

Elena I. Dashevskaya, Ilya Litvin, and Evgeny E. Nikitin*

On the Relation between Population Kinetics and State-to-State Rate Coefficients for Vibrational Energy Transfer

DOI 10.1515/zpch-2015-0597

Received March 20, 2015; accepted July 28, 2015

Abstract: The relation between time-dependent population of vibrational state and collision-induced state-to-state rate coefficients is discussed within the Landau–Teller kinetic equations for the relaxation of harmonic oscillators in a heat bath. In particular, the increase of the populations in the first and the second vibrational state of an initially cold oscillator shows a considerable variety of its relation to a single Landau–Teller state-to-state rate coefficient. It is suggested that this variety should be kept in mind when experimental studies of the relaxation of specific level are analyzed.

Keywords: Reaction Kinetics.

Dedicated to Prof. Dr. Dr. h.c. mult. Jürgen Troe on the occasion of his 75th birthday

1 Introduction

Vibrational relaxation and dissociation of diatomic molecules in a heat bath provide a simple example for transient multilevel kinetics. There are extensive solutions of the respective master equations, employing various models for collision-induced state-to-state (StS) vibrational transitions and transitions to the dissocia-

***Corresponding author: Evgeny E. Nikitin**, Schulich Faculty of Chemistry, Technion – Israel Institute of Technology, 32000, Haifa, Israel; and Max-Planck-Institut für Biophysikalische Chemie, Am Fassberg 11, D-37077 Göttingen, Germany, e-mail: enikiti@mpibpc.mpg.de

Elena I. Dashevskaya: Schulich Faculty of Chemistry, Technion – Israel Institute of Technology, 32000, Haifa, Israel; and Max-Planck-Institut für Biophysikalische Chemie, Am Fassberg 11, D-37077 Göttingen, Germany

Ilya Litvin: Institut für Physikalische Chemie, Universität Göttingen, Tammannstrasse 6, D-37077 Göttingen, Germany

tion continuum (see e.g. [1–7]). For not too high temperatures, relaxation and dissociation are decoupled, implying that the former establishes a non-equilibrium quasi-stationary distribution before a noticeable fraction of molecules has chance to arrive at the dissociation. Under this condition, the vibrational relaxation can be treated disregarding dissociation. The form of the kinetic relaxation equations and the general properties of their solution are well documented (see e.g. the texts [8–11]). While a variety of approximations for setting up the relaxation equations is available, a closer look at the simplest of these equations appears worthwhile, in particular when analytical solutions are possible. We are motivated for this work through our recent reinterpretation of the vibrational relaxation NO in Ar [12, 13]. Originally, the experimental data were reported either in terms of the first-order (FO) rate laws [14, 15] or within a simplified two-state (TS) approximation [16] where the kinetics was characterized by apparent state-specific (SSp) rate coefficients.

In order to arrive at a transparent relation between the StS and SSp rate parameters, in this article we adopt the Landau–Teller (LT) approach to multi-state kinetics. We first consider some general features of TS and LT models (Section 2), then discuss possible relations between the apparent SSp and the fundamental StS rate coefficients (Section 3). Finally we apply these relations to the relaxation of population of the first and second vibrational states of an initially cold harmonic oscillator (Section 4). Section 5 concludes the paper.

2 Two state (TS) vs. Landau–Teller (LT) model

The first relaxation models [17, 18] employed a TS concept (for the ground and the first excited vibrational states). The TS model allows one to derive well-defined apparent state-specific SSp rate coefficient that describes the exponential change of population of the excited vibrational state of a diatom, and relates this to the StS rate coefficient that describes the transfer of population from the excited to the ground state. The TS relaxation equation contains a single StS kinetic parameter, $k_{10}^{\text{TS}}(T)$, that is related to the collisional deactivation of the first vibrational state in the $1 \rightarrow 0$ transition upon collisions of the diatom with the atoms X at the heat bath of temperature T . An analytical solution for the time dependent population of the first level, $x_1^{\text{TS}}(t)$ (and hence that of the zeroth level, $x_0^{\text{TS}}(t)$, due to the normalization $x_0^{\text{TS}}(t) + x_1^{\text{TS}}(t) = 1$) which asymptotically approaches its final

equilibrium value $x_{1f}^{\text{TS}} = x_{1f}^{\text{TS}}(T)$ starting from its initial value x_{1i}^{TS} reads

$$\frac{x_{1f}^{\text{TS}} - x_{1i}^{\text{TS}}(t)}{x_{1f}^{\text{TS}} - x_{1i}^{\text{TS}}} = F_1^{\text{TS}}(t) = \exp(-[X]k_1^{\text{TS}}(T)t) \quad (1)$$

Here k_1^{TS} is a SSp relaxation rate coefficient which is related to the state-to-state rate coefficient k_{10}^{TS} by

$$k_1^{\text{TS}}(T) = k_{10}^{\text{TS}}(T) (1 + b(T)) \quad (2)$$

where $b(T)$ is the Boltzmann factor for level $v = 1$ above the level $v = 0$ with the energy difference ΔE_{10} , $b(T) = \exp(-\Delta E_{10}/k_B T)$. Equation (1) defines the SSp rate coefficient $k_1^{\text{TS}}(T)$ and provides the relation to the StS rate coefficient $k_{10}^{\text{TS}}(T)$ by Equation (2).

After papers [17, 18], it was quickly realized [19], with the citation of the Landau and Teller's work published later [20], that a two-level scheme, except for special particular cases, is not adequate. The LT model represents a multi-level vibrational manifold of harmonic oscillator states which are weakly coupled to a stochastic Boltzmann reservoir and which are only allowing the nearest-neighbor transitions $v \leftrightarrow v \pm 1$ with linear dependence of the StS rate coefficient on the vibrational quantum number:

$$\begin{aligned} k_{v,v-1} &= vk_{10} \\ k_{v-1,v} &= vk_{10}b \end{aligned} \quad (3)$$

Similar to the TS model, the LT model requires a single StS rate coefficient $k_{10}(T)$ only. However, for this model, the relaxation kinetics for the population of a specific vibrational state is not exponential, and therefore well-defined SSp rate coefficients do not exist. Thus, the question arises whether ill-defined apparent SSp rate coefficients $k_v(T)$ nevertheless can be related to the well-defined StS rate coefficient $k_{10}(T)$.

The LT relaxation equations for the populations $x_v(t)$ employing StS rate coefficients from Equation (3), possess the remarkable property that the mean energy E^{LT} of the ensemble of the harmonic oscillators (HO) exponentially relaxes from its initial value E_i towards its final, thermally equilibrium, value E_f . This is described by the LT expression (also cited sometimes as Bethe–Teller equation [21, 22]):

$$F_E^{\text{LT}}(t) \equiv \frac{E_f^{\text{HO}} - E^{\text{LT}}(t)}{E_f^{\text{HO}} - E_i^{\text{HO}}} = \exp(-[X]k_E t) \quad (4)$$

Here where k_E is an energy relaxation rate coefficient which is related to the state-to-state rate coefficient k_{10} by

$$k_E = k_{10}(1 - b). \quad (5)$$

In Equation (4) $E_i = E^{LT}(t)|_{t=0}$, and $E_f^{HO} = \Delta E_{10}b/(1 - b)$. Note that Equation (4) is valid irrespective of an initial distribution of populations, x_{vi}^{HO} , of vibrational states that defines the quantity E_i by $E_i = \sum_{v=0}^{\infty} v\Delta E_{10}x_{vi}^{HO}$.

The evolution of the population of individual states, $x_v^{LT}(t)$, is described by analytical solution of the LT kinetic equations [23], and it depends on the initial distribution x_{vi}^{HO} . A particular case, as discussed below, is the relaxation starting from an initial Boltzmann distribution of temperature T_0 , for which

$$\begin{aligned} x_{vi}^{HO} &= (1 - b_0)b_0^v, \\ E_i &= \Delta E_{10}b_0/(1 - b_0) \end{aligned} \quad (6)$$

with $b_0 = \exp(-\Delta E_{10}/k_B T_0)$. The Boltzmann-to-Boltzmann (from T_0 to T) relaxation of the harmonic oscillators within the LT model then occurs through a set of Boltzmann distributions (the so-called canonical invariance):

$$x_v^{LT}(\tau, b_0, b) = (1 - a(\tau, b_0, b))a^v(\tau, b_0, b) \quad (7)$$

where τ is the reduced time, $\tau = [X]k_E t$, related to the rate of the energy relaxation, see Equation (4). The explicit form for the function $a(\tau, b_0, b)$ reads [23]:

$$a(\tau, b_0, b) = \frac{(1 - b_0) - \exp(-\tau)(1 - b_0/b)}{(1 - b_0)/b - \exp(-\tau)(1 - b_0/b)} \quad (8)$$

with the initial and final values given by

$$\begin{aligned} a(\tau, b_0, b)|_{\tau=0} &= b_0, \\ a(\tau, b_0, b)|_{\tau=\infty} &= b. \end{aligned} \quad (9)$$

The expression

$$\frac{x_{vf}^{HO} - x_v^{LT}(\tau, b_0, b)}{x_{vf}^{HO} - x_{vi}^{HO}} \equiv F_v^{LT}(\tau, b_0, b) \quad (10)$$

with $x_{vf}^{HO} = (1 - b)b^v$ then is the the LT counterpart of Equation (1) for an initial Boltzmann distribution. However, the expression in Equation (10), in contrast to Equation (1), does not have exponential form.

3 Apparent SSp rate coefficients for LT model

Though $F_v^{\text{LT}}(\tau, b_0, b)$ in Equation (10) is not exponential in time, one may try to fit it by an exponential in analogy to first order (FO) kinetics

$$F_v^{\text{LT}}(\tau, b_0, b) \approx F_v^{\text{LTFO}}(\tau, b_0, b) = \exp(-\kappa_v^{\text{LTFO}}(b_0, b)\tau). \quad (11)$$

Here τ should cover a reasonable range dictated by the experimental conditions and it corresponds to the trial value of the apparent rate coefficient, $\kappa_v^{\text{LTFO}}(b_0, b)$, which can be regarded as SSp rare coefficient for the LT model. This implies that κ_v^{LTFO} will depend, beside the heat bath parameters b_0 and b , also on a certain parameter p that governs the choice of the above “trial value”, i.e. $\kappa_v^{\text{LTFO}} = \kappa_v^{\text{LTFO}}(b_0, b, p)$. Once κ_v^{LTFO} is chosen, it relates a SSp rate coefficient k_v to a StS rate coefficient k_{10} by requiring that F_v^{LTFO} from Equation (11) coincides with its SSp counterpart

$$F_v^{\text{SSp}}(\tau, b_0, b) = \exp(-\kappa_v(b_0, b)\tau). \quad (12)$$

In this way one gets an expression

$$k_v(b_0, b, p) = \kappa_v^{\text{LTFO}}(b_0, b, p)k_{10}(b)(1 - b), \quad (13)$$

which relates the multitude of experimentally measured rates $k_v(b_0, b, p)$ to a single LT rate coefficient $k_{10}(b)$.

A possibility of such a fitting is illustrated by Figure 1 which shows the drop of the function $F_v^{\text{LT}}(\tau, b_0, b)$, for $b_0 = 1/10, b = 1/2$, from 1 to 0.1, i.e. by one order of magnitude such as relevant to the experimental conditions. The approximately linear dependence of $\log F_v^{\text{LT}}(\tau, b_0, b)$ on τ across this interval is observed for $v = 1, 2, 3$ but noticeable non-linear incubation periods are clearly apparent for higher v ; these are due to the late arrival of populations at higher levels from the lower ones.

The quality of the exponential fitting is illustrated by Figure 2 for $b_0 = 1/10, b = 1/2$. It clearly shows the difficulties with this type of fit for $v = 3$; for $v = 4$, the exponential fitting appears inadequate. However, one can improve the LTFO fitting by introducing a delayed LTFO exponential (DLTFO) which corresponds to a first-order kinetic equation as

$$F_v^{\text{DLTFO}}(\tau, \tau_d, b_0, b) \approx \exp[-\kappa_v^{\text{DLTFO}}(b_0, b, \tau_d)(\tau - \tau_d)\Theta(\tau - \tau_d)] \quad (14)$$

$$dF_v^{\text{DLTFO}}/d\tau = -\kappa_v^{\text{DLTFO}}(b_0, b, \tau_d)\Theta(\tau - \tau_d)F_v^{\text{DLTFO}} \quad (15)$$

where Θ is the step function, and τ_d is a delay time. We see from Figure 2 that, for $v = 4$, the DLTFO graph noticeably differs from the LTFO graph but reproduces reasonably well the LT graph.

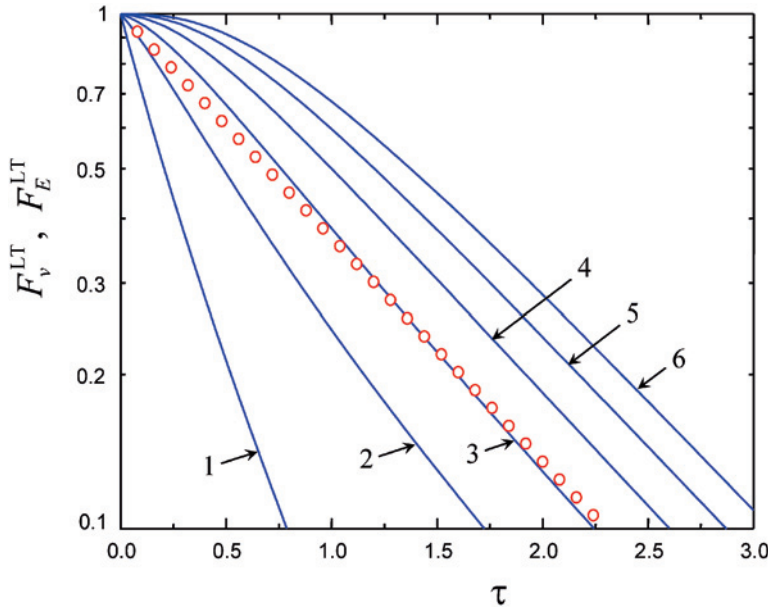


Figure 1: Single-level LT relaxation curves (log scale), $F_v^{LT}(\tau, b_0, b)$ vs. τ (labeled by quantum numbers v) for $b_0 = 1/10, b = 1/2$ (full lines). Open circles correspond to the exponential relaxation of the oscillator mean energy, $F_E^{LT}(\tau, b_0, b)$ vs. τ . Interestingly, the population in level $v = 3$ relaxes approximately at the same rate as the mean energy (for these values of b_0 and b).

One way to choose SSp rate coefficients and to inspect the corresponding accuracy of the exponential approximation consists in the following procedure: one forces Equation (11) to pass through the point $F_v^{LTFO} = p$ at the time $\tau_v = \tau_v(b_0, b, p)$, such as found from the requirement that the solution of the LT kinetic equation describes the drop of F_v^{LT} by the same factor p during the time period $\tau_v = \tau_v(b_0, b, p)$. In this way, the SSp rate coefficient $k_v(b_0, b, p)$ is expressed through StS rate coefficient k_{10} as

$$k_v(b_0, b, p) = K_v(b_0, b, p)k_{10}(b) \tag{16}$$

with

$$K_v(b_0, b, p) = -\frac{(1-b) \ln p}{\tau_v(b_0, b, p)}. \tag{17}$$

Here, τ_v is found from the equation

$$F_v^{LT}(\tau, b_0, b) \Big|_{\tau=\tau_v(b_0, b, p)} = p. \tag{18}$$

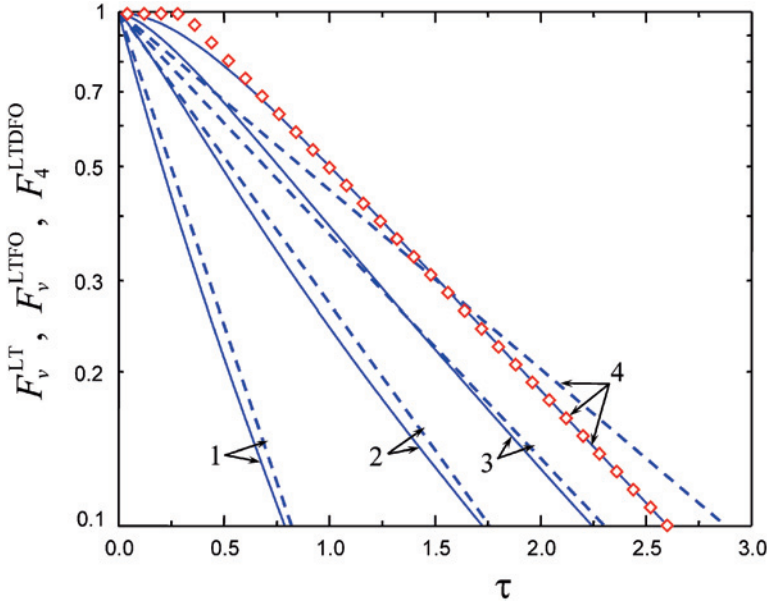


Figure 2: Single-level LT relaxation curves (log scale), $F_v^{LT}(\tau, b_0, b)$ (full curves), their FO fitting $F_v^{LTFO}(\tau, b_0, b)$ (dashed straight lines) for $b_0 = 1/10$, $b = 1/2$ (labeled by quantum numbers v). Fitted rate coefficients are $\kappa_1^{LT}(b_0, b) = 2.8$, $\kappa_2^{LT}(b_0, b) = 1.3$, $\kappa_3^{LT}(b_0, b) = 1$, $\kappa_4^{LT}(b_0, b) = 0.8$. For $v = 4$, the DLTFO fitting $F_4^{DLTFO}(\tau, b_0, b, \tau_d)$ (diamonds) corresponding to $\kappa_4^{DLTFO}(b_0, b, \tau_d) = 1$ and $\tau_d = 0.3$ is also shown.

The variety of $\kappa_v^{LTFO}(b_0, b, p)$ found from a variation of p across a “reasonable” range (as determined by the experimental conditions) characterizes the accuracy of the exponential approximation.

4 Relaxation of initially cold oscillator

We illustrate the preceding analysis by the case of an initially cold oscillator with $b_0 \ll 1, b$ (typical conditions for relaxation in shock waves). Then, Equation (8) becomes

$$a(\tau, b_0, b)|_{b_0 \ll 1, b} = \frac{1 - \exp(-\tau)}{1/b - \exp(-\tau)} \tag{19}$$

and the expressions for $F_v^{\text{LT}}(\tau, b_0, b)$ are simplified. For instance, $F_1^{\text{LT}}(\tau, b_0, b)|_{b_0 \ll b, 1} \equiv \tilde{F}_1^{\text{LT}}(\tau, b)$ becomes:

$$\tilde{F}_1^{\text{LT}}(\tau, b) = 1 - \frac{1 - \exp(-\tau)}{(1 - b \exp(-\tau))^2} \quad (20)$$

In this case, equation Equation (18) can be solved analytically yielding, together with Equation (17), the following expression for $K_1(b_0, b, p)|_{b_0 \ll b, 1} \equiv \tilde{K}_1(b, p)$:

$$\tilde{K}_1(b, p) = \frac{(1 - b) \ln p}{\ln M(b, p)} \quad (21)$$

$$M(b, p) = \frac{2b(1 - p) - 1}{2b^2(1 - p)} + \sqrt{\left(\frac{2b(1 - p) - 1}{2b^2(1 - p)}\right)^2 + \frac{p}{b^2(1 - p)}} \quad (22)$$

The graphs of $\tilde{K}_1(b, p)$ are shown in Figure 3 for three values of p : $p = 1/2$, $p = 1/e$ and $p = 1/5$. Had the decay been exponential, all three curves would coincide. The difference between curves for various values of p characterize the

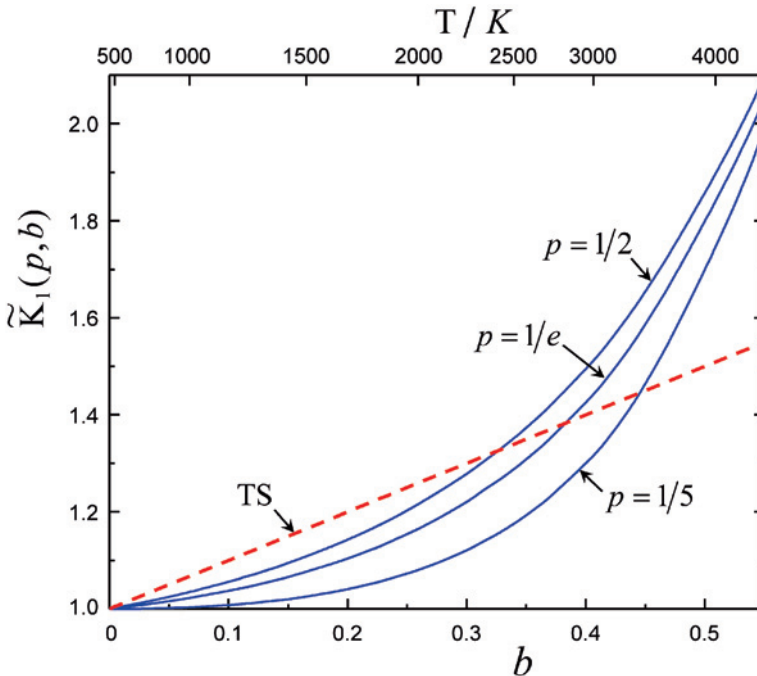


Figure 3: Coefficients $\tilde{K}_1(p, b)$ in Equation (21) vs b for different values of p (solid lines). Also shown is the result for a TS model (dashed line). The upper abscissa axis refers to temperatures for NO molecule with $\Delta E_{10}/k_B = 2700$ K.

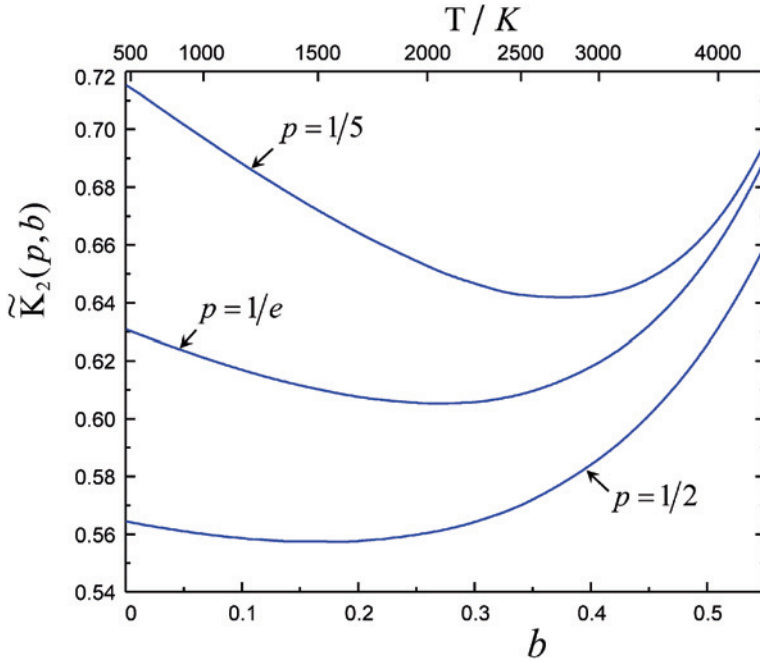


Figure 4: Similar to Figure 3 but for $\tilde{K}_2(p, b)$.

accuracy of the exponential approximation. For instance, with $T = \Delta E_{10}/k_B$ (i.e. $b = \exp(-1) = 0.368$), the difference in $\tilde{K}_1(b, p)$ for $p = 1/2$ and $p = 1/5$ equals 0.20, while the mean value of K for these two values of p is about 1.35. Also shown in this Figure is $K_1^{\text{TS}}(b) = (1 + b)$, the respective quantity for the two-states approximation, see Equation (2). The convergence of $\tilde{K}_1(b, p)$ to $K_1^{\text{TS}}(b)$ with decreasing b is a manifestation of progressively better performance of the TS approximation when transitions to (and from) higher states are ignored. On the other hand, a sharp increase of $\tilde{K}_1(b, p)$ for b about 1/2 and higher is related to the overshoot phenomenon (see below).

Similar plots, but for $\tilde{K}_2(b, p)$, are shown in Figure 4. Here the curve for the TS model is absent since it is not applicable to the case $v = 2$.

As a practical example, we consider now the vibrational relaxation of NO in Ar behind a shock wave studied experimentally in Ref. [15, 16] in a wide temperature range. For relaxation in $v = 1$ state, the relation between the measured rate coefficients k_1 [15, 16] and the fundamental rate coefficients k_{10} , as predicted by the above treatment, is given in Table 1 as a list of conversion factors $K_1 = k_1/k_{10}$ for different temperatures and parameters p that determines the point at which

Table 1: Conversion factors \tilde{K}_1 between SSp rate coefficients k_1 and StS rate coefficients k_{10} for the relaxation of NO ($\nu = 1$) for different temperatures T and various values of the fitting parameters p .

| T | 1800 K | 2100 K | 2400 K | 2700 K | 3000 K |
|-----------|--------|--------|--------|--------|--------|
| $p = 1/5$ | 1.05 | 1.10 | 1.15 | 1.23 | 1.31 |
| $p = 1/e$ | 1.13 | 1.19 | 1.26 | 1.35 | 1.44 |
| $p = 1/2$ | 1.17 | 1.24 | 1.32 | 1.41 | 1.51 |

the exponential LTFO kinetics (see Equation (11)) is fitted to the non-exponential LT kinetics.

For a fixed value of p , the temperature dependence of K_ν demonstrates the manifestation of the multiple-state relaxation kinetics in an approximate first order single state kinetics. For a fixed temperature, the dependence of K_ν on p indicates uncertainties in the approximation of non-exponential kinetics by an exponential decay.

Turning now to relaxation in $\nu = 1$ and $\nu = 2$ states, we show in Figure 5 the predicted time dependence of populations of the vibrational states $\nu = 1$ and $\nu = 2$ of NO behind a shock wave at $T = 2700$ K in a heat bath which was initially at room temperature. For this case, b_0 is about 3×10^{-4} , and $b = 0.368$. The figure shows graphs of $\tilde{F}_1^{\text{LT}}(\tau, b)$ and $\tilde{F}_2^{\text{LT}}(\tau, b)$ (full lines) which clearly demonstrate the change of slopes in the former (dashed lines) and the appearance of an incubation period in the latter (open symbols). Also shown are the graphs for $\tilde{F}_1^{\text{LTFO}}(\tau, b)$ and $\tilde{F}_2^{\text{LTFO}}(\tau, b)$ with $\kappa_1^{\text{LTFO}} = 1.7$, $\kappa_2^{\text{LTFO}} = 1.1$. For $\nu = 1$, the straight line is defined by the condition that it connects the correct initial and final points of $\tilde{F}_1^{\text{LT}}(\tau, b)$. For $\nu = 2$, the straight line is defined by the condition that it starts at the correct initial point of $\tilde{F}_2^{\text{LT}}(\tau, b)$ and then asymptotically runs parallel to $\tilde{F}_2^{\text{LT}}(\tau, b)$. The ratio $\kappa_2^{\text{LTFO}}/\kappa_1^{\text{LTFO}}$, equals 0.647, while the ratio of the experimental rate coefficients k_2/k_1 is 0.65 (see Ref. [15], Table 1). If one goes to lower temperatures, the difficulties with FO interpretation of the relaxation increases due to the longer induction period for $\nu = 2$ state.

One more interesting feature should be mentioned. For high enough temperature T , the populations of some lying levels pass, in the relaxation course, through a single maximum (the overshoot phenomenon), so that the function $\tilde{F}_\nu^{\text{LT}}(\tau, b)$ changes its sign before disappearing at equilibrium. For a given value of ν , the overshoot occurs under condition $b > \nu/(\nu + 1)$. For $\nu = 1$, the asymptotic (for $\tau \gg 1$) form of $\tilde{F}_1^{\text{LT}}(\tau, b)$ is

$$\tilde{F}_1^{\text{LT}}(\tau, b) \Big|_{\tau \gg 1} = (1 - 2b) \exp(-\tau) + (2b - 3b^2) \exp(-2\tau) + O(\exp(-3\tau)). \quad (23)$$

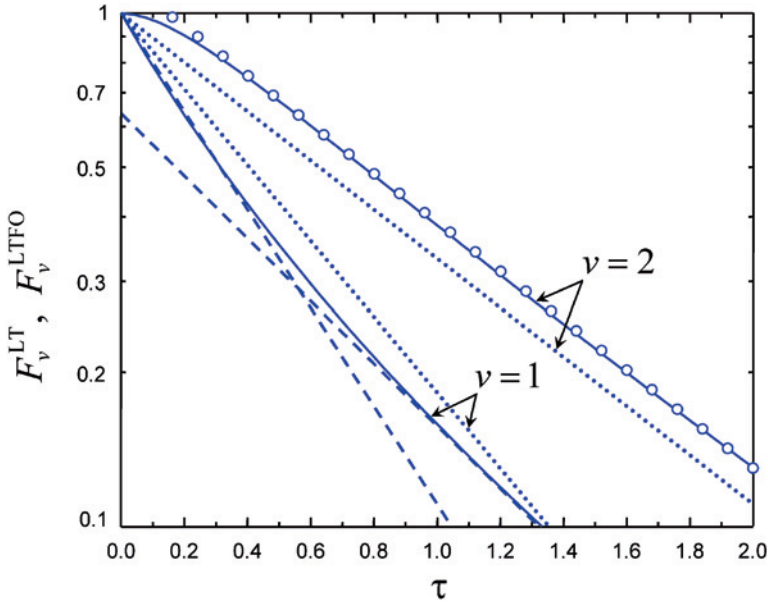


Figure 5: Single-level LT relaxation curves (NO + Ar, log scale), $\tilde{F}_1^{LT}(\tau, b)$ and $\tilde{F}_2^{LT}(\tau, b)$ for $b_0 \approx 3 \times 10^{-4}$ (room temperature before the shock front) and $b = 0.368$ ($T = 2700$ K behind the shock front) for $\Delta E_{10}/k_B = 2700$ K (solid curves). Dashed lines show the change of slopes in the linear approximation of the exponent for $\nu = 1$, and symbols indicate the existence of the induction period for $\nu = 2$. Also shown are the graphs for $\tilde{F}_1^{LTFO}(\tau, b)$ and $\tilde{F}_2^{LTFO}(\tau, b)$ with $\kappa_1^{LTFO} = 1.7, \kappa_2^{LTFO} = 1.1$ (dotted lines). For $\nu = 1$, the straight line is defined by the condition that it connects the correct initial and final points of $\tilde{F}_1^{LT}(\tau, b)$. For $\nu = 2$, the straight line is defined by the condition that it starts at the correct initial point of $\tilde{F}_2^{LT}(\tau, b)$ and then asymptotically runs parallel to $\tilde{F}_2^{LT}(\tau, b)$.

Here, the threshold value of b that corresponds to the overshoot is $1/2$. For $b < 1/2$, the function $\tilde{F}_1^{LT}(\tau, b)$ approaches zero from above, and for $b > 1/2$ from below (overshoot). In both cases, the time dependence of $\tilde{F}_1^{LT}(\tau, b)$ is governed by the lowest eigenvalue of the LT kinetic matrix (factor of unity in front of τ in the exponent of the first term in the r.h.s. of Equation (23)). For $b = 1/2$, the first term in Equation (23) vanishes, and the long-time decay of $\tilde{F}_1^{LT}(\tau, b)$ is governed by the second eigenvalue (factor of two in front of τ in the remaining term in the r.h.s. of Equation (23)). Figure 6 shows examples of $\tilde{F}_1^{LT}(\tau, b)$ for the values of $b = 1/2$ as well as below ($b = 1/4$) and above ($b = 3/4$) it. Also shown are possible exponential approximations to these three cases.

Finally we emphasize that our analysis refers to Boltzmann-to-Boltzmann relaxation (shock wave conditions) and not to a relaxation of an initial non-Boltzmann distribution (e.g. an optical excitation of a single vibrational state).

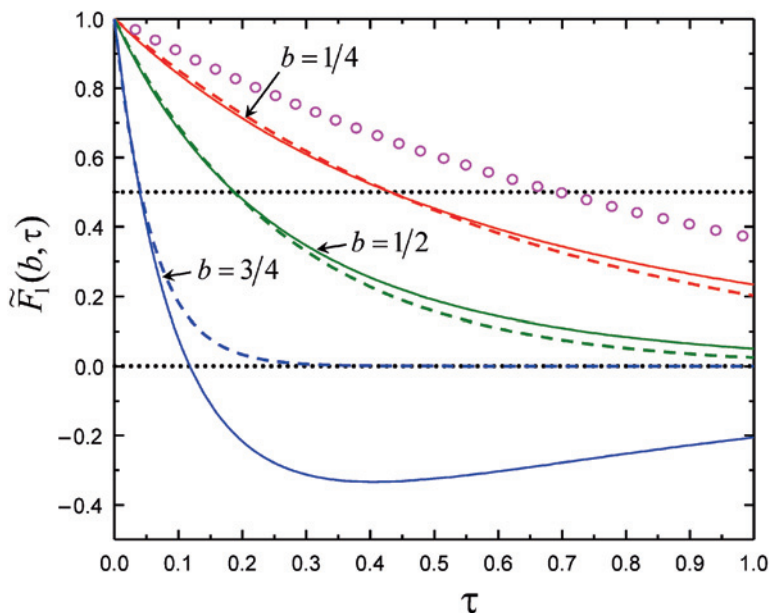


Figure 6: Illustration of the overshoot for $v = 1$. Plots of $\tilde{F}_1(\tau, b)$ vs. τ for $b = 1/4, 1/2, 3/4$ (solid lines) and approximations of $\tilde{F}_1(\tau, b)$ by exponentials $\exp(-\beta\tau)$ with $\beta = 1.61, 3.68, 17.5$ respectively (dashed lines). These exponentials are fitted by the requirement that they coincide with $\tilde{F}_1(\tau, b)$ at points where $\tilde{F}_1(\tau, b) = 1$ and $\tilde{F}_1(\tau, b) = 0.5$. The exponential with $\beta = 1$ (open circles) correspond to the energy relaxation.

5 Conclusion

The interpretation of the vibrational relaxation kinetics in terms of state-specific relaxation rate coefficient meets some difficulties. First, this quantity cannot be strictly defined on the basis of a relaxation master equation since the population change of a single state is not exponential. Second, if it is defined on the basis of experimental data as an effective rate coefficient, one should carefully indicate the time interval across which the change of the population was measured. The latter information can be used in forcing non-exponential relaxation to be represented by an exponential, thus allowing one to relate SSp rate coefficients to StS rate coefficients which enter into the master equations and which can, in principle, be calculated theoretically.

The outlined concept has no advantage compared to a direct *numerical* solution of the relevant rate equations provided they contain well-defined state-to-state rate coefficients. However, if the latter are taken in a trial numerical form,

it is difficult to adjust them to a single effective rate coefficient derived from the experimental kinetics of the population change. Moreover, such an adjustment (many unknown to one known quantity) will suffer from several uncertainties. We therefore decided to use an *analytical* solution of Landau–Teller rate equation that contains a single state-to-state rate coefficient. This allows to see the accuracy and possibility of adjustment of an exponentially-fitted experimental kinetics of a single-level population to the theoretical non-exponential kinetics. In this respect the present approach is superior (compared to numerical solution of kinetic equations with fitted state-to-state rate coefficients) for an evaluation of experiments since it is more transparent. Its performance was demonstrated in Section 3 by introducing a concept of the delayed first-order relaxation, and in Section 4 by a overshoot phenomenon. However, a simple case of single-level relaxation during thermal heating of the ensemble of initially cold oscillators (e.g. behind the shock wave front) shows ambiguities in the use of SSp rate coefficients for the single-state relaxation kinetics. Fortunately, for the first vibrational state, the StS and a set of related SSp rate coefficients do not differ much and sometimes their difference falls into the accuracy range of the experiment provided that the heat bath temperature is noticeably below the overshoot threshold. The situation can be completely different for higher vibrational states where the population kinetics in the Boltzmann-to-Boltzmann relaxation shows an incubation delay. Similar difficulties arise when the initial state does not correspond to a Boltzmann distribution (e.g. it is prepared by an optical excitation).

Acknowledgement: This work acknowledges many stimulating discussions with Professor Juergen Troe and his continuing interest in our work.

References

1. V. A. LoDato, D. L. S. McElwain, and H. O. Pritchard, *J. Am. Chem. Soc.* **91** (1969) 7688.
2. J. E. Dove and D. G. Jones, *J. Chem. Phys.* **55** (1971) 1531.
3. J. E. Dove and J. Troe, *Chem. Phys.* **35** (1978) 1.
4. H. Teitelbaum, *Can. J. Chem.* **61** (1983) 1253.
5. H. Teitelbaum, *Can. J. Chem.* **61** (1983) 1267.
6. H. Teitelbaum, *Can. J. Chem.* **61** (1983) 1276.
7. H. Teitelbaum, *Chem. Phys.* **124** (1988) 55.
8. I. V. Adamovich, S. O. Macheret, J. W. Rich, and C. E. Treanor, *AIAA J* **33** (1995) 1070.
9. M. Capitelli (Ed.), *Nonequilibrium Vibrational Kinetics*, Springer, Berlin Heidelberg (1986).
10. M. Capitelli, C. M. Ferreira, B. F. Gordiets, and A. I. Osipov, *Plasma kinetics in Atmospheric Gases*, Springer, Berlin Heidelberg New York (2000).

11. R. Brun (Ed.), *High Temperature Phenomena in Shock Waves*, Springer, Berlin Heidelberg (2012).
12. E. I. Dashevskaya, E. E. Nikitin, and J. Troe, *Phys. Chem. Chem. Phys.* **17** (2015) 151.
13. E. I. Dashevskaya, I. Litvin, E. E. Nikitin, and J. Troe, *J. Chem. Phys.* **142** (2015) 164310.
14. G. Kamimoto and H. Matsui, *J. Chem. Phys.* **53** (1970) 3987.
15. K. Glaenger and J. Troe, *J. Chem. Phys.* **63** (1975) 4352.
16. K. Glaenger, *Chem. Phys.* **22** (1977) 367.
17. A. J. Rutgers, *Ann. Phys.* **16** (1933) 350.
18. A. Eucken and R. Becker, *Z. Phys. Chem. B* **27** (1934) 235.
19. A. Eucken and H. Jaacks, *Z. Phys. Chem. B* **30** (1935) 85.
20. L. Landau and E. Teller, *Phys. Z. Sowjetunion* **10** (1936) 34.
21. H. A. Bethe and E. Teller, *Ballistic Research Labs. Rept. X-117*, Aberdeen Proving Ground (1945)
22. H. A. Bethe, *Selected Works of Hans A. Bethe*, Ch. 14: Deviations from Thermal Equilibrium in Shock Waves (with E. Teller), p. 295, World Scientific, Singapore (1997).
23. E. W. Montroll and K. E. Shuler, *J. Chem. Phys.* **26** (1957) 454.