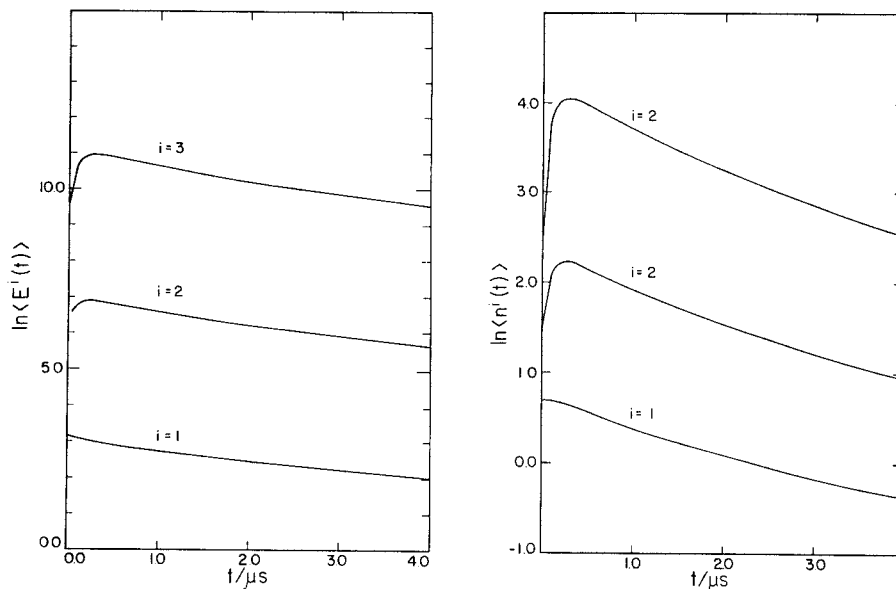


Figure 8. (a) Time evolution of the first three energy moments; $\langle E^i(t) \rangle$, $i=1, 2, 3$. At early times the first moment $\langle E(t) \rangle$ has almost pure exponential decay (time in μs). (b) Time evolution of the first three moments of vibrational quanta; $\langle n^i(t) \rangle$, $i=1, 2, 3$.

shown to relax in the following pure exponential manner

$$\langle M(t) \rangle = \langle M(t^*) \rangle + [\langle M(0) \rangle - \langle M(t^*) \rangle] \exp(-t/\tau), \quad (3.11)$$

where $\langle M(0) \rangle$ and $\langle M(t^*) \rangle$ are the initial and quasi-equilibrium values of the moments respectively. If $M(t^*)$ is greater than $M(0)$, as was found to be the case for the second and third moments, then $\langle M(t) \rangle$ will increase from $t=0$ to $t=t^*$; otherwise it will decay. Although these general features are approximately displayed in figure 8 it is clear that the superposition cannot be the whole story. This is especially born out by the behaviour of the first moments. The almost pure exponential decay of $\langle E(t) \rangle$ would strongly support the superposition model but the different behaviour of $\langle n(t) \rangle$ could equally well contradict it!

The behaviour of the moments, or more generally the macroscopic observables, is of central importance in obtaining the maximal entropy distributions. This is described in the following section.

4. ENTROPY

We now turn to the use of entropy as a means of characterizing certain features of the relaxation process described in the previous sections.

4.1. Entropy deficiency and vibrational entropy

In figure 9 we plot the entropy deficiency (2.7) as a function of time for the relaxation processes corresponding to figure 2. As expected, ΔS shows a

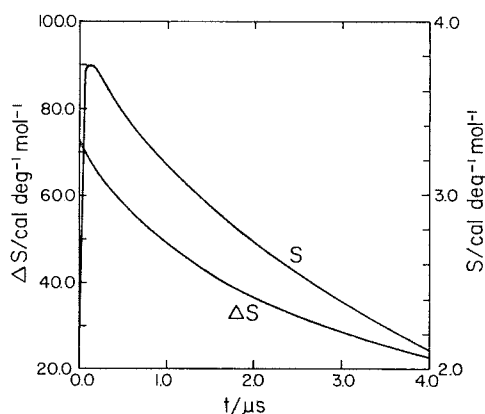


Figure 9. Time dependence of the entropy deficiency (left ordinate) and of the vibrational entropy (right ordinate) for population evolution with initial distribution as in figure 2 (a). The maximum in S corresponds to the smearing out of the population around figure 2 (d) (time in μs).

smooth monotonic decrease with the approach to equilibrium. Plots such as this are common to the relaxation of all the initial distributions examined.

In contrast to the entropy deficiency, the entropy of the vibrational distribution $S = - \sum_n P(n, t) \ln P(n, t)$ (as opposed to the entropy of the whole system, heat bath plus sub-system) does not necessarily have to display monotonic behaviour. In figure 9 we plot S as a function of time for the population evolution corresponding to figure 2. The sharp initial rise in S reflects the increase in entropy as the well ordered initial distribution (figure 2 (a)) relaxes to the smeared out intermediate distribution (figure 2 (d)). However, beyond this point the entropy then starts to decrease as the distribution narrows down towards the final equilibrium distribution. If one notes that the equilibrium distribution takes the form

$$P^0(n) = Q^{-1} \exp(-E_n/kT), \quad (4.1)$$

where Q is the partition function and T the (bath) temperature, then the entropy can be expressed in the following form :

$$\begin{aligned} S &= - \sum_n P(n, t) \ln P(n, t), \\ &= - \sum_n P(n, t) \ln \left[\frac{P(n, t)}{P^0(n)} \right] - \sum_n [P(n, t) - P^0(n)] \ln P^0(n) \\ &\quad - \sum_n P^0(n) \ln P^0(n), \\ &= -\Delta S + \frac{1}{kT} [\langle E(t) \rangle - \langle E(\infty) \rangle] + S_0, \end{aligned} \quad (4.2)$$

where S_0 is the entropy of the equilibrium distribution, ΔS the entropy deficiency and the term $1/kT[\langle E(t) \rangle - \langle E(\infty) \rangle]$ represents the amount of entropy transferred to the heat bath. This equation enables us to represent ΔS in the form

$$\Delta S = \frac{1}{kT} \Delta E - (S - S_0). \quad (4.3)$$

The second law of thermodynamics requires that $\Delta S \geq 0$ and hence we must always have $\Delta E \geq kT(S - S_0)$. If we now consider just the first stage of the relaxation process and let S_0 represent the entropy of the quasi-equilibrium distribution we can deduce the following. In certain cases of strong population inversion we may have $S > S_0$ (as opposed to our case where $S < S_0$) and hence more entropy must be transferred to the heat bath to ensure $\Delta S \geq 0$. We can now see that this is facilitated by having a lower temperature T . Hence we can draw the general conclusion that the lower the bath temperature the greater the possible population inversion.

4.2. The maximal entropy distribution

Finally we examine the maximal entropy procedure as a means of reproducing the evolving population distribution. It has been shown that this procedure is of a variational type and that the maximal entropy distribution will converge monotonically to the exact one as more and more (independent) constraints are included [2, 3]. Clearly the procedure will be most useful when one can obtain accurate results using the least number of constraints. Hence our aim is to find those constraints that contain the most information pertinent to the relaxation process.

The results of § 3.4 show that the behaviour of the moments $\langle E_n(t) \rangle$ and $\langle n(t) \rangle$ reflect quite a few features of the relaxation process and particularly the early V-V stage. Accordingly, as a first attempt to find a suitable maximal entropy distribution we maximize the entropy $S = - \sum_n P(n, t) \ln P(n, t)$ subject to the constraints $\langle E_n(t) \rangle$ and $\langle n(t) \rangle$. This standard procedure yields

$$P(n, t) = Q^{-1} \exp [-\lambda_1(t)E_n - \lambda_2(t)n], \quad (4.4)$$

where λ_1 and λ_2 are time dependent Lagrange multipliers and Q the (time dependent) partition function. The precise behaviour of $\lambda_1(t)$ and $\lambda_2(t)$ will depend on the behaviour of the corresponding moments but we do know the asymptotic behaviour, i.e.

$$\lambda_1(t) = 1/kT \quad \text{and} \quad \lambda_2(t) = 0 \quad (t \rightarrow \infty), \quad (4.5)$$

where T is the bath temperature. The distribution (4.4) resembles that suggested by Treanor *et al.* [6] to describe the quasi-stationary state that would be obtained for a pure V-V relaxation process. However, in our case we are interested in obtaining the form of the distribution function that is valid throughout the entire relaxation process and not just the quasi-stationary distribution.

Returning to the distribution (4.4) we can rewrite it in the form

$$P(n, t) = Q^{-1} \exp [-\lambda_1(t)(E_n - E_n^0) - \lambda_3(t)E_n^0], \quad (4.6)$$

where E_n^0 is the harmonic oscillator energy level,

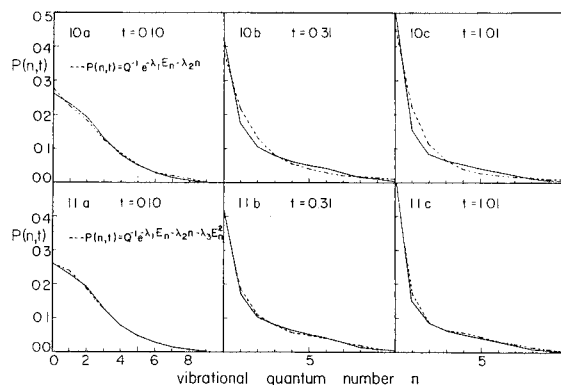
$$E_n^0 = (n + \frac{1}{2})\hbar\omega, \quad \text{and} \quad \lambda_3(t) = [\lambda_1(t) + \lambda_2(t)/\hbar\omega].$$

Since $E_n < E_n^0$ we see that for sufficiently large λ_1 (depending, of course, on the behaviour of λ_3) $P(n, t)$ can display strong (in fact diverging) population

inversion. Note that in the limit of zero anharmonicity (4.4) reduces to the canonically invariant form [1]

$$P(n, t) = Q^{-1} \exp [-\lambda_1(t)E_n^0];$$

the multiplier $\lambda_2(t)$ has vanished since $\langle n \rangle$ is no longer an informative moment, now being (trivially) linearly dependent on $\langle E_n^0 \rangle$. Although the two-parameter distribution (4.4) may be adequate at short times it will break down at large ones since it fails to take into account the de-excitation of higher vibrational levels by the V-T processes. Clearly additional constraints are required. One might consider trying $\langle n^2(t) \rangle$ but this is not informative since it is linearly dependent on $\langle E_n \rangle$ and $\langle n \rangle$ (see equation (3.3)). We can, however, use $\langle E_n^2(t) \rangle$ and in figures 10 and 11 we compare the exact distribution at a number of times



Figures 10 and 11. Comparison of exact (full line) distributions with two (figure 10) and three (figure 11) constraints maximal entropy distributions (broken line) at a number of times (μ s). The third constraint is almost linearly dependent on the previous ones (cf. [21] for the definition of linear dependence and its implications).

with the maximal entropy distributions using $\langle E_n(t) \rangle$ and $\langle n \rangle$, and $\langle E_n(t) \rangle$, $\langle n(t) \rangle$ and $\langle E_n^2(t) \rangle$ as constraints. It can be seen that the three-parameter distribution gives a good fit to the exact one for all times shown. As expected, the two-parameter distribution, although adequate at very short times, is particularly poor at longer times. Clearly though, other combinations of constraints are possible. We also compared (not shown) the exact distributions with those using $\langle E_n(t) \rangle$ and $\langle E_n^2(t) \rangle$ and $\langle E_n(t) \rangle$, $\langle E_n^2(t) \rangle$ and $\langle E_n^3(t) \rangle$ as constraints. The latter distribution gives excellent results and one must conclude that this combination of constraints contains more information than the other three-parameter distribution tried. This is perhaps not surprising since the combination $\langle E_n \rangle$, $\langle E_n^2 \rangle$ and $\langle E_n^3 \rangle$ implicitly contains information about all vibrational moments up to $\langle n^6 \rangle$ whereas $\langle E_n \rangle$, $\langle n \rangle$ and $\langle E_n^2 \rangle$ only includes terms up to $\langle n^4 \rangle$. However, our results should be considered as phenomenological at this stage and we have simply shown that the evolving population distribution can be accurately fitted with a three-parameter distribution. Our choice of constraints has been guided by physical intuition but we cannot tell at this stage whether there are other combinations of constraints that would be more informative and hence give even better results. Finally, we mention that

the numerical determination of the Lagrange multipliers was carried out by means of a recently devised linear programming technique [21].

4.3. Constraints

The previous discussion clearly identified the procedure that is still missing in the maximal entropy formalism. One needs to be able to identify the constraints directly without computing the probabilities first. For the time evolution under the Liouville equation this procedure has already been implemented [22]. It is thus possible to obtain an exact solution of the Liouville equation via the maximal entropy formalism. Work is in progress on deriving corresponding results for the master equation. Until such results are available, the role of the maximal entropy formalism is either that of providing a compact expressions for the populations or that of inducing the most likely (or most conservative or least biased) population distribution subject to given average values of a few constraints (which, by themselves, do not suffice to determine uniquely the distribution). The procedure that is still missing specifies a set of constraints whose average values, when used in the maximal entropy formalism, determine an exact solution of the master equation.

5. CONCLUDING REMARKS

We have investigated the vibrational relaxation of diatomic molecules in a heat bath by direct numerical integration of the master equation, using a comprehensive set of exponential gap state-to-state rate constants. The anharmonicity of the energy levels gives rise to a number of interesting features ; principally, that the relaxation process can be divided into two stages : first, a very fast up-pumping stage dominated by V-V exchange collisions which leads to a type of quasi-equilibrium intermediate distribution and secondly, a very much slower V-T dominated stage during which the intermediate distribution relaxes towards thermal equilibrium. This second stage appears to be quite independent of the precise form of the initial distribution. The first stage can be fitted quite well by a linear superposition of the initial and quasi-equilibrium distributions. The evolution of the moments of energy and vibrational quanta reflect the various stages of the relaxation process. We then proceeded to show how entropy can be used to characterize the relaxation process. The entropy deficiency displays a smooth monotonic decay with the approach to equilibrium. On the other hand, the entropy of the relaxing subsystem need not display monotonic decay and, indeed, varies according to the relative ordering of the evolving population distribution. The maximal entropy distribution was used to describe the evolving population distribution. Although a two-constraint distribution provided an adequate fit to the V-V dominated stages of the relaxation it was found necessary to add at least a third constraint to account for later, V-T dominated, stages of the process.

Although further numerical work would be of interest ; e.g. to consider the effect of changes of temperature and other parameters, more theoretical work is called for. At the kinetic level it is of great practical importance to devise models that will explain the transition from V-V dominated to V-T dominated collisions and hence predict the degree of possible population inversion. At the thermodynamic level it is important to devise criteria for selecting the most

informative constraints in order to obtain the most accurate maximal entropy distributions.

We may also point out that the procedures outlined here for computing vibrational state populations evolving in time subject to V-V and V-T relaxation may be of great utility in numerical modelling of chemical lasers [23]. In these models, a great deal of computational effort is expended in calculating state-to-state rate constants and in solving non-linear master equations of the type of equation (3.4). We suggest that incorporation of explicit expressions for $dP(n)/dt$ would greatly reduce the time required for these modelling calculations.

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APPENDIX

It is a simple matter to show [1] the equivalence between the stochastic equation

$$P(r, t + \Delta t) = \sum_{s, m, n} \Pi(rs|mn)P(m, t)P(n, t) \quad (\text{A } 1)$$

and the non-linear master equation

$$\frac{dP(r, t)}{dt} = \sum_{s, m, n} \{k(r, s \leftarrow m, n)P(m, t)P(n, t) - k(m, n \leftarrow r, s)P(r, t)P(s, t)\}. \quad (\text{A } 2)$$

The state-to-state rate constants $k(r, s \leftarrow m, n)$ satisfy the condition of detailed balance with the equilibrium distributions, i.e.

$$k(r, s \leftarrow m, n)P^0(m)P^0(n) = k(m, n \leftarrow r, s)P^0(r)P^0(s). \quad (\text{A } 3)$$

Using this condition the master equation (A 2) can be rewritten in the following form

$$\frac{dP(r, t)}{dt} = \sum_{s, m, n} k(r, s \leftarrow m, n)P^0(m)P^0(n) \left[\frac{P(m, t)P(n, t)}{P^0(m)P^0(n)} - \frac{P(r, t)P(s, t)}{P^0(r)P^0(s)} \right]. \quad (\text{A } 4)$$

We wish to find the rate of entropy production $-d\Delta S/dt$, i.e.

$$-\frac{d\Delta S}{dt} = -\frac{d}{dt} \sum_r P(r, t) \ln \left[\frac{P(r, t)}{P^0(r)} \right] = -\sum_r \frac{dP(r, t)}{dt} \ln \left[\frac{P(r, t)}{P^0(r)} \right], \quad (\text{A } 5)$$

which we write in the 'symmetrized' form

$$\begin{aligned} -\frac{d\Delta S}{dt} = & -\frac{1}{4} \sum_r \frac{dP(r, t)}{dr} \ln \left[\frac{P(r, t)}{P^0(r)} \right] - \frac{1}{4} \sum_s \frac{dP(s, t)}{ds} \ln \left[\frac{P(s, t)}{P^0(s)} \right] \\ & - \frac{1}{4} \sum_m \frac{dP(m, t)}{dm} \ln \left[\frac{P(m, t)}{P^0(m)} \right] - \frac{1}{4} \sum_n \frac{dP(n, t)}{dn} \ln \left[\frac{P(n, t)}{P^0(n)} \right]. \end{aligned} \quad (\text{A } 6)$$

By using the master (A 4) we can reduce (A 6) to

$$-\frac{d\Delta S}{dt} = \frac{1}{4} \sum_{r,s,m,n} k(r, s \leftarrow m, n) P^0(m) P^0(n) \left[\frac{P(m, t) P(n, t)}{P^0(m) P^0(n)} - \frac{P(r, t) P(s, t)}{P^0(r) P^0(s)} \right] \\ \times \left\{ \ln \left[\frac{P(m, t) P(n, t)}{P^0(m) P^0(n)} \right] - \ln \left[\frac{P(r, t) P(s, t)}{P^0(r) P^0(s)} \right] \right\} \quad (\text{A } 7)$$

and since $(x - y)(\ln x - \ln y) \geq 0$ we have the desired result

$$-\frac{d\Delta S}{dt} \geq 0. \quad (\text{A } 8)$$

An interesting difference between this derivation and the more general one described in § 2 is that here it is necessary to invoke the detailed balance condition (A 3).

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