

# The influence of intramolecular vibrational relaxation on the pressure dependence of unimolecular rate constants

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We study the rate constant in a bistable two degree of freedom system subject to impulsive BGK collisions. We find that the rate constant is very sensitive to the coupling of the degrees of freedom in the low collision regime. RRKM theory often overestimates the low collision rise—especially at higher collision rates, where the rate constant rises much more slowly making the molecule appear to have fewer degrees of freedom. We argue that such effects should be seen in experiments extending over a very wide range of pressures.

The dependence of a unimolecular rate constant of a polyatomic molecule on pressure (or equivalently collision frequency) has been studied extensively using RRKM theory.<sup>1,2</sup> At low collision rates the rate constant rises proportionally to the collision rate due to energy activation. Let us focus on impulsive strong collision models so that the rate constant is well approximated by<sup>1-3</sup>

$$k_{\text{low}} \simeq \alpha \frac{1}{(n-1)!} (\beta Q)^{n-1} e^{-\beta Q}, \quad (1)$$

where  $\beta Q$  is the barrier height in units of thermal energy,  $\alpha$  is the collision rate, and  $n$  is the total number of degrees of freedom of the molecule. At high collision rates the rate constant decreases inversely proportional to the collision rate as<sup>1</sup>

$$k_{\text{high}} = k_{\text{TST}} \frac{\omega_B}{\alpha}, \quad (2)$$

due to spatial diffusion where  $\omega_B$  is the frequency of the unstable mode of the saddle point. The rate constant is always smaller than the value given by transition state theory<sup>1,2</sup>

$$k_{\text{TST}} = \frac{1}{2\pi} \frac{\prod_i \omega_i^{(0)}}{\prod_i \omega_i^{(s)}} e^{-\beta Q}, \quad (3)$$

where  $\omega_i^{(s)}$  and  $\omega_i^{(0)}$  are the stable normal mode frequencies of the saddle and the wells, respectively. A simple approximation for the rate constant valid for any collision rate is<sup>4</sup>

$$k^{-1} \simeq k_{\text{low}}^{-1} + k_{\text{TST}}^{-1} + k_{\text{high}}^{-1}. \quad (4)$$

Therefore, as a function of collision frequency the rate constant for a polyatomic molecule increases at first then goes through a broad maximum near the transition state value and decreases again. The initial rise is slow for a molecule with few degrees of freedom and very rapid for a polyatomic with many degrees of freedom.

This approach, however, makes the important assumption inherent in RRKM theory that the energy flow between vibrational modes of the molecule is very rapid (fast IVR). A simple example where this assumption breaks down is a polyatomic molecule where the reaction coordinate is completely decoupled from all the other degrees of freedom (infinitely slow IVR). In this example the rate constant will be described by a one degree of freedom model and will exhibit a slow rise at low collision rates [ $n = 1$  in Eq. (1)]. There-

fore, the RRKM theory is not valid in this case. Obviously there will be some kind of transition between these two extremes of strong coupling (fast IVR) and weak coupling (slow IVR). There has been some speculation on the nature of this transition.<sup>5</sup> However, there have been no studies of such non-RRKM effects on rate constants using specific model systems, mainly because of numerical difficulties calculating rate constants. Recently, however, a rapid method for calculating rate constants based on reactive flux ideas has been suggested by Straub and Berne.<sup>6,7</sup> In this paper we use this rapid method to calculate rate constants in a non-RRKM molecule subject to impulsive collisions. We use the two degree of freedom “polyatomic” studied by De Leon and Berne with the Hamiltonian<sup>8</sup>

$$H = 4(\dot{x}^2 + \dot{y}^2) + 4y^2(y^2 - 1)e^{-z\lambda x} + 10(1 - e^{-\lambda x})^2 + 1. \quad (5)$$

The potential energy consists of a quartic bistable potential ( $y$  coordinate) of unit barrier height and a Morse oscillator ( $x$  coordinate) which are completely decoupled for  $z = 0$ . For nonzero  $z$  the modes become nonlinearly coupled and the system shows a quite complex pattern of regular and chaotic motion for different choices of the parameters  $\lambda$  and  $z$ . The equations of motion are solved using a Runge-Kutta method.<sup>9</sup> The system is subjected to random collisions with a mean collision frequency  $\alpha$ . After each collision both velocities are resampled from a Maxwell-Boltzmann distribution with a temperature  $\beta^{-1} = 0.1$ . This BGK model<sup>10</sup> mimics a bath gas composed of heavy hard spheres. The rate constants obtained by the rapid method<sup>6,7</sup> are shown in Fig. 1. The solid line is the prediction of the rate theory using the RRKM assumption (rapid IVR) for two degrees of freedom [Eqs. (1)–(4) with  $n = 2$ ].<sup>11</sup> The dashed line is the same theory but applied to the quartic  $y$  degree of freedom [Eqs. (1)–(4) with  $n = 1$ ]. Note that at low collision rates the rate constant for one degree of freedom (dashed line) lies below the rate constant for two degrees of freedom (full line). In Fig. 1(a) we show the simulation data for a strongly irregular surface ( $\lambda = 1.95$  and  $z = 2.3$ ). The corresponding isolated system is accurately described by a RRKM rate constant.<sup>8</sup> The thermal rate constant shown in Fig. 1(a) is in good agreement with the two degree of freedom theory. In Fig. 1(b) we show the results for the uncoupled system ( $z = 0$ ). Here the rate constant is correctly given by the one

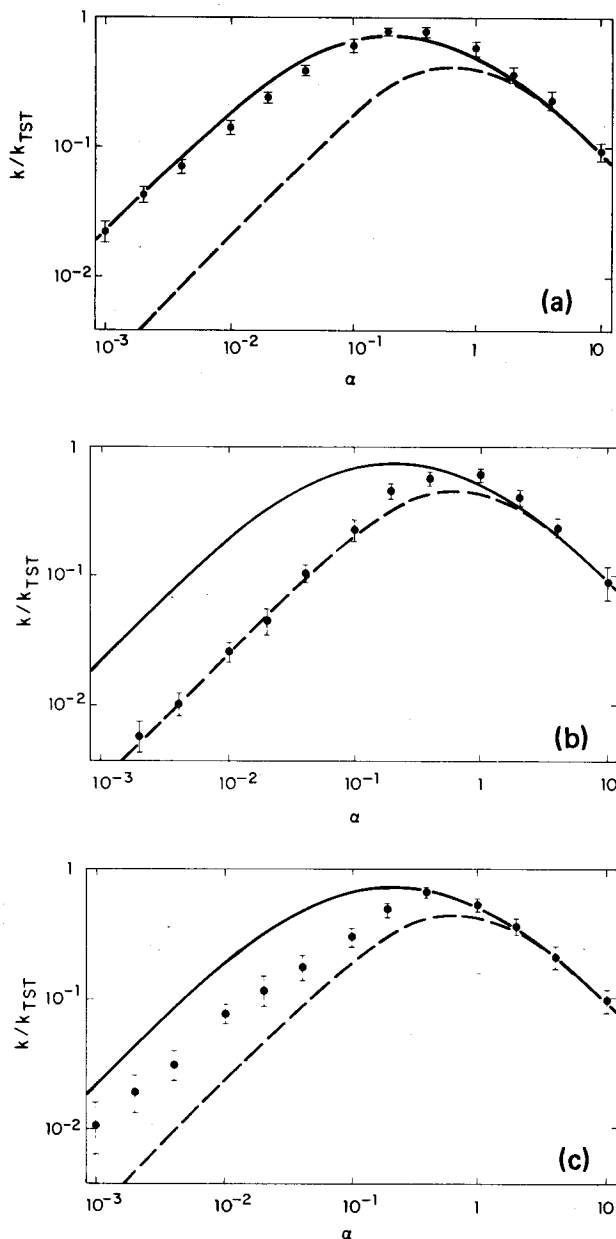


FIG. 1. A log-log plot of the rate constant as a function of collision frequency for a BGK model applied to a bistable two degree of freedom potential. The dots are simulation results with 95% confidence intervals (Ref. 24). The solid line is RRKM theory for two degrees of freedom assuming rapid energy partitioning [Eqs. (1)–(4) with  $n = 2$ ]. The dash-dotted line is the same theory but applied only to a single degree of freedom [Eqs. (1)–(4) with  $n = 1$ ]. (a) Strong coupling between the modes with rapid energy partitioning ( $\lambda = 1.95$  and  $z = 2.3$ ). (b) No coupling between the modes with infinitely slow energy partitioning ( $\lambda = 1.0$  and  $z = 0.0$ ). (c) Typical intermediate coupling between the modes ( $\lambda = 2.8$  and  $z = 1.0$ ).

degree of freedom theory except near the maximum where the approximation formula [Eq. (4)] is inaccurate.

Actually we were surprised to find that for our Hamiltonian Eq. (5) the two degree of freedom RRKM theory does not work for most other parameter choices. A typical intermediate case ( $\lambda = 2.8$  and  $z = 1$ ) is shown in Fig. 1(c). The data lie in between the predictions of the one and two degrees of freedom theories. Figure 1(c) suggests that the rate con-

stant is approximately described by the two degrees of freedom theory at very low collision rates, whereas at higher collision rates it is described preferably by a model with one degree of freedom. Such behavior can be explained qualitatively in terms of slow energy migration between the reactive and nonreactive mode as follows.<sup>5</sup> If the collision rate is slow compared with the IVR rate all activated trajectories can cross to the product side. Thus all phase space is available and the rate constant rises rapidly according to RRKM theory. If on the other hand the collision rate is fast compared with the IVR rate, any activated trajectory having most of its energy in the nonreactive mode gets deactivated before it can transfer its energy to the reactive mode and has therefore no possibility to react. This reduces the available phase space and leads to a slower rise of the rate constant as a function of the collision rate.

The physically intuitive concept of “energy in a vibrational mode” can be made more precise using the notion of “vague tori.”<sup>8,12</sup> On a short time scale a trajectory will move on such a vague torus and resemble quasiperiodic motion.<sup>13</sup> On a longer time scale (reciprocal IVR rate) the vague tori get destroyed and trajectories cover the energy shell in an irregular fashion. It has also been suggested that “cantori” (unstable tori) can represent surfaces in phase space which are difficult to cross resulting in trapping in a region of phase space.<sup>14</sup>

From these considerations one might think a quantitative theory of such non-RRKM effects must be intrinsically complicated. Fortunately, as we show below, a simple property of the isolated non-RRKM molecule determines the rate constant in the “strong collision approximation”<sup>2,3</sup> where each collision resamples the total energy of the molecule. The rate constant can be defined as the correlation time of the correlation function<sup>15</sup>

$$C(t) = \frac{\langle \delta\theta(0)\delta\theta(t) \rangle}{\langle \delta\theta^2 \rangle}, \quad (6)$$

where  $\theta$  is the characteristic function for the reactants, i.e., in our case the step function of  $y$  and  $\delta$  denotes a fluctuation from the equilibrium value. For the strong collision approximation any correlation function  $C(t)$  at a finite collision rate  $\alpha$  is related to the same correlation function in the absence of collisions  $C^{(0)}(t)$  by<sup>16,17</sup>

$$\tilde{C}(s) = \frac{\tilde{C}^{(0)}(s + \alpha)}{1 - \alpha\tilde{C}^{(0)}(s + \alpha)}, \quad (7)$$

where  $\tilde{C}(s)$  is the Laplace transform of  $C(t)$ . It turns out that in practice it is much easier to evaluate the time derivative of  $C^{(0)}(t)$ , i.e.,

$$\dot{C}^{(0)}(t) = -k_{\text{TST}}k^{(0)}(t), \quad (8)$$

where

$$k^{(0)}(t) = \frac{\langle \delta(y)\dot{y}\theta[y(t)] \rangle}{\langle \delta(y)\dot{y}\theta(t) \rangle} \quad (9)$$

is the normalized reactive flux [ $k^{(0)}(t \rightarrow 0^+) = 1$ ] for the isolated molecule in the absence of collisions and  $\delta(y)$  is Dirac's  $\delta$  function. Using the fact that  $k_{\text{TST}}$  is exponentially small and that the correlation time is the Laplace transform at  $s = 0$ , Eqs. (7)–(9) give a simple expression for the rate constant

$$\frac{k_{\text{SCA}}}{k_{\text{TST}}} = \alpha \bar{k}^{(0)}(\alpha) = \alpha \int_0^\infty dt e^{-\alpha t} k^{(0)}(t), \quad (10)$$

where we have neglected exponentially small terms. Since  $k^{(0)}(t)$  can be evaluated from a trajectory calculation on the isolated molecule quite easily, Eq. (10) represents a simple way for calculating the rate constant in the strong collision approximation including all non-RRKM effects. Note that very similar relations are used in chemical activation studies.<sup>18</sup> Let us consider the limiting behavior of Eq. (10). At high  $\alpha$  Eq. (10) reduces to unity, i.e., the rate constant is given by the transition state value. At low  $\alpha$  Eq. (10) reduces to<sup>16</sup>

$$k_{\text{SCA}} \rightarrow \alpha k_{\text{TST}} \int_0^\infty dt k^{(0)}(t) = X^\neq k_{\text{low}} \quad (\alpha \rightarrow 0), \quad (11)$$

where in the second equality we have introduced  $X^\neq$ , the thermal average of the measure in phase space of crossing trajectories.<sup>16</sup> In a system of three or more degrees of freedom Arnold diffusion<sup>13</sup> connects all irregular regions of phase space and  $1 - X^\neq$  is the measure of trapping tori. However, in a two degree of freedom system an irregular trajectory may be bounded by a trapping torus so that it will never cross and therefore will not contribute to  $X^\neq$ . In either case the explicit value of  $X^\neq$  can be evaluated from Eq. (7) by performing the time integral numerically. If the phase space is completely irregular all trajectories are crossing ( $X^\neq = 1$ ) and Eq. (11) reduces to Eq. (1). However, if there is a measurable portion of trapping tori ( $X^\neq < 1$ ) then the rise at low collision frequency is slower than predicted by Eq. (1). Physically this means that if an activated trajectory moves on a trapping torus it will never be able to cross over to the product side and therefore the next collision will always be deactivating. This results in a reduced low collision rate constant.

To apply these ideas we have considered the Hamiltonian [Eq. (5)] with  $\lambda = 2.8$  and  $z = 1.0$ . We ran  $10^4$  trajectories on the surface Eq. (4) without any collisions and determined the survival probability  $P^{(0)}(t)$ , i.e., the fraction of the trajectories which have not yet recrossed the transition state as a function of time.<sup>7</sup> One can calculate the Laplace transform of the normalized reactive flux  $\bar{k}^{(0)}(s)$  by numerically determining the Laplace transform of the survival probability  $\bar{P}^{(0)}(s)$  and using

$$\bar{k}^{(0)}(s) \simeq \frac{\bar{P}^{(0)}(s)}{2 - s\bar{P}^{(0)}(s)}, \quad (12)$$

which is a quite accurate approximation for the symmetric double well.<sup>7</sup> From  $\bar{k}^{(0)}(s)$  one can then calculate the rate constant in the strong collision approximation using Eq. (10). The result is shown by the solid line in Fig. 2. As a check of this procedure we simulated the strong collision approximation<sup>2,4</sup> (after each collision one resamples velocities as well positions from an equilibrium distribution in a given well) on the Hamiltonian [Eq. (5)]. The results (points in Fig. 2) are in perfect agreement with the prediction of Eq. (10). Therefore, we are confident that the rate constant in the strong collision approximation can be accurately determined using the free molecule trajectories in practice. In this case Eq. (11) gives  $X^\neq \simeq 0.85$ .

Turning back to the impulsive BGK model (resampling

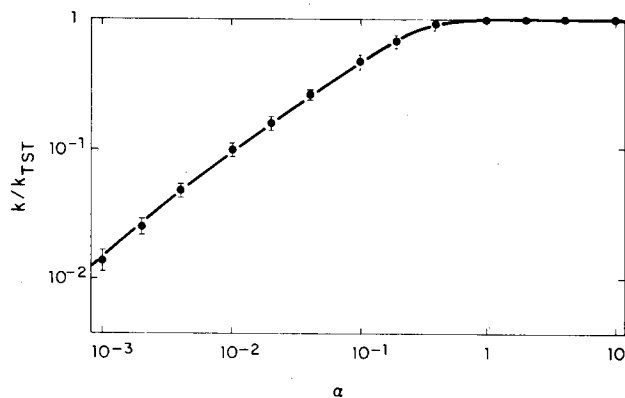


FIG. 2. Strong collision approximation applied to the moderately weakly coupled bistable two degree of freedom system shown in Fig. 1(c). ( $\lambda = 2.8$  and  $z = 1.0$ ). The solid line is the prediction of the exact non-RRKM theory [Eq. (10)] using the reactive flux for the isolated molecule as input. The dots are the simulation data.

velocities only) we use an approximate model to explain the simulation data which are shown in Fig. 1(c) and replotted in Fig. 3 (dots). The solid line in Fig. 3 is an approximate theory where we use the strong collision approximation [Eq. (10)] and the spatial diffusion result [Eq. (2)] in the interpolation formula

$$k^{-1} \simeq k_{\text{SCA}}^{-1} + k_{\text{high}}^{-1}. \quad (13)$$

This approximate theory is in semiquantitative agreement with the data.

One expects that such non-RRKM effects will play a similar role in weak collision models<sup>2,3</sup> (e.g., Kramers frictional model<sup>1</sup>). We also think that such non-RRKM effects become more important for a molecule with more than two degrees of freedom. Unfortunately the computational effort for the two degree of freedom system in the low collision regime is already substantial. Even when done by the rapid method<sup>6,7</sup> one rate constant usually requires several hours on the FPS-164 attached processor. With every degree of freedom added the reactive flux decays roughly by a factor of  $\beta Q$  more slowly to the plateau value, and it will be very costly to obtain accurate data on a larger system at low collision frequencies.

If these non-RRKM effects are important in real mole-

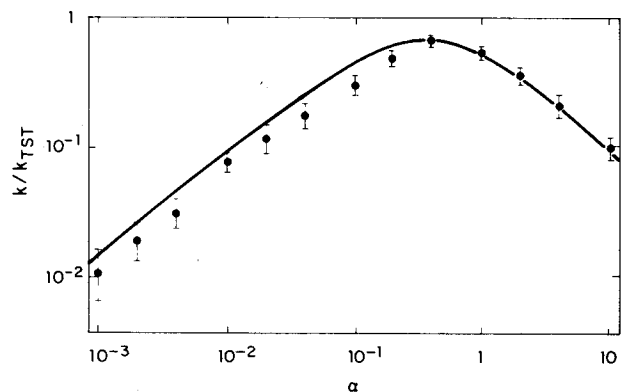


FIG. 3. BGK model applied to the moderately weakly coupled bistable two degree of freedom system shown in Fig. 1(c). The solid line is the prediction of the approximate non-RRKM theory [Eqs. (10) and (13)] using the reactive flux for the isolated molecule as input. The dots are the same simulation data as shown in Fig. 1(c).

cule measurements of the rate constant as a function of pressure should show initially a rapid rise which goes through a plateau and then subsequently rises more slowly. The present study suggests that such transitions from rapid to slower rise are probably very smooth and stretch over several decades in pressure. Since most gas phase experiments are not performed over more than two orders of magnitude in pressure, it is not surprising that no such effects have been observed. Because of practical difficulties there are very few experiments on polyatomics which cover many orders of magnitudes of density.<sup>19-21</sup> In cyclohexane there indeed seems to be a rapid rise at lower pressures<sup>19</sup> changing into a slower rise at higher pressures.<sup>20</sup> In fact Zawadski and Hynes recognized this discrepancy between predictions of simple RRKM barrier crossing theories and experimental data.<sup>22</sup> Studies on stilbene<sup>21</sup> also seem to suggest such behavior. Unfortunately, in either case, the experimental data are not conclusive enough. It is therefore quite possible that future studies along these lines might show such effects. Good candidates are recombinations or isomerizations of molecules where the reactive degree of freedom is a low frequency mode and the molecule has some high frequency modes.

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