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 theo-

\[ k_{\text{low}} \approx \alpha \frac{1}{(n-1)!} (\beta Q)^{n-1} e^{-\beta Q}, \]

where \( Q \) 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 con-
stant decreases inversely proportional to the collision rate as

\[ k_{\text{high}} = k_{\text{TST}} \frac{\omega_0}{\alpha}, \]

due to spatial diffusion where \( \omega_0 \) is the frequency of the
unstable mode of the saddle point. The rate constant is always
smaller than the value given by transition state theo-

\[ k_{\text{TST}} = \frac{1}{2\pi} \frac{\Pi \omega_0^{(0)}}{\Pi \omega_i^{(0)}} e^{-\beta Q}, \]

where \( \omega_0^{(0)} \) and \( \omega_i^{(0)} \) are the stable normal mode frequencies of
the saddle and the wells, respectively. A simple approxima-
tion for the rate constant valid for any collision rate is

\[ k^{-1} \approx k^{-1}_{\text{low}} + k_{\text{TST}} + k^{-1}_{\text{high}}. \]

Therefore, as a function of collision frequency the rate con-
stant 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 assump-
tion 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 com-
pletely decoupled from all the other degrees of freedom (in-
finity slowly IVR). In this example the rate constant will be

\[ \text{fore}, \text{the RRKM theory is not valid in this case. Obviously}
\]

\[ \text{there will be some kind of transition between these two ex-
}

\[ \text{tremes of strong coupling (fast IVR) and weak coupling}
\]

\[ \text{(slow IVR). There has been some speculation on the nature of}
\]

\[ \text{this transition. However, there have been no studies of}
\]

\[ \text{such non-RRKM effects on rate constants using specific}
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\[ \text{model systems, mainly because of numerical difficulties cal-
}

\[ \text{culating rate constants. Recently, however, a rapid method}
\]

\[ \text{for calculating rate constants based on reactive flux ideas has}
\]

\[ \text{been suggested by Straub and Berne. In this paper we use}
\]

\[ \text{this rapid method to calculate rate constants in a non-}
\]

\[ \text{RRKM molecule subject to impulsive collisions. We use the}
\]

\[ \text{two degree of freedom "polyatomic" studied by De Leon}
\]

\[ \text{and Berne with the Hamiltonian}
\]

\[ H = 4(\chi^2 + \psi^2) + 4y^2(y^2 - 1)e^{-4x} + 10(1 - e^{-4x})^2 + 1. \]

The potential energy consists of a quartic bistable potential
(\( \psi \) coordinate) of unit barrier height and a Morse oscillator
(\( \chi \) 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. The system is subjected to random collisions with a
mean collision frequency \( \alpha \). After each collision both veloci-
ties are resampled from a Maxwell–Boltzmann distribution
with a temperature \( \beta^{-1} = 0.1 \). This BGK model mimics a
bath gas composed of heavy hard spheres. The rate constants
obtained by the rapid method 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
[Eqns. (1)–(4) with \( n = 2 \)]. The dashed line is the same
theory but applied to the quartic \( \psi \) degree of freedom [Eqns.
(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 irregu-
lar surface (\( \lambda = 1.95 \) and \( z = 2.3 \)). The corresponding iso-
lated system is accurately described by a RRKM rate con-
stant. 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

The rate constant 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. 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.” On a short time scale a trajectory will move on such a vague torus and resemble quasiperiodic motion. 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.

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” where each collision resamples the total energy of the molecule. The rate constant can be defined as the correlation time of the correlation function

\[ C(t) = \frac{\langle \delta\theta(0)\delta\theta(t) \rangle}{\langle \delta\theta^2 \rangle}, \]

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

\[ \tilde{C}(s) = \frac{\tilde{C}^{(0)}(s + \alpha)}{1 - \alpha \tilde{C}^{(0)}(s + \alpha)}, \]

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.,

\[ \dot{C}^{(0)}(t) = -k_{\text{TST}} k^{(0)}(t), \]

where

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

is the normalized reactive flux \([k^{(0)}(t) = 0^+ = 1]\) 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.
\[
\frac{k_{\text{SCA}}}{k_{\text{TST}}} = a k^{(0)}(a) = a \int_0^\infty \, dt \, e^{-\alpha t} k^{(0)}(t),
\]
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.\(^{18}\) 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
\[
k_{\text{SCA}} = \alpha k_{\text{TST}} \int_0^\infty \, dt \, k^{(0)}(t) = X^* k_{\text{low}} (\alpha \to 0),
\]
where in the second equality we have introduced \(X^*\), the thermal average of the measure in phase space of crossing trajectories.\(^{16}\) In a system of three or more degrees of freedom Arnold diffusion\(^{17}\) connects all irregular regions of phase space and \(1 - X^*\) 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 \(X^*\). In either case the explicit value of \(X^*\) can be evaluated from Eq. (7) by performing the time integral numerically. If the phase space is completely irregular all trajectories are crossing \((X^* = 1)\) and Eq. (11) reduces to Eq. (1). However, if there is a measurable portion of trapping tori \((X^* < 1)\) 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.\(^7\) One can calculate the Laplace transform of the normalized reactive flux \(\tilde{k}^{(0)}(s)\) by numerically determining the Laplace transform of the survival probability \(\tilde{P}^{(0)}(s)\) and using
\[
\tilde{k}^{(0)}(s) \sim \frac{\tilde{P}^{(0)}(s)}{2 - s\tilde{P}^{(0)}(s)},
\]
which is a quite accurate approximation for the symmetric double well.\(^7\) From \(\tilde{k}^{(0)}(s)\) 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\(^{2,4}\) (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 \(X^* \approx 0.85\).

Turning back to the impulsive BGK model (resampling 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
\[
k^{-1} \approx k_{\text{SCA}}^{-1} + k_{\text{high}}^{-1}.
\]
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\(^{5,3}\) (e.g., Kramers frictional model\(^1\)). 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\(^6,7\) 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 \(\beta g\) 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-
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. In cyclohexane there indeed seems to be a rapid rise at lower pressures changing into a slower rise at higher pressures. In fact Zawadski and Hynes recognized this discrepancy between predictions of simple RRKM barrier crossing theories and experimental data. Studies on stilbene 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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M. Borkovec and B. J. Berne, J. Phys. Chem. 89, 3994 (1985). There are many similar approximation formulas. See, for example, Ref. 1. Equation (4) is probably the simplest one.


The equations of motion are integrated with a relative energy conservation of 10-7.


For a symmetric double well potential Eq. (1) is reduced by a factor of 2. We have also evaluated the exact expressions discussed in Ref. 3 for the rate constants using Monte Carlo sampling and used these values instead of Eq. (1) where necessary. In the cases studied Eq. (1) agreed with the correct value always better than 10%.

See, for example, W. Reinhardt, J. Phys. Chem. 86, 2158 (1982).


There are many equivalent definitions of the rate constant. See, for example, Ref. 1.


B. J. Berne and R. Pecora, Dynamic Light Scattering (Wiley, New York, 1976), and references therein. Such relations were originally used in the theory of rotational diffusion.

See, for example, R. A. Marcus, W. L. Hase, and K. N. Swamy, J. Phys. Chem. 88, 6717 (1984), and references therein.


W. L. Hase and H. B. Schlegel, J. Phys. Chem. 86, 3901 (1982). These authors have shown however that thermal rate data on methylisocyanoacetate are in good agreement with RRKM theory.