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DETERMINATION OF VIBRATIONAL RELAXATION RATES FROM DECAY CONSTANTS

by

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Determination of Vibrational Relaxation Rates From Decay Constants

by Yan Haixing
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Paper received on June 29, 1978.

The vibrational relaxation process of a molecule plays an important role in the processes of high speed gasdynamics, chemodynamics and ultrasound, especially in the molecular laser [1]. A lot of relaxation experiment data have been accumulated [2]. However, only some macroscopic physical quantities are able to be measured in experiments; for instance, in a shock tube or laser fluorescence experiment, the relaxation process of a corresponding vibrational mode can be monitored by observing the variation of a spectral radiation with time [3, 4]. This variation follows the form of $I - I_{\infty} = I_0 e^{-\lambda t}$, except in the beginning short moment. The decay constants, λ , contain information of various relaxation rates of the system. However, this does not simply represent the rate of one particular process, except for a pure biatomic molecule. This paper presents the topic of how to determine the relaxation rate from decay constants. *Chinese language, translation, (original) ←*

Simplified processes are adopted by most of the past works. The models used in analyses are too imperfect, and application range is restricted; moreover, Schafer formula [5] which is used

to process V-T data has no relation with the one used to process V-V data.

A universal data process method is presented in this paper, and a formula which is suitable for various concrete conditions (such as single λ and double λ) is thus obtained. The methods for both V-V and V-T rate processes are also unified. This explains that the Schafer formula is an approximation of this universal formula under special conditions. Inaccurate data presented in Ref. [2-4] are also pointed out by giving an example of CO₂ system.

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1. Method and Universal Formula

First, for an experiment system a relaxation equation set describing various energy transferring processes is listed based on a certain relaxation mechanism. Then these equations are expanded with respect to a relative bias,

$$X_i = 1 - \frac{E_i}{E_i(T)} \quad (1)$$

A relationship between the exponent constant, λ , and the rate, K , is thus obtained by solving the characteristic equation, $f(\lambda, K_i)$ of the linearized equation set. The function of $K_i = K(\lambda, K_i)$ can then be solved reversely. The desired K_i can be calculated by a given K_i and the experiment data,

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Based on a CO system as an example, an equation set is given. In CO-N₂-H₂O mixture, its relaxation mechanism is $n_1 \leftrightarrow T$, $n_2 \leftrightarrow CO(n_1)$, $CO(n_1 \leftrightarrow n_1 + n_2)$, $CO(n_1 \leftrightarrow 2n_2)$, $CO(n_2) \leftrightarrow T$. Its relaxation equation set is

$$\begin{cases} \frac{dE_1}{dt} = \left(\frac{dE_1}{dt}\right)_{n_1 \leftrightarrow T} - \theta_1 \left(\frac{dE_1}{dt}\right)_{n_1 \leftrightarrow n_2} \\ \frac{dE_2}{dt} = \left(\frac{dE_2}{dt}\right)_{n_1 \leftrightarrow n_2} - \frac{\theta_2}{\theta_1} \left(\frac{dE_1}{dt}\right)_{n_1 \leftrightarrow n_2} + \left(\frac{dE_2}{dt}\right)_{n_2 \leftrightarrow T} \\ \frac{dE_3}{dt} = -\frac{\theta_3}{\theta_1} \left(\frac{dE_1}{dt}\right)_{n_1 \leftrightarrow n_2} + \left(\frac{dE_3}{dt}\right)_{n_2 \leftrightarrow T} \\ \frac{dE_4}{dt} = \left(\frac{dE_4}{dt}\right)_{n_2 \leftrightarrow T} - \frac{\theta_4}{\theta_1} \left(\frac{dE_1}{dt}\right)_{n_1 \leftrightarrow n_2} \end{cases} \quad (2)$$

where the relaxation terms are defined in Ref. [1, 6]. The associated solution of the linearized equation set of X_i is

$$X_i = \sum C_k e^{-\lambda_k t} \quad (3)$$

where C_{ij} is a constant associated with the initial conditions. The characteristic equation which satisfies the exponent constant is a fourth order polynomial of λ .

Since a Fermi resonance exists, the $n_1 \rightarrow 2n_2$ rate is high. Moreover, because precise and complete data for this process is lacking, it is practical to choose an approximation in which n_1 and n_2 are in balance. In other words, the $n_1 \rightarrow 2n_2$ rate is much higher than λ and other rates. Therefore, the characteristic equation becomes

$$\begin{aligned}
K(\lambda) = & \frac{1}{\tau_N \tau_{1-N}} \cdot \frac{(1-\rho_1)(1-\rho_2)}{(1-\rho_N)(1-\rho_1)^2} + \frac{1}{\tau_{1-N}} \left[\frac{1}{\tau_N \tau_1} \cdot \frac{1-\rho_1}{(1-\rho_1)^2} + \frac{1}{\tau_N \tau_{1-N}} \right. \\
& \cdot \frac{\rho_1}{2\rho_1(1-\rho_1)(1-\rho_N)} + \frac{1}{\tau_1 \tau_{1-N}} \cdot \frac{\phi_1 \rho_1 (1-\rho_1)}{\phi_N \rho_N (1-\rho_1)^2} \left. \right] - \left[\frac{1}{\tau_1 \tau_N} \cdot \frac{1-\rho_1}{(1-\rho_1)^2} \right. \\
& + \frac{1}{\tau_N \tau_{1-N}} \cdot \frac{(1-\rho_1)(1-\rho_2)}{(1-\rho_1)^2(1-\rho_N)} + \frac{1}{\tau_N \tau_{1-N}} \cdot \frac{2\rho_1(1-\rho_1)}{\rho_1(1-\rho_1)(1-\rho_N)} + \frac{1}{\tau_1 \tau_{1-N}} \\
& \cdot \frac{\phi_1 \rho_1 (1-\rho_N)(1-\rho_1)}{\phi_N \rho_N (1-\rho_1)(1-\rho_1)^2} + \frac{1}{\tau_1 \tau_{1-N}} \cdot \frac{(1-\rho_1)(1-\rho_2)}{(1-\rho_1)^2(1-\rho_N)} \left. \right] \lambda - \frac{\lambda}{\tau_{1-N+1}} \left\{ \left[\frac{1}{\tau_N} \right. \right. \\
& + \frac{1}{\tau_{1-N}} \cdot \frac{\phi_1 \rho_1 (1-\rho_N)}{\phi_N \rho_N (1-\rho_1)} \left. \right] \cdot \left[\frac{\rho_1}{2\rho_1(1-\rho_1)(1-\rho_2)} + \frac{1-\rho_1}{(1-\rho_1)^2} \right. \\
& + \frac{2\rho_1(1-\rho_1)}{\rho_1(1-\rho_1)(1-\rho_2)} \left. \right] + \frac{1}{\tau_1} \cdot \frac{1-\rho_1}{(1-\rho_1)^2} + \frac{1}{\tau_{1-N}} \cdot \frac{\rho_1}{2\rho_1(1-\rho_1)(1-\rho_N)} \left. \right\} \\
& + \left\{ \frac{1}{\tau_1} \cdot \frac{1-\rho_1}{(1-\rho_1)^2} + \frac{1}{\tau_{1-N}} \cdot \frac{(1-\rho_1)(1-\rho_2)}{(1-\rho_1)^2(1-\rho_N)} + \frac{1}{\tau_{1-N}} \cdot \frac{2\rho_1(1-\rho_1)}{\rho_1(1-\rho_1)(1-\rho_N)} \right. \\
& + \left[\frac{1}{\tau_N} + \frac{1}{\tau_{1-N}} \cdot \frac{\phi_1 \rho_1 (1-\rho_N)}{\phi_N \rho_N (1-\rho_1)} \right] \cdot \left[\frac{1-\rho_1}{(1-\rho_1)^2} + \frac{2\rho_1}{\rho_1(1-\rho_1)} \right] \left. \right\} \lambda^2 + \frac{\lambda^2}{\tau_{1-N+1}} \\
& \cdot \left[\frac{\rho_1}{2\rho_1(1-\rho_1)(1-\rho_2)} + \frac{1-\rho_1}{(1-\rho_1)^2} + \frac{2\rho_1(1-\rho_1)}{\rho_1(1-\rho_1)(1-\rho_2)} \right] \\
& - \left[\frac{1-\rho_1}{(1-\rho_1)^2} + \frac{2\rho_1}{\rho_1(1-\rho_1)} \right] \lambda^2 - \dots
\end{aligned} \tag{4}$$

where

$$\rho_i = \exp(-\theta_i/T) \tag{5}$$

In process A,

$$\frac{1}{\tau_A} = N^{\text{vib}} \sum_i \rho_i \cdot K(A; N) \tag{6}$$

where ρ_i is gram molecule fraction, θ_i is vibrational characteristic temperature, N is the particle number in unit volume.

Equation (6) is the summation of all components of the system, and K is the relaxation rate of this process.

Under a resonance condition, it is not difficult to prove that the spectral radiation intensity, I , of which the jumping quantum number is 1, is proportional to the vibrational energy E of that particular mode [7]. In the experiment, the time history of the spectral radiation density is measured, and its decay constant is then determined. Obviously, this decay constant should perfectly correspond to the eigen values of X_i for that particular mode. If some of the eigen values are large, their effect on Equation (3) will be reduced to zero in a very short period. Thus, for those systems containing multiple eigen values, only one of two decay constants can be measured from experiments. For a single λ , the desired rate can be calculated from Equation (4) by giving this λ and other known rates, and then the unknown $K[A; N]$ can be determined from Equation (6) by a giving λ and $K[A; C]$ which is obtained in a pure CO_2 experiment. If two λ , can be measured in an experiment, then both $f(\lambda_1) = 0$ and $f(\lambda_2) = 0$ have to be solved simultaneously to obtain two desired rates.

In a pure CO_2 and a CO_2-H_2O systems, only $CO_2 \rightarrow CO_2 + \nu_1$, $CO_2 \rightarrow CO_2 + \nu_2$, $CO_2 \rightarrow CO_2 + \nu_3$ appear in the relaxation process. Take the characteristic equation when ν_1 and ν_2 are in equilibrium, which is equivalent to take $\frac{1}{\tau_{1-0}} = \frac{1}{\tau_{2-0}} = 0$ in Equation (4). For a single λ ,

$$\frac{1}{\tau_{1-0}} = \left\{ \frac{\lambda}{\tau_1} \cdot \frac{1-\rho_1}{(1-\rho_1)^2} - \lambda^2 \left[\frac{1-\rho_1}{(1-\rho_1)^2} + \frac{2\rho_1}{\rho_1(1-\rho_1)} \right] \right\} / \left\{ \frac{\lambda}{\tau_1} \cdot \frac{1-\rho_1}{(1-\rho_1)^2} - \lambda^2 \left[\frac{2\rho_1}{2\rho_1(1-\rho_1)(1-\rho_1)} + \frac{1-\rho_1}{(1-\rho_1)^2} + \frac{2\rho_1(1-\rho_1)}{\rho_1(1-\rho_1)^2(1-\rho_1)} \right] \right\} \quad (7)$$

If $\nu_1 \rightarrow 3\nu_1$ is chosen as a V-V exchange mechanism in a CO² molecule, $\nu_1 \rightarrow \nu_1 + \nu_1$ in Equation (2) has to be substituted by $\nu_1 \rightarrow 3\nu_1$. Compare the approximation of the characteristic equation which assumes ν_1 and ν_2 in equilibrium, and with Equation (4) and (7), there exists a simple relationship as

$$\frac{1}{\tau_{1-2}} = \frac{(1-\rho_1)^2}{1-\rho_1} \cdot \frac{1}{\tau_{2-1+2}} \quad (8)$$

2. V-T Rate Formula in a Limiting Case

The Schafer Formula of V-T relaxation time, τ_s , at the minimum vibrational energy level of a system which is converted from the total relaxation time, τ_2 , measured in some conventional experiments (such as ultrasound and a shock tube) [5]

$$\tau_1 = \frac{C_v(\nu_1)}{C_v} \cdot \tau_s \quad (9)$$

where C_v is the total vibrational constant volume specific heat; $C_v(\nu_1)$ is the part contributed by ν_1 mode. This formula is still being extensively used.

Actually, the V-T rate formula can be derived from the limiting case when the V-V rate is much greater than the V-T rate. For the pure CO² case, the final form of Equation (7) is similar to Equation (9) in the case of $\frac{1}{\tau_{2-1+2}} \gg \frac{1}{\tau_2}$. After substituting the expression form of the vibrational specific heat

into Equation (9), it clearly indicates that the Schafer formula is an approximation form in this limiting case. From Table 1, it shows that this approximation is good for CO₂ when the temperature is low.

Similar conclusions can be drawn for other systems and relaxation mechanisms.

Table 1 Comparison of the Schafer formula and the limiting case of Equation (7)

T(K)	(7)式的因子(1)	Schafer 公式的因子(2)	相对误差(%) (3)
1576	0.5966	0.5511	-7.3
1052	0.6472	0.6092	-5.9
800	0.7007	0.6691	-4.5
400	0.9419	0.9191	-0.5

Key: (1) Factors of Equation (7); (2) Factors of Schafer; (3) Relative error (%).

3. Results

Table 2 and 3 show the results of Case K_{TB}. K_{TB} and K_{RWG} are obtained from the approximation of Ref. [2, 3] and Ref. [4], respectively, or extracted directly from literature. K is the result of this paper (data of decay constants are taken from Ref. [3, 4]).

It shows in these tables that the differences can be as large as 40%, except in the CO₂-H₂O case. Since errors caused by the temperature variation are different, additional bias can be introduced into those temperature dependent relations.

Table 2 Results of single decay constant
K unit: 10^{15} cm³/part.sec

(1) 体系	T(K)	K _{TD}	K	(2) 相对偏差(%)
(3) 纯 CO ₂	2297	287	228	25.9
	1520	243	201	20.9
	1000	151	132	14.4
	800	82.3	74.2	10.9
	500	26.9	25.9	3.9
	300	9.18	9.16	0.2
CO ₂ -H ₂ O	970.6	500.7	530.8	-5.7
	787.3	683.9	709.5	-3.6
	500	935.0	939.6	-0.49
	300	798.96	799.02	-0.0075
CO ₂ -N ₂	1380	919.8	1435.1	-35.9
	1192	157.2	234.8	-33.0
	1056	97.35	100.7	-3.3
	968.0	58.45	46.69	25.2
	852.0	38.46	38.23	4.0
	798.0	47.68	35.84	33.0

Key: (1) System; (2) Relative error; (3) Pure CO₂

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Table 3 Results of double decay constant

T(K)	400	700	900	1000
K _{app}	44.18	17.36	7.72	3.02
K	49.52	21.39	8.911	2.776
(1) 相对偏差(%)	-10.8	-10.8	-13.5	8.7

Key: (1) Relative error.

4. Discussion

The base of the method presented in this paper is to linearize a nonlinear relaxation equation set. Both experimental measurement and theoretical analysis indicate that X_i decays exponentially with respect to time. This implies that the second order higher terms approach to zero much faster than the first order term. This also means that effects of the high order terms on the signal are noticeable only at the beginning short moment; however, what we are interested is the decay situation after a long period of time, and this should mainly depend upon the linear term. The estimation which is drawn from the conditions of an laser fluorescence experiment indicates that the linear term still plays the major role even in the initial highly non-equilibrium stage. This linearization approximation is especially good for those experiments which have small bias from equilibrium ($X_i \ll 1$).

Both TB [2, 3] and RWG [4] are processed for single λ and double λ , respectively. Let's analyze their approximation characteristics. It is not difficult to prove that the formulae used by them can be derived from the original equation presented in this paper and takes $\frac{1}{r_i} \rightarrow \infty$ (this is equivalent to $X_2 = 0$). Obviously, this approximation is too inexact.

The relaxation mechanism is the starting point of the data process. Generally, the relaxation mechanism is determined through theoretical analysis. In recent years, much progress [8] has been made on the relaxation mechanism through the combination of theories and experiments. It is pointed out that different mechanisms could possibly exist in different mixtures, even in a the same system under a different temperature condition.

The V-T rate which is derived from Schafer formula has a certain error. It is not suitable to use the Schafer formula, especially when the V-V rate is not much greater than the V-T rate. The formula presented in this paper, however, is appropriate for processing this type of data.

Since all process rates are calculated from a certain process data, therefore, if the data used as the base are not accurate, the calculated rates may appear as large errors or may even be nonsense (such as a negative value). Similar situations appear in the photosound method. Therefore, one has to be careful to select the rate for data processing. From another standpoint, this provides a powerful mean to examine and inspect against those existing data rates.

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