SIMULTANEOUS VIBRATIONAL RELAXATION AND RADIATIVE DECAY OF INITIAL BOLTZMANN DISTRIBUTIONS☆

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Exact solutions for the probabilities of occupation of the states of a harmonic oscillator undergoing simultaneous (vibrational) relaxation and (radiative) decay are obtained for initial Boltzmann distributions and it is shown that they maintain their Boltzmann form throughout the process.

Although there has been considerable recent interest [1–5] in the experimental study of the vibrational relaxation of excited molecules with the help of their time-dependent emission spectra, exact calculations for reasonable models are not available. An oft-used analysis [e.g. 6], wherein emission is assumed to occur *after* the entire relaxation process has ended, is valid only for situations in which relaxation times are much smaller than times characterizing emission, and can clearly provide no information about the relaxation process. The other extreme, involving zero relaxation has also been considered in the literature [7]. The importance of intermediate situations has been emphasized e.g., by Dexter and collaborators [7,8]. For such situations an analysis of the coupled relaxation and decay is necessary and in this note we report some exact results of such an analysis.

Vibrational relaxation in the absence of emissive decay has often been studied in terms of an equation proposed by Montroll and Shuler (MS) [9]. Based on the Landau and Teller prescription [10] for the rate calculation, it describes the evolution of the system among a semi-infinite manifold of equally spaced energy states via nearest-neighbor transition rates. The characteristics of the harmonic oscillator (which the equation purports to describe) are reflected in (i) the equal spacing of the energy levels, and (ii) the linear dependence of the transition rates of the larger of the two energies in question. The nearest-neighbor character of the rates may be said to arise from an interaction linear in the displacement of the oscillator.

While solutions of the MS equation are well-known in the literature, consequences of appending an energy-dependent decay rate to the equation are not. We therefore consider the latter situation and write our modified form of the MS equation

$$\frac{\mathrm{d}P_n}{\mathrm{d}t} = -\alpha_n P_n + k\{(n+1)P_{n+1} + n\,\mathrm{e}^{-\beta}P_{n-1} - [n+(n+1)\,\mathrm{e}^{-\beta}]P_n\}\,. \tag{1}$$

Here P_n is the probability of occupation of the nth state, k characterizes the relaxation rate, $\beta = \hbar\omega/k_B T$, ω and T are the oscillator frequency and temperature respectively, and the "bias factors" $\mathrm{e}^{-\beta}$ ensure the thermalization of the decayless system. The form of the decay rate α_n, describing a loss of the "excitation", must be specified before attempting a solution of (1). The choice of an energy-independent α_n leads to a trivial solution of (1) as it merely multiplies the MS solutions by an exponential factor. A non-trivial choice is

$$\alpha_n = b + cn = b + \left(\frac{c}{\hbar\omega}\right)\epsilon_n\,, \tag{2}$$

where ϵ_n is the energy of the nth state, and b and c are constants. We have shown elsewhere [11] that eq. (2) results from the well known expression [6] for α_n and is correct to second order in a perturbation series for α_n in powers of the Huang–Rhys factor.

Eq. (1) with α_n described by (2) may be solved by defining

$$G(z,t) = \sum_{n=0}^{\infty} z^n P_n(t)\,\mathrm{e}^{bt}\,, \tag{3}$$

which yields

$$\frac{\partial G}{\partial t} = k e^{-\beta} \left\{ [z^2 - z(e^\beta + 1 + \gamma) + e^\beta] \frac{\partial G}{\partial z} + (z-1)G \right\} \quad (4)$$

where $\gamma = (c/k)e^\beta$. The solution of eq. (4) using the method of characteristics [12] is straightforward and the coefficient of the nth power of z in the expression thus obtained for $G(z,t)$, yields $P_n(t)$ when multiplied by e^{-bt} (see eq. (3)). The general solution of eq. (4) which we have obtained [11] naturally involves $G(z,0)$ explicitly and it is through the latter that the initial configuration of the oscillator is fed into the problem. Initial Boltzmann distributions at temperatures different from the environmental temperature are of considerable interest. For such a case, described by

$$P_n(0) = e^{-n\beta_0} \cdot (1 - e^{-\beta_0}), \quad (5)$$

with $\beta_0 = \hbar\omega/k_B T_0$, T_0 being the initial temperature, eq. (3) gives

$$G(z,0) = (1 - e^{-\beta_0})/(1 - z e^{-\beta_0}). \quad (6)$$

Substitution of (6) in the general solution of (4) can be shown to yield

$$G(z,t) = Y(t)/(1 - zA(t)), \quad (7)$$

where $A(t)$ and $Y(t)$ *are independent of* z. It follows immediately that the probabilities $P_n(t)$ are given by

$$P_n(t) = e^{-bt} Y(t) [A(t)]^n = e^{-bt} Y(t) e^{-n\beta(t)}, \quad (8)$$

where $\beta(t)$ is defined as $\ln[1/A(t)]$.

Equation (8) contains the striking result that apart from the decay described by $e^{-bt}Y(t)$, the $P_n(t)$'s always maintain a Boltzmann distribution with a time-dependent temperature $T(t) = \hbar\omega/k_B \beta(t)$. Of importance is the fact that n occurs in $P_n(t)$ *only* as a factor multiplying $\beta(t)$ in the exponent. The time dependent temperature $T(t)$ has the form

$$[T(t)]^{-1} = \frac{k_B}{\hbar\omega} \cdot \ln \left(\frac{M' - e^{-\tau}N'}{M - e^{-\tau}N} \right), \quad (9)$$

where

$$\tau = t \left\{ 2 k e^{-\beta} \left[\left(\frac{e^\beta - 1 + \gamma}{2} \right)^2 + \gamma \right]^{Y_2} \right\}, \quad (10)$$

and M', N', M, N are constants whose values depend on k, β, β_0 and C. It can be shown from eqs. (9) and (10) that $T(0) = T_0$ but $T(\infty) \neq T$. The latter result is of some relevance to the Stepanov problem [13,14].

We have thus shown that for decay rates *linear in the energy*, initial Boltzman distributions maintain the Boltzmann form throughout the simultaneous processes of relaxation and decay. Such a behavior appears to have been assumed in the literature but has, to our knowledge, never been proved for a decaying system.

We have also obtained the explicit solution of eq. (1) with (2) for the localized initial condition $P_n(0) = \delta_{nm}$. From the superposition of these the solution for any initial condition, (such as the Poisson, relevant to electronic excitation from a zero-temperature ground state) can be easily obtained. The general formalism can also be applied to a quantitative analysis of experimental situations [1–5] and these and other results will be reported elsewhere [11]. We also wish to mention that our present analysis, as well as that of Montroll and Shuler [9], explores the exact (not approximate) consequences of a master (not Schrödinger) equation, and thus belongs to a different category from other well known calculations [15,16].

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