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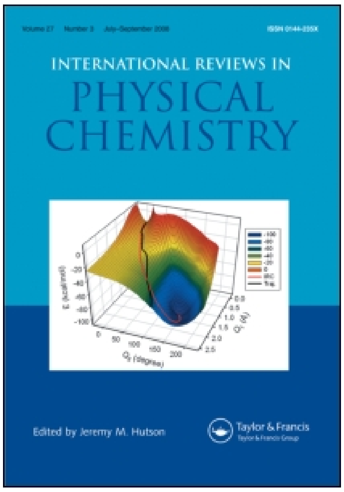

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Theory of collisional energy transfer of highly excited molecules

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The method of obtaining collisional energy transfer data for collisions between a highly excited polyatomic and a bath gas from classical trajectories is discussed. The technique yields the mean(-square) energy transferred per collision from a comparatively small (≈ 500) number of trajectories. Results compare favourably, qualitatively and quantitatively, with experiment for all except the lightest bath gases (where the interaction potential is uncertain). Simple analytical models are also examined. These yield methods of obtaining energy transfer data of practical use in predicting and interpreting falloff data for unimolecular and recombination reactions. It is shown that quantum effects are unimportant for such systems.

1. Introduction

This review discusses the theory of collisional energy transfer of a highly excited polyatomic substrate molecule colliding with a bath gas. 'Highly excited' in this context means superthermal (e.g. 20–200 kJ mol^{-1}) internal (vibrational and rotational) excitation, in the ground electronic state; such energies are those typically involved in falloff behaviour of unimolecular and recombination reactions (Gilbert and Smith 1990). 'Polyatomic' refers to four or more atoms. As will be shown, for systems of this size and energy, classical mechanics supplies an accurate description of the dynamics of collisional energy transfer, the computations, and development of approximate models, being simplified by the statistical behaviour of a large number of atoms at high energy.

The theory discussed here provides a basis for calculating the rates of collisional energy transfer where such quantities are required to predict or fit falloff effects (i.e. the pressure dependence of unimolecular and recombination rate coefficients). Such studies are of intrinsic scientific interest. Reliable theory (with a preference that such theory also be relatively easy to apply) is moreover of considerable technical application. For example, many of the reactions involved in combustion and aerochemical modelling are in the falloff regime, and rate coefficients for many of such reactions either cannot be measured experimentally in the desired range of temperatures and pressures, or are quite unknown, and hence modellers must rely on theoretical estimates.

Collisional energy transfer is quantified as the rate coefficient $R(E, E')$ for the process whereby a substrate molecule, with initial energy E', undergoes a collision with a bath gas molecule and ends up with internal energy E. In this review, we first show how to find this quantity from classical trajectories. We start by looking at the type of behaviour that would be expected in these collisions, so as to find the general features of $R(E, E')$. We next examine approximate models, and compare full trajectory results and approximate models with each other and with experiment. Finally, the importance of quantum effects is examined. This review does not concern itself with how such information can be used in the solution of the master equation, which relates $R(E, E')$ to

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thermal rate coefficients; this topic has been discussed extensively elsewhere (Gilbert and Smith 1990, Oref and Tardy 1990).

$R(E, E')$ is defined as the number of collision events per unit time, per substrate molecule, per bath-gas molecule, that start with the substrate having energy E' in the active degrees of freedom and finish with this energy lying between E and $E+\mathrm{d}E$. This rate coefficient has dimensions (energy^{-1} volume time^{-1}). It may also be expressed in terms of a *probability of energy transferred per collision*, $P(E, E')$, defined by

$$P(E, E') = \frac{[\mathrm{M}]R(E, E')}{\omega(E')} = \frac{R(E, E')}{Z(E')}, \tag{1}$$

where $\omega(E')$ is a total collision frequency, [M] the number concentration of bath gas, and $Z(E')$ the collision number. For notational convenience, we adopt the common assumption that $\omega(E')$ and $Z(E')$ are independent of the initial energy E' (we shall examine its validity in section 3). One then has the following normalization condition for $P(E, E')$

$$\int_0^\infty P(E, E')\,\mathrm{d}E = 1. \tag{2}$$

However, it is *essential* (Lim and Gilbert 1990a) to be aware that the true observable in any experiment is the *rate coefficient* $R(E, E')$ (or one of its averages), not $P(E, E')$, etc., and the factorization into 'per collision' quantities such as $P(E, E')$ and $\langle \Delta E \rangle$ is purely as an aid to intuition: except for hard spheres, one can never define a 'collision'.

In an unimolecular or recombination reaction, the thermal rate coefficient k is determined from the solution to the master equation

$$-kg(E) = [\mathrm{M}] \int_0^\infty [R(E, E')g(E') - R(E', E)g(E)]\,\mathrm{d}E' - k(E)g(E), \tag{3}$$

where $g(E)$ is the population of substrate molecules with energy E, and $k(E)$ the microscopic rate coefficient for molecules with energy E.

An important objective is to develop methods that can give sufficient information on $R(E, E')$ to predict the pressure dependence of k with sufficient accuracy (i.e. falloff behaviour). It is important to realize that for falloff behaviour, and for so-called 'direct' experiments (which measure the time evolution of the average energy in a non-reacting system, e.g. Barker 1984, Shi and Barker 1988, Yerram, Brenner, King and Barker 1990, Hippler, Lindermann and Troe 1985, 1989), it is usually unnecessary to know the complete functional form of $R(E, E')$, but rather only to known the value of a single moment: for example, the mean rate of energy transfer $R_{E',1}$ (or equivalently the mean energy transferred per collision, $\langle \Delta E \rangle$), or the mean-squared rate $R_{E',2}$ (or equivalently the mean-square energy transferred per collision, $\langle \Delta E^2 \rangle$). These moments are defined by

$$R_{E',n} = \int_0^\infty (E-E')^n R(E, E')\,\mathrm{d}E, \qquad \langle \Delta E^n \rangle = \int_0^\infty (E-E')^n P(E, E')\,\mathrm{d}E. \tag{4}$$

Approximate proofs of the insensitivity of the rate coefficients to all except one moment of $R(E, E')$ have been derived (e.g. Keck and Carrier 1965), but these proofs are valid only in the limit of very weak collisions; in fact, numerical solution of the master equation (e.g. Gilbert and Smith 1990) shows this independence almost always holds to a quite acceptable approximation. However, it should be noted that certain types of experiments are sensitive to more than one moment of the distribution (e.g. Pashutski and Oref 1988, Morgulis, Sapers, Steel and Oref 1989, Löhmannsröben and Luther 1988, Luther and Reihs 1988, King, Nguyen and Gilbert 1981); particular attention will be paid to the results of such experiments at a later point. Moreover, certain experiments ('direct' or 'physical' ones; Oref and Tardy 1990) give a relatively direct measure of the first moment, $R_{E',1}$ or $\langle \Delta E \rangle$, whereas the second momement $R_{E',2}$ or $\langle \Delta E^2 \rangle$ gives a measure of the width of $R(E, E')$, and (as will be apparent from subsequent discussions) also arises naturally in models for the energy transfer process.

Although it is unnecessary to know extremely precise information about the functional form of $R(E, E')$ for many purposes, it must be borne in mind that the insensitivity to higher momements is *not* exact, and the difference between values of, say, unimolecular rate coefficients calculated with the same value of $\langle \Delta E \rangle$, etc., but different functional forms for $R(E, E')$, can be as much as 50%. It is therefore advisable to have a functional form for $R(E, E')$ that is as physically correct as possible; this point will be further discussed in subsequent sections.

It is seen from their defining equations that $\langle \Delta E \rangle$, $\langle \Delta E^2 \rangle$ and any other single measure of $R(E, E')$ depend on the initial energy E'. This is explicitly taken into account in the notation $R_{E',2}$. Strictly speaking, one should therefore always report as accurately as possible the initial energy when giving experimental or theoretical values for any of these quantities. Fortunately, the initial-energy dependence of $R_{E',2}$ is quite weak over typical ranges of energy (see below).

Another common measure of $R(E, E')$ or $P(E, E')$ is the average *downward* energy transferred per collision

$$\langle \Delta E_{\text{down}} \rangle = \frac{\int_0^{E'} (E' - E) P(E, E') \, \mathrm{d}E}{\int_0^{E'} P(E, E') \, \mathrm{d}E}. \tag{5}$$

This is the average value of the energy transferred for collisions where the molecule loses energy, as distinct from $\langle \Delta E \rangle$, which covers both gains and losses of energy. Like $\langle \Delta E^2 \rangle^{1/2}$, $\langle \Delta E_{\text{down}} \rangle$ is always positive, and is an approximate measure of the width of $P(E, E')$. It is frequently employed because, if one adopts the simple exponential-down model, then $P(E, E') \propto \exp(-|E - E'|/\langle \Delta E_{\text{down}} \rangle)$ for downward collisions, and approximate solutions to the master equation for this functional form have been found (e.g. Troe 1977). Each of the measures of $R(E, E')$ discussed here, namely, $\langle \Delta E \rangle$, $\langle \Delta E^2 \rangle$ and $\langle \Delta E_{\text{down}} \rangle$, can be readily computed from any other of these measures, given the form of $R(E, E')$ and the molecular parameters (e.g. Gilbert and Smith 1990).

2. Calculation from classical trajectories

We now show how $R(E, E')$ and its moments can be obtained through classical trajectory calculations, given a potential function describing the system under study. $R(E, E')$ is a phase-space average of the energy transferred by many individual trajectories, each of which starts with a set of random initial conditions chosen from an ensemble corresponding to the experimental conditions. These initial conditions are specified by the impact parameter, the phase and energy of each vibrational mode, the rotational energy, orientation of the substrate, and the relative substrate/bath-gas translational energy, given that the initial value of the substrate energy is E'. The average must be taken over a sufficiently large number of trajectories that the required quantity converges to within a prescribed tolerance. There are publicly-available programs (e.g. Lim and Hase 1990) which enable one to implement such trajectory calculations for a wide variety of potentials.

Figure 1 shows a series of 'snapshots' from a single trajectory of azulene colliding with Xe, the energy of the azulene being about $3 \times 10^4\,\mathrm{cm}^{-1}$ above the zero-point energy, and the relative translational energy being 1·2 kcal mol^{-1} (corresponding to the mean energy of a system at 300 K; it will be seen from (5) below that the mean translational energy corresponding to a given temperature in these systems is $2k_BT$). Note the large distortions of the azulene during the interaction. Moreover, the substrate usually undergoes at least one rotation during the interaction; note also that the collision involves interaction of the bath gas with many substrate atoms (partly because the azulene is rotating on a timescale that is somewhat faster than the duration of the collision). This can also be seen in figure 2, which shows, for a single trajectory, the time evolution of $E_i(t)$, the energy of the substrate during the collision; the required distribution function $R(E, E')$ is that of $E_i(t=+\infty)$, given that $E_i(t=-\infty)=E'$. Note also the duration of the collision, which is of the order of picosecond (the collision is however usually shorter than a picosecond with lighter bath gases). Note also that the substrate energy undergoes a large number of peregrinations during the collision, as the bath gas interacts with a number of substrate atoms with random vibrational phases. That is, the collision involves multiple interactions of the bath gas with one or more of the substrate atoms: a 'chattering' collision. These and other features will be discussed in more detail in connection with the development of approximate models.

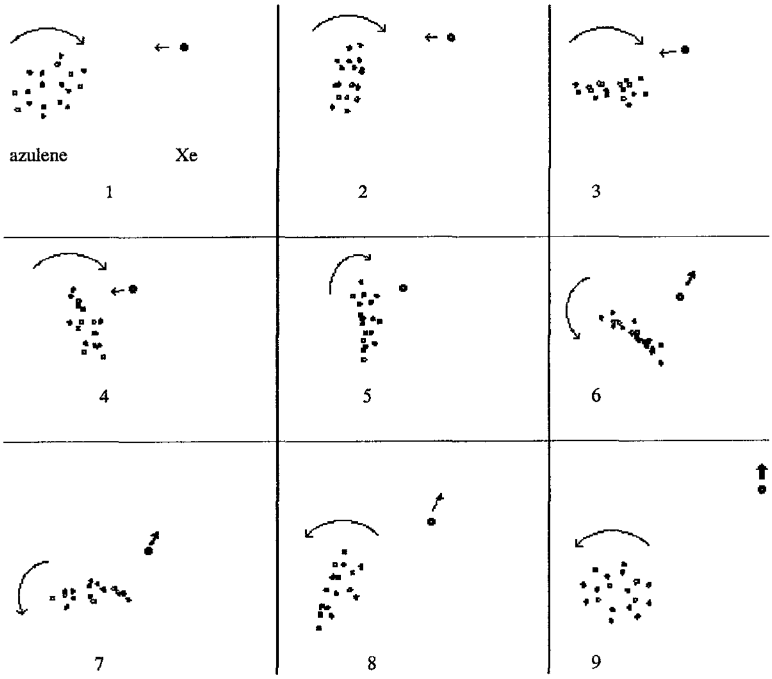

Figure 1. A series of snapshots of an excited azulene/Xe collision (energy transfer ≈ $-500\,\mathrm{cm}^{-1}$). Arrows indicate direction of rotation of azulene (which changes between the fifth and sixth snapshot), and direction of motion of Xe (which also changes between the same snapshots). For clarity, the sizes of the points representing the atoms are much smaller than the van der Waals radii. Note the large distortions of the azulene ring during the interaction.

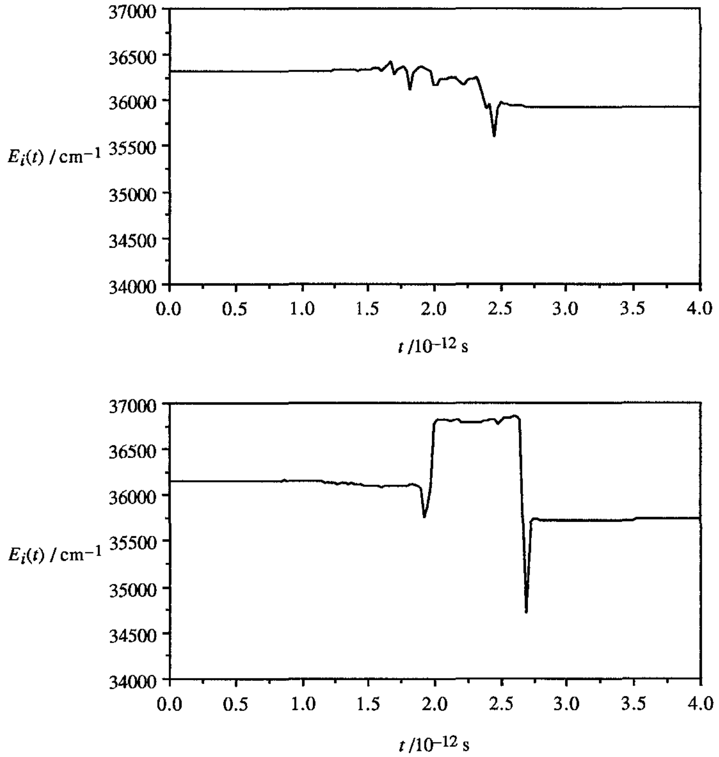

Figure 2. Data from two trajectories showing azulene energy $E_i(t)$ during collision of excited azulene colliding with Xe, relative translational energy corresponding to 300 K.

The method for obtaining $R(E, E')$ from trajectory calculations (Lim and Gilbert 1990a) is as follows. The rate coefficient for collisions between a substrate and a bath gas in translational equilibrium is given by (Porter and Raff 1976)

$$R(E,E')=\left(\frac{8k_{\mathrm{B}}T}{\pi\mu}\right)^{1/2}\frac{1}{(k_{\mathrm{B}}T)^2}\int_0^\infty \mathrm{d}b\,2\pi b\int_0^\infty \mathrm{d}E_{\mathrm{T}}\exp(-E_{\mathrm{T}}/k_{\mathrm{B}}T)E_{\mathrm{T}}B(E,E',E_{\mathrm{T}},b). \quad (6)$$

Here μ is the reduced mass of the substrate/bath-gas pair, E_{T} the relative kinetic energy, b the impact parameter, and B the probability of the event in question occurring. For simplicity, we have taken the bath gas to be monatomic (the extension required to include a bath gas with internal structure is straightforward; Lim and Gilbert 1990a). The presence of the factor $(k_{\mathrm{B}}T)^{-2}\exp(-E_{\mathrm{T}}/k_{\mathrm{B}}T)E_{\mathrm{T}}$ in the integrand implies that the mean translational energy is $2k_{\mathrm{B}}T$, the average value of this function.

Before proceeding, we note that $R(E, E')$ and $P(E, E')$ must obey the microscopic reversibility (also called detailed balance) relationship

$$f(E')R(E,E')=f(E)R(E',E), \qquad f(E')P(E,E')=f(E)P(E',E), \qquad (7)$$

where $f(E)=\rho(E)\exp(-E/k_{\mathrm{B}}T)$, $\rho(E)$ being the density of states of the substrate. These give the relationship between the rates of upward and downward energy transfer. These equations, which can be proved from (6), are *exact*; they arise from the time reversibility of the quantum and classical equations of motion, averaged over a Boltzmann distribution of translational energies of the bath gas (e.g. Gilbert and Smith 1990).

The rate coefficient $R_{E',n}$, i.e. the nth moment of $R(E,E')$, can be obtained from (6) as

$$R_{E',n}=\left(\frac{8k_BT}{\pi\mu}\right)^{1/2}\frac{1}{(k_BT)^2}\int_0^\infty db\,2\pi b\int_0^\infty dE(E-E')^n \times\int_0^\infty dE_T\exp(-E_T/k_BT)E_TB(E,E',E_T,b). \quad (8)$$

The probability $B(E,E',E_T,b)$ can be found from classical trajectories as follows. In addition to the variables of integration considered explicitly in (6) and (8), the system has many more degrees of freedom: the positions and momenta of each atom in the substrate, which may take any value subject only to the constraint of the given values of b, E and E_T. These will be chosen in a Monte-Carlo fashion from an appropriate distribution. For example, the value of E_T is chosen from the distribution $f(E_T)=(k_BT)^{-2}E_T\exp(-E_T/k_BT)$, and b from $f(b)=2\pi b/\pi b_{max}^2$, where b_{max} is the maximum impact parameter to be considered (i.e. the numerical value of 'infinity' in the integral over b); the other initial conditions (coordinates and momenta corresponding to the specified internal energy, rotational energy and orientation) must also be chosen from appropriate distributions using, for example, orthant sampling (Bunker and Hase 1973). Implementation of the statistics (Lim and Gilbert 1990a) gives the following expression for the evaluation using classical trajectories

$$R_{E',n}=\lim_{b_{max}\to\infty}\lim_{N\to\infty}\left(\frac{8k_BT}{\pi\mu}\right)^{1/2}\pi b_{max}^2\frac{1}{N}\sum_{i=1}^{N}(\Delta E_i)^n. \quad (9)$$

The corresponding formula for the distribution $R(E,E')$ is

$$R(E,E')=\lim_{b_{max}\to\infty}\lim_{N\to\infty}\lim_{\varepsilon\to 0}\left(\frac{8k_BT}{\pi\mu}\right)^{1/2}\pi b_{max}^2\frac{1}{\varepsilon N}\sum_{i=1}^{N}\chi_i(E,E';\varepsilon). \quad (10)$$

Here N is the number of trajectories, ΔE_i is the energy change in the ith trajectory, and the characteristic function $\chi_i(E,E';\varepsilon)$ is unit if the ith trajectory has its final energy in the range E to $E+\varepsilon$, and is zero otherwise (i.e. ε is the bin width).

Note that in (9) and (10) one never makes any attempt to define a 'collision', in the form of choosing some prescription for b_{max}; instead, one takes the proper limit as this maximum impact parameter becomes infinitely large, and calculates the energy transfer rate coefficient. The subdivision into 'per collision' quantities such as ω and $\langle\Delta E\rangle$ is certainly convenient, and indeed essential for developing approximate models, but depends on an *arbitrary* definition of the collision number. The requisite expressions for these are as follows. One defines a collision number Z (see (1)) with reference to a convenient hard-sphere diameter d

$$Z_{HS}=\left(\frac{8k_BT}{\pi\mu}\right)^{1/2}\pi d^2, \quad (11)$$

where d can be found by a physically reasonable estimate (e.g. Lennard-Jones) using the methods discussed below for finding the collision frequency in approximate models. 'Per-collision' quantities are then simply calculated from the values of the equivalent rate coefficients, $R(E,E')$ and its moments, using the definitions

$$P(E,E')=\frac{1}{Z_{HS}}R(E,E'), \qquad \langle\Delta E^n\rangle=\frac{1}{Z_{HS}}R_{E',n}. \quad (12)$$

To evaluate average energy transfer quantities, one chooses a maximum impact parameter $b_{\max}$ sufficiently large (say, 50% greater than the Lennard-Jones diameter) that trajectories beyond this do not exchange significant amounts of energy. One then chooses initial conditions randomly (from the appropriate distributions for E_{T}, b and the positions and momenta of the atoms) and runs a sufficiently large number of trajectories so that the chosen moment converges. It is important to note this point about the selection of initial conditions. Equation (9) is a deceptively simple recipe for the (moments of) the rate of energy transfer. The values of ΔE_i therein (i.e. the energy transfer for each trajectory) in this summation are not weighted according to the probability of that trajectory, because this weighting is assumed in the derivation to be already taken into account in the selection of initial conditions. If one is examining, for example, the dependence of the energy transfer rate on E_{T}, then equivalent expressions to (9) with $f(E_{\mathrm{T}})=\delta(E'_{\mathrm{T}}-E_{\mathrm{T}})$ must be used (Clarke, Oref, Gilbert and Lim 1991).

Figure 3 shows the distribution function $R(E, E')$ obtained for thermal collisions of highly excited azulene with Xe; for convenience, the ordinate is given as the number of trajectories, i.e. the factors $(8k_{\mathrm{B}}T/\pi\mu)^{1/2}\pi b_{\max}^2/\varepsilon N$ in (10) have been omitted. Figure 3 was calculated using the potential of Clarke *et al.* (1991) (bends, stretches and wags for the azulene, and Lennard-Jones atom–atom interactions between the azulene and Xe). The data of figure 3 were determined using $N=600$ trajectories, which while not a sufficiently large number to give an accurate representation of the full distribution function for $R(E, E')$, is quite adequate to show the general features (as will be seen, this number of trajectories is sufficient to evaluate the second moment, $R_{E',2}$, with acceptable accuracy). Note that the average energy per oscillator in this calculation is about one quantum above the zero-point energy, which is typical of that of moderate-size polyatomic molecules undergoing reaction (in a polyatomic with many degrees of freedom, and average of one quantum of excitation per oscillator adds up to a large total energy).

There are three noticeable features of $R(E, E')$:

(1) $R(E, E')$ falls away to zero for large energy changes ($|E-E'|\gg 0$). This is because the transfer of a very large amount of energy could only occur if the collision duration were sufficient for complete randomization of energy between all degrees of freedom of the substrate and the bath gas. However, the collision duration (*c.* 1 ps or less) is much too short for this to occur, particularly in view of the very weak interaction between substrate and bath gas. It should be noted that the foregoing argument will not necessarily be applicable if the bath gas molecule has a large number of degrees of freedom. In this case, the collision can last much longer (a 'sticky' collision) and there is an increased likelihood of greater randomization between the substrate's internal energy and the kinetic and internal energies of the bath gas. There could then well be large amounts of energy transferred, and $R(E, E')$ could be large for large $|E-E'|$. This case of having a large amount of energy transferred in most collisions (applicable if the bath gas molecule contains, say, ten or more atoms) is a *strong* collision.

(2) $R(E, E')$ assumes large values for small energy changes ($E\approx E'$); a so-called *elastic peak* is present at $E=E'$. This arises from energy transfer in collisions which occur with large impact parameters (recall that (9) and (10) can only be properly evaluated in the limit of an infinite range of b): clearly, trajectories with very large b cannot transfer significant amounts of energy. There is correspondingly a large number of trajectories with high b, since the density of trajectories

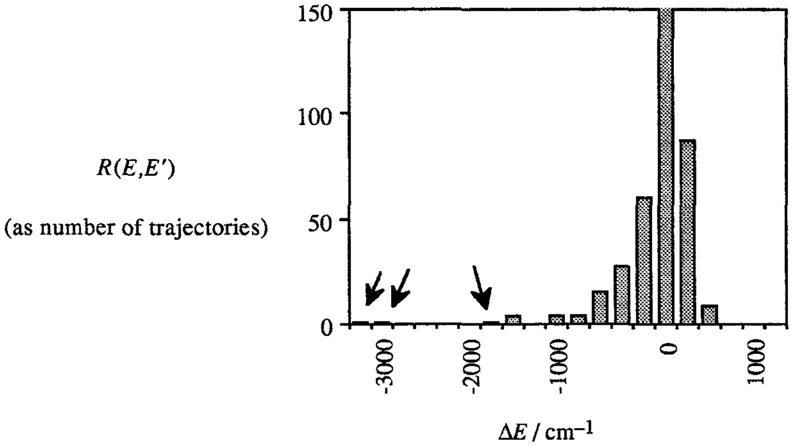

Figure 3. $R(E, E')$, in the form of a histogram of the number of trajectories with a given energy transfer. Elastic peak has been truncated. These trajectories all had the same translational energy $E_T = 1{\cdot}2\,\mathrm{kcal\,mol^{-1}}$ (corresponding to a thermal energy of 300 K), $E' = 30\,644\,\mathrm{cm^{-1}}$; total number of trajectories = 600. Arrows point to single trajectories transferring c. 1500, 3000 and $3300\,\mathrm{cm^{-1}}$. Calculated from the data of Thompson *et al.* (1991).

with impact parameter b is proportional to $2\pi b$ (6). Indeed, this elastic peak in $R(E, E')$ must (classically) be infinite when $E = E'$. However (e.g. Gilbert and Smith 1990), measures of the overall energy transfer rate (e.g. a unimolecular rate coefficient in the falloff regime) are always finite. That is, there are many collisions which transfer a tiny amount of energy, but these contribute vanishingly to the overall energy transfer rate and to the rate coefficient.

(3) There is a small number (about 1%) of 'supercollisions' (indicated with arrows in figure 3), which transfer amounts of energy very much greater than the average. These have been observed experimentally (Pashutski and Oref 1988, Morgulis *et al.* 1989, Löhmannsröben and Luther 1988, Luther and Reihs 1988), as well as being seen in trajectory calculations (Lendvay and Schatz 1990, Clarke *et al.* 1991); this qualitative accord between an unusual effect seen both in simulations and experiment suggests the qualitative correctness of both the trajectory approach and of the potential functions employed. The explanation of this effect (Clarke *et al.* 1991) is that these unusual collisions involve a substrate atom (hydrogen in the present case) being squashed between the bath gas atom and the bulk of the substrate molecule; this forces the squashed atom high up the repulsive wall between it and the bath gas atom, resulting in a large energy transfer on the recoil. It should be noted that these supercollisions have a small but significant (say, 20%) effect on the overall mean energy transfer.

Having considered the full distribution function, $R(E, E')$, we next consider calculations of its moments, as in (9): it will be recalled that for purposes of modelling falloff behaviour and 'direct' experiments, it is usually sufficient to know only $R_{E',1}$ or $R_{E',2}$. It is more efficient to calculate $R_{E',2}$, since all contributions to the summation in (9) will be positive, and thus one expects convergence for a smaller value of N than for calculating $R_{E',1}$, when contributions will have both positive and negative sign. Typically, 500–1000 trajectories are sufficient for adequate convergence of $R_{E',2}$. Note that earlier studies had suggested that only 100 trajectories were sufficient (Lim and Gilbert 1990b); however, this misconception arose because the presence of supercollisions (see above) was not realized in these earlier calculations, and these supercollisions strongly affect the convergence properties of the summations in (9). This convergence is illustrated in figures 4, which shows $R_{E',2}$ (for convenience converted to a root-mean-square energy transfer per collision, $\langle \Delta E^2 \rangle^{1/2}$) as a function of the reciprocal of the number of trajectories N (obviously, the properly converged value of the required quantity is the limit as N^{-1} approaches zero). Note the occasional jumps up, followed by a steady decrease: this is caused by the occasional supercollision.

Next, consider the convergence of (9) for increasingly large values of the maximum impact parameter $b_{\max}$. This can be seen in the *pseudo-opacity function*, $p(b)$, which is defined in the usual way, except that the function considered here has different units from conventional opacity functions (an appropriate to the units of the dynamical quantity we are considering): for example, we write (8) (for $n=2$) as

$$R_{E',2}=\int_0^\infty 2\pi b\,\mathrm{d}b\,p(b), \tag{13}$$

where

$$p(b)=\left(\frac{8k_\mathrm{B}T}{\pi\mu}\right)^{1/2}\frac{1}{(k_\mathrm{B}T)^2}\int_0^\infty \mathrm{d}E\,(E-E')^n\int_0^\infty \mathrm{d}E_\mathrm{T}\exp(-E_\mathrm{T}/k_\mathrm{B}T)E_\mathrm{T}B(E,E',E_\mathrm{T},b). \tag{14}$$

The function $p(b)$ is easily obtained from trajectory data [note that this differs from the quantity denoted $I(b)=2\pi bp(b)$ in Gilbert and Smith (1990)]. A typical $p(b)$ is shown in figure 5.

As stated, the energy transfer is governed by chattering: many impulsive, essentially atom/atom, interactions (this also holds for rotational energy transfer, e.g. Evans, Evans and Hoffman 1990). The energy transfer must therefore depend significantly on

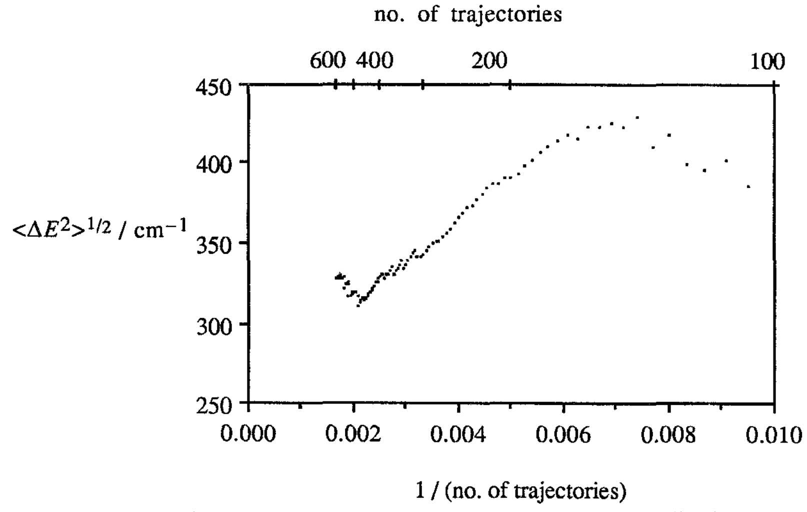

Figure 4. Convergence of mean-squared rate of energy transfer (normalized to root-mean-squared energy transfer per collision, $\langle \Delta E^2 \rangle^{1/2}$, using $d=6{\cdot}97\,\text{Å}$) with number of trajectories, for azulene/Xe collisions at $T=300\,\mathrm{K}$, with $E'=30\,664\,\mathrm{cm}^{-1}$. Calculated from the data of Thompson *et al.* (1991).

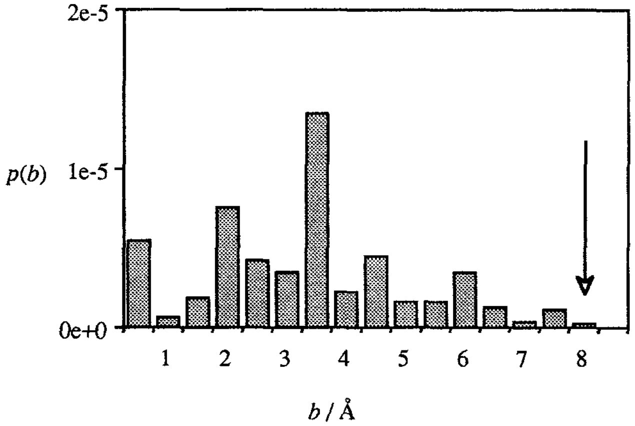

Figure 5. Pseudo-opacity function $p(b)$ for thermal ($T=300$ K) azulene/Xe collisions; $E'=17500\,\mathrm{cm}^{-1}$. Arrow shows the Lennard-Jones radius $\sigma(\Omega^*_{2,2})^{1/2}$ (see (17)), where $\sigma=5{\cdot}05$ Å. Calculated from the data of Clarke *et al.* (1991), with 600 trajectories.

the repulsive part of the interaction potential. This can explain the observation (e.g. Oref and Tardy 1990) that average energy transfer values have similar magnitudes for a wide range of substrates interacting with the same bath gas, and also that they do not depend strongly on the detailed structure of the substrate. Consider for example a homologous series of alkane/monatomic bath gas collisions. All must be dominated by the same carbon/bath gas plus hydrogen/bath gas repulsive interactions, which will all be similar for similar substrates. Hence the lack of variation can be understood directly from the chattering nature of the collision dynamics. Of course, the precise value of the energy transfer rate coefficient for a particular system will depend on the full details of the interaction potential.

Lastly, in this section, we note that the energy E in (8)–(10) can in fact be one of several different kinds: it can refer to any of

(1) The *total* energy of the substrate (which is what is used in figures 2–5).

(2) The *rotational* energy of the substrate. This is useful for computing falloff curves when the conservation of the J quantum number (angular momentum conservation) of the master equation must be taken into account (Forst 1973, Smith and Gilbert 1988, Smith, McEwan and Gilbert 1989). When the moment of inertia of the activated complex significantly exceeds that of reactant, one needs to have information about the rate of collisional energy transfer involving two-dimensional (conserved) external rotational energy, E_{rot}. This is achieved (Whyte and Gilbert 1989) by determining the conserved rotational component as follows. One diagonalizes the inertia tensor I and transforms the resulting angular velocity vector ω to the principal axis system. E_{rot} is then given by $(I_{\mathrm{a}}\omega_{\mathrm{a}}^2+I_{\mathrm{b}}\omega_{\mathrm{b}}^2)/2$, where I_{a} and I_{b} are the principal moments of inertia corresponding to the two-dimensional inactive rotor, and ω_{a} and ω_{b} are the corresponding angular speeds. Since vibration changes the value of E_{rot} even at infinite separation, this quantity must be averaged over the longest vibrational period once the two moieties have reached a sufficiently large separation.

(3) The energy of active modes, i.e. the total energy less the energy of the two-dimensional (conserved) external rotation E_{rot}. This energy of active modes is that which may be used in an isolated molecule to undergo reaction.

Trajectory simulations can be used to explore the rates of different types (total, internal and rotational) of energy transfer, data which as yet are not available from experiment. Such data are starting to be accumulated (Clarke *et al.* 1991). As yet, no obvious interrelations or trends with regard to the type of energy transfer being measured have been discovered, except the following.

(1) Average internal, rotational and total mean-squared energy transfer values for thermal collisions involving monatomic bath gases are all of similar magnitude: of the order of a few $k_B T$. One important implication of this is that it can often be used to provide comparatively simple solutions of the master equation incorporating angular momentum conservation (Smith and Gilbert 1988).

(2) The variation of the mean-square energy transfer rate with the translational energy of the bath gas [i.e. using $\delta(E_T - E'_T)$ instead of a thermal distribution in (8), giving all bath gas molecules the same translational energy E'_T] shows (Clarke *et al.* 1991) a comparatively weak dependence on E'_T. For example, the mean-square rate of energy transfer for azulene colliding with Xe is found to vary approximately as $(E'_T)^{0 \cdot 4}$ for $E'_T < 2\,\text{kcal mol}^{-1}$, and as $(E'_T)^{1 \cdot 1}$ for $2 \leqslant E'_T < 10\,\text{kcal mol}^{-1}$. From (8), it can be shown (Clarke *et al.* 1991) that this 'microcanonical' dependence of the mean-squared rate on translational energy implies the same exponents for the dependence of the thermal ('canonical') mean-squared rate on temperature. That is, these simulations suggest that the *temperature dependence of the mean-square energy transfer rate is weak.*

(3) The dependence of the second moment $R_{E',2}$ (or $\langle \Delta E^2 \rangle$) on initial substrate energy E' is also quite weak, e.g. a variation of only *c.* 20% as E' varies over the range 3000 to 30 000 cm^{-1}. Note however that the corresponding first moments show a strong E' dependence; however, as will be given in detail in section 6, a knowledge of $R_{E',2}$ is sufficient to specify the value of $R_{E',1}$, and hence the energy variation of the first moment is inherent in the lack of E' variation of the second moment.

It is essential to make two reservations with regard to trajectory calculations. First, the relevance to experiment depends on the *correctness of the assumed potential function.* In favourable cases, the sensitivity to the assumed potential is not very strong; in others, it is. A commonly-used potential is a valence force field for the internal Hamiltonian of the substrate and a Lennard-Jones atom/atom interaction between the substrate and the bath gas. Current comparisons between theory and experiment (see below) suggest that this can yield values for $R_{E',2}$ which are of an acceptable accuracy provided that the bath gas is not too light (e.g. it seems to be invalid for He and Ne, but valid for heavier bath gases). Qualitative and quantitative information on the form of typical substrate/bath gas potential functions is at present lacking, and should be an important area for future research. Second, there may be significant *quantum effects.* This second point will be discussed in section 7.

Before concluding this section, we note that, instead of determining energy transfer rates from trajectories and then using the results in solution of the master equation, an alternative numerical technique (Bruehl and Schatz 1988) is to solve *both* the energy transfer *and* master equation problems simultaneously. The computational requirements are approximately the same as those for implementation of the two techniques separately. The simultaneous technique is however entirely numerical, and does not permit a physical interpretation of the average energy transfer rate coefficients.

3. Models for the collision number

As stated above, *a priori* calculations of the energy transfer rate coefficient, or of its moments, do not require any reference to a collision frequency. There is no need ever to define a 'collision', and indeed (since deflections will occur for trajectories of arbitrarily large impact parameters for any real potential) it is impossible to make a rigid definition of a collision for anything except those of hard spheres (or other artificial potentials of finite range). However, all current models for the energy transfer make use of *per collision* quantities, as expressed by the factorization of (1). This invokes the intuitively appealing concepts of the average energy, and root-mean-square (r.m.s.) energy, transferred per collision. These quantities would be expected to be semi-quantitatively deduced from approximate models and/or from comparison with data for similar collision partners. For such purposes, it is useful to examine the approximate separation of $R(E, E')$ into Z and $P(E, E')$, and to have models for both these quantities separately. The notion of a collision number is the object of this section.

The total collision number Z can be defined as the integral of $R(E, E')$ over all final energies E. However, as is apparent from figure 3, this integral may in fact be *infinite* because of the elastic peak in $R(E, E')$, even though this elastic peak does not contribute to the overall reaction rate. However, the separation into a probability and collision number requires one to have a physically reasonable means of defining an appropriate Z, and, moreover, that this should lead to a finite value for this quantity.

The basic assumption that would enable one to make a valid definition of a collision number is the following: that the variation with impact parameter b of the rate coefficient for energy transfer can be assumed negligible beyond some maximum value $b_{\max}$. One can then use this $b_{\max}$ to define a collision number for energy transfer, by putting $d = b_{\max}$ in (11). The simplest case would be if the pseudo-opacity function of (13) were a simple step function, or at least if one could specify some $b_{\max}$ beyond which energy transfer is negligible and which also corresponds to some physically reasonable definition of a collision.

This assumption of being able to define a $b_{\max}$ can be tested against the results of classical trajectory calculations. Figure 5 showed the dependence of $R_{E',2}$ upon the maximum impact parameter. One sees that energy transfer in fact does *not* suddenly cease at a particular impact parameter. However, it is also apparent that the energy transfer rate coefficient indeed assumes negligible values beyond a sufficiently large impact parameter, which is the order of (although significantly greater than) the hard-sphere radius. Hence an *approximate* separation of the energy transfer rate coefficient into a total collision number and a probability does have some practical meaning. In general, one would expect the form of $p(b)$, and hence of $b_{\max}$ and $Z(E')$, to depend on the initial energy E'. Such a possibility is explicitly ignored in most treatments.

The total collision number could always be found by generating plots such as figure 5, and making some arbitrary but consistent definition of where to define $b_{\max}$, but this would defeat the purpose of finding approximate models, and it is necessary to resort to a semi-empirical treatment.

The simplest approach to finding a maximum impact parameter would be the hard-sphere collision number; however, it is apparent from figure 5 that this is inadequate (since the hard-sphere diameter corresponding to the potential used to generate figure 5 is about 5 Å). Suppose, as an improvement, one were to use the spherically-average potential, and find the total elastic collision rate, either classical or quantum mechanical? One problem here is that the total classical elastic collision rate is *infinite* (although clearly our classical *inelastic* energy transfer rate is well defined, as is apparent from figure 5 and the well behaved convergence of (9) as $b_{\max}$ is taken to arbitrarily high values). Moreover, the total quantum elastic rate (Bernstein 1966, Child 1974), although finite, is extremely large, and corresponds to maximum impact parameters much greater than those contributing to the energy transfer processes under consideration.

This difficulty can be overcome (Kohlmaier and Rabinovitch 1962), albeit in a non-rigorous way, by using the fact that the classical expression for the *viscosity* is finite, even for potentials such as the Lennard-Jones function that have an infinite range. Now, the classical viscosity for a realistic potential is related to the hard-sphere value by a simple factor, the collision integral. Since viscosity represents momentum- and energy-transfer phenomena, one then empirically assumes that this same collision integral can be used to deduce a total collision number for energy transfer in the type of system under consideration. One has (e.g. Present 1958)

$$Z_{\text{real}} = Z_{\text{HS}}\Omega^*_{2,2}, \tag{15}$$

where $\Omega^*_{2,2}$ is a reduced collision integral. For a Lennard-Jones potential with parameters σ and ε, this may conveniently be approximated by (Neufeld, Janzen and Aziz 1972)

$$\Omega^*_{2,2} = \frac{1{\cdot}16145}{(T^*)^{0{\cdot}14874}} + \frac{0{\cdot}52487}{\exp(0{\cdot}7732\,T^*)} + \frac{2{\cdot}16178}{\exp(2{\cdot}437887\,T^*)}, \tag{16}$$

where $T^* = k_B T/\varepsilon$. The differences between the collision frequencies calculated from the hard sphere and (15) are not large at high temperatures, but are of the order of a factor of 2 at low ones. It is apparent from figure 5 that the maximum impact parameter defined from (15) and (11), by putting

$$d = \sigma(\Omega^*_{2,2})^{1/2}, \tag{17}$$

does indeed define a maximum impact parameter that encompasses the range contributing significantly to energy transfer.

There are some experimental results (e.g. Lawrance and Knight 1983) on total energy transfer rate coefficients to test against the above model. In these experiments, a molecule of moderately large size was prepared in a single rovibronic level to give a moderately high density of states. The total energy transfer rate coefficient was then found from the time evolution of the absorption intensity from the initial state, in the presence of added bath gas. The total energy transfer rate coefficient was found to be adequately approximated by the Lennard-Jones expression given above, except when the bath gas was very light (He or H_2). The origin of this may perhaps be the inapplicability of the Lennard-Jones potential for the lightest bath gases (see below).

For systems involving ion/molecule collisions, the interaction potential is quite different from the Lennard-Jones 12–6 model, and alternative formulae must be used. The simplest of these is the well-known Langevin expression for the collision between an ion and a bath gas which has no dipole moment

$$Z_{\text{ID}} = 2\pi q\left(\frac{\alpha}{4\pi\varepsilon_0\mu}\right)^{1/2}. \tag{18}$$

Here q is the electronic charge, α the polarizability of the bath gas, and ε_0 the permittivity of free space. Equation (18) yields a collision number which is considerably greater than that for a hard sphere or Lennard-Jones interaction, as to be expected because of the long-range nature of the interaction potential. However, there are at present no adequate experimental data or classical simulations for collisional energy transfer involving highly excited ionic species, and it is only speculation that the assumptions leading to the adoption of such an expression (viz., that the form of $p(b)$ is qualitatively similar to that of figure 5, with b_{max} corresponding to (18)) are justified. The methodology discussed above should therefore only be used with extreme caution for collisions involving a highly excited ionic species and a bath gas, and experimental and classical trajectory calculations for such systems are an important area for future work.

4. Models for energy transfer: functional forms

As stated above, it is useful both for phenomenological understanding and for purposes of fitting and predicting data to factorize $R(E, E')$ into a collision number Z and a probability of energy transfer per collision, $P(E, E')$. We now examine some of the approximate models employed for $P(E, E')$. Attention here is confined to systems where the substrate contains more than a few atoms: here, a classical statistical models are quantitatively applicable. A variety of theoretical approaches have been developed to describe energy transfer among small (diatomic or triatomic) species (reviewed by Orr and Smith 1987) where quantum effects are important and statistical treatments are invalid.

We begin with more detailed examination of the collision dynamics as exemplified in figures 1 and 2. The Hamiltonian for the *entire* substrate/bath gas system is

$$H_{tot} = H_{substrate} + V + H_{bath\ gas}. \tag{19}$$

Here $H_{substrate}$ is the Hamiltonian for the isolated molecule; $H_{bath\ gas}$ is the Hamiltonian of the bath gas; and V is the interaction potential between the two moieties. $P(E, E')$ is the probability that the value of $H_{substrate}$ after the collision is E, given that its initial value is E'. The dynamics of the system are described by the time variation of $H_{substrate}$ *during* the collision; figure 2 shows a typical variation of the substrate energy $H_{substrate}(t) \equiv E_i(t)$, for a polyatomic substrate colliding with a monatomic bath gas. These show some obvious features:

(1) The collision is short: *c.* a picosecond or less. This time is too short for randomization of energy between the two moieties, but is significantly longer than a typical vibrational period.

(2) The substrate energy undergoes a large number of oscillations during the collision; these oscillations are not apparently of constant phase or amplitude, and will be discussed in more detail in connection with the biased random walk collision model below.

(3) The qualitative features of $R(E, E')$ must also be borne in mind: (*a*) The functional form for $P(E, E')$ should ideally have an elastic peak [although strictly speaking this will not contribute to most experimental observations, and indeed is precluded by the approximations involved in factorizing $R(E, E')$ into a *finite* collision number a probability per collision]. (*b*) $P(E, E')$ should decrease for large energy differences between initial and final states. (*c*) It must obey microscopic reversibility, (7). (*d*) The presence of supercollisions should also be included.

We now consider specific models for $P(E, E')$, bearing in mind this dynamical behaviour. There are two objectives here. The first is to obtain information on the general type of *functional form* for this quantity, e.g. if it can be approximated by an exponential or Gaussian. The second is to obtain reliable quantitative estimates of *parameter values* to use in these functional forms for the purposes of predicting or fitting experimental data. It will emerge that no approximate model obeys all the criteria set out above, although some models do satisfy most of them: in particular, the biased random walk model, and the impulsive ergodic collision theory model, furnish (for different situations) curate's eggs which are edible.

4.1. *Exponential-down model*

This model is given by

$$P_{\text{EXP}}(E,E')=\frac{1}{N(E')}\exp\left(\frac{-|E-E'|}{\langle\Delta E_{\text{down}}\rangle}\right),\qquad E<E', \tag{20}$$

where $N(E')$ is a normalization constant determined by (2), and with the form for $E>E'$ being fixed by microscopic reversibility, (7). Equation (20) satisfies the physical requirement that it decreases for sufficiently large $|E-E'|$, but otherwise has no particular basis in any model for the collision dynamics. A variant is the double-exponential model

$$\begin{aligned} P_{\text{EXP}}(E,E')&=\frac{1}{N(E')}\exp\left(\frac{E-E'}{\alpha}\right),\qquad E<E',\\ P_{\text{EXP}}(E,E')&=\frac{1}{N(E')}\exp\left(\frac{E'-E}{\gamma}\right),\qquad E>E', \end{aligned} \tag{21}$$

where the quantity γ is determined by microscopic reversibility, but is assumed to be energy-independent. One can approximate γ to be energy-independent if $f(E)$ is approximately exponential over the energy range of interest (e.g. Troe 1977). In such cases, the double-exponential model has the advantage that an approximate analytical solution of the master equation can be obtained (e.g. Troe 1977). It is therefore often employed to fit experimental data.

4.2. *Biased random walk* (*BRW*) *model*

This model (Gilbert 1984, Lim and Gilbert 1986, 1990c) takes account of the oscillations in $E_i(t)$ noted above, and of constraints imposed by microscopic reversibility and energy conservation; however, it takes no account of supercollisions. It is deduced as follows.

$E_i(t)$ shows a large number of apparently uncorrelated oscillations during the collision. This is because the vibrational phases of the different modes of the highly excited substrate will be random, and thus any group of atoms will show quasi-random motion. This in turn will be reflected by the motion of the bath gas atom as it interacts with these atoms during a collision (figure 1).

If the time variation of $E_i(t)$ during a collision is indeed random, then the required probability distribution can be obtained from the theory of the diffusion of a Brownian particle (e.g. McQuarrie 1976). That is, one can treat the motion as being a (diffusive) *random walk*, representing the collision dynamics, although this takes place in 'energy space', not in the ordinary cartesian space of a Brownian particle. Because the constraint of microscopic reversibility specifies the relationship between the up and down steps (i.e. as if the drunken sailor, conventionally used to anthropomorphize a random walk, were staggering on a sloping path), the random walk is *biased*.

The test of randomness is provided by the autocorrelation function of the time derivative of $E_i(t)$, $\langle \dot{E}_i(t)\dot{E}_i(0)\rangle$. Figure 6 shows a typical energy derivative autocorrelation function, and indeed, one sees that on the timescale of a collision (say, a picosecond: see figure 2), the autocorrelation has decreased significantly, as expected if the energy exchange during the collision were pseudo-random. This suggests that the flow of energy between substrate and collider can be described as a diffusive process in the substrate energy during a collision event.

Given the assumption of a random walk constrained by microscopic reversibility, one obtains a simple functional form for $P(E, E')$, as follows. The 'diffusion coefficient' in energy space for random variation of $E_i(t)$ during a collision will be the integral of the energy derivative autocorrelation function (e.g. McQuarrie 1976)

$$D=\int_0^\infty \langle \dot{E}_i(t)\dot{E}_i(0)\rangle\,\mathrm{d}t. \tag{22}$$

The constraint on the random energy migration caused by microscopic reversibility is given by the equation for diffusion in an external field. Specifically, it is assumed that the distribution function $B(E_i, E', t)$ for the probability of the substrate, with initial energy E', having energy E_i at time t during the collision, is given by the Smoluchowski equation (e.g. McQuarrie 1976)

$$\frac{\partial B}{\partial t}=D\frac{\partial\left(zB+\dfrac{\partial B}{\partial E_i}\right)}{\partial E_i}, \tag{23}$$

where z is a quantity arising from microscopic reversibility. The probability distribution $P(E, E')$ can then be identified as $B(E_i \equiv E, E', t=t_c)$, where t_c is the duration of a collision. It is of course recognized that there is no rigorous way of defining the beginning and end of a collision, but this assumption of some sharp beginning and end is inherent in developing the model; figure 2 shows that the onset and cessation of significant bath gas/substrate interaction are indeed fairly sharp. If D and z are independent of t and of E_i, then the solution of (23) is

$$P_{\mathrm{BRW}}(E, E')=(4\pi s^2)^{-1/2}\exp\left[\frac{-(zs^2+E-E')^2}{4s^2}\right], \tag{24}$$

where the value of z is identified from the microscopic reversibility relation for $P(E, E')$ of (7) yielding

$$z=-\frac{\partial \ln f(E)}{\partial E}, \tag{25}$$

and the quantity s, which has the dimensions of energy, is given by

$$s^2=Dt_c. \tag{26}$$

The BRW form for $P(E, E')$ of (24) yields

$$\langle \Delta E\rangle=-s^2 z, \tag{27}$$

$$\langle \Delta E^2\rangle=2s^2+s^4z^2. \tag{28}$$

In many situations $s^4z^2 \ll 2s^2$, and so one can primitively approximate the second moment to $2s^2$ in the BRW model, i.e. the second moment appears in a natural (albeit approximate) way in the functional form for $P(E, E')$ of (24).

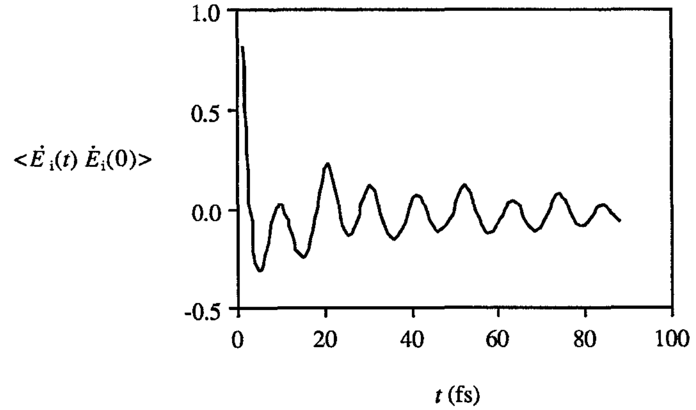

Figure 6. Normalized autocorrelation function $\langle \dot{E}_i(t)\dot{E}_i(0)\rangle$ for azulene/Ar collisions at $E' = 17\,500\,\mathrm{cm}^{-1}$. Redrawn from the data of Lim and Gilbert (1990c).

Equation (24) was derived with the assumption that z in (25) is energy-independent, i.e. that $f(E)$ is exponential. One regime where this assumption will always break down is for large molecules and/or at high temperatures, when $f(E)$ goes through a maximum. Under those circumstances (Gilbert and Oref 1991), it is acceptable to assume $f(E)$ to be Gaussian

$$f(E) = \frac{1}{2\pi^{1/2}c}\exp\left[-\left(\frac{E-\bar{E}}{2c}\right)^2\right], \tag{29}$$

where c and $\bar{E}$ are constants determined from the actual population distribution. Applying the same treatment used to obtain (24), one obtains (with minor but very accurate approximations)

$$P_{\mathrm{BRW}}(E, E') = \left(\frac{1}{4\pi c^2(1-q^2)}\right)^{1/2} \exp\left[\frac{-[E-\bar{E}-(E'-\bar{E})q]}{4c^2(1-q^2)}\right] \text{(high temperature)}, \tag{30}$$

where $q = \exp(-bt_c)$ and b is the solution of the equation $\exp(-bt_c) = (D/2c^2b) - 1$. It is noteworthy that if one takes the limit of very short collisions ($t_c \rightarrow 0$), then the right-hand side of (30) reduces to $\delta(E-E')$, i.e. no energy transfer, just as one expects for very short, i.e. very weak, collisions. If on the other hand one takes the limit of extremely long collisions ($t_c \rightarrow \infty$), then the right-hand side of (30) reduces to that of (29), i.e. to $f(E)$, which is the strong-collision form. Hence the high temperature functional form of the BRW model has the pleasing characteristic of having infinitely weak and strong cases as the appropriate limits for very short and very long collisions.

Although not considered further here, it should be noted that the BRW model is also able to yield useful information on the functional form for the dependence of collisional *rotational* energy transfer on initial and final rotational energy (Smith and Gilbert 1988).

4.3. *Strong collision model*

The strong collision model for $P(E, E')$ assumes that the collision probability is proportional to the equilibrium population of the *final* energy, and independent of the *initial* energy

$$P_{\mathrm{SC}}(E, E') = f(E), \qquad E < E', \tag{31}$$

where $f(E)$ here has for convenience been normalized so that $\int f(E)\mathrm{d}E=1$. This functional form was often used because it leads to a simple solution of the master equation (e.g. Gilbert and Smith 1990). However, the model is completely unphysical. Because $f(E)$ is usually a decreasing function of substrate energy E, the strong collision model implies that a molecule having a very high energy is most likely to finish with a very low energy after a single collisional encounter. It therefore predicts extremely large values of $\langle\Delta E\rangle$: values of the order of $10^4\,\mathrm{cm}^{-1}$, which is one or more orders of magnitude above those actually observed. This error can be partially (but improperly) corrected through a 'collision efficiency' β, which assumes that only one in every $1/\beta$ collisions actually transfers energy, but that the probability is still greatest for going to low energies from high ones. This is in qualitative contradiction to trajectory simulations. The only case where the strong collisional model is very approximately applicable is where the bath gas is a very large polyatomic, since then the falloff curve predicted by the strong collision model is indistinguishable from that found for a physically realistic form for $P(E,E')$.

4.4. *Impulsive ergodic collision theory*

These models are based upon the ideas inherent in the strong collision model, but take better account of the actual collision dynamics. These models assume some form of ergodicity between the degrees of freedom of substrate and bath gas. Now, this cannot be accurate for many situations, for example when the bath gas is not a large polyatomic (since then the collision is too short for significant randomization of the energy between the substrate and the bath gas). Such models may however be valid when the bath gas is a moderately large polyatomic, and indeed in such cases the results can be in acceptable accord with experiment. The best of these ergodic models is the 'impulsive ergodic collision theory' (IECT) of Nordholm and co-workers (Schranz and Nordholm 1981), which assumes that the collision is ergodic in the *kinetic energy* alone (rather than the kinetic plus potential energy). Given this assumption, one can deduce the probability of energy transfer in terms of ratios of the densities of states of *translational* degrees of freedom of substrate and bath gas before and after the collision. Appropriate ensemble averaging and approximate evaluation of the translational densities of states yields the following form for $P(E,E')$

$$P_{\mathrm{IECT}}(E,E')=\frac{1}{Q}\int_{\max(0,K-K')}^{\infty}\mathrm{d}K''\,\rho_1(K)\rho_2(K''+K'-K)\frac{\rho_2(K'')\exp(-K''/k_{\mathrm{B}}T)}{\rho_{12}(K'+K'')},\quad(32)$$

where K refers to kinetic energy, ρ refers to densities of states, the subscripts 1, 2 and 12 refer to substrate, bath gas and the combined system respectively, and the partition function

$$Q=\int\mathrm{d}K\,\rho_2(K)\exp(-K/k_{\mathrm{B}}T).$$

5. Models for energy transfer: parameter estimation

We next consider how the parameters required in the approximate models for $R(E,E')$ discussed in the preceding section can be evaluated, for the purposes of predicting and fitting experimental data, and, more importantly, in gaining phenomenological understanding. Note that the *exponential* model, because it has no physical basis, does not provide any *a priori* means to estimate the requisite energy transfer parameter (i.e. $\langle \Delta E_{\mathrm{down}} \rangle$ in (20)). The *strong collision* model contains no parameters except those required for the calculation of $f(E)$, namely, the vibrational frequencies and rotational constants of the substrate.

The *biased random walk* model is written in terms of a single parameter s, (24), which in turn requires the collision time t_c and the 'energy-space diffusion coefficient' D. Recent work (Clarke *et al.* 1991) has shown that these can be obtained with quite acceptable reliability using what has been denoted 'Model B' (Lim and Gilbert 1990c). This approximate treatment of the dynamics is as follows (see Lim and Gilbert 1990c, for further details).

First, the collision time is taken to be the average time for traversing the spherically averaged substrate molecule/bath gas interaction potential $V_{\mathrm{av}}(r)$, starting from a closest interaction distance d, and having translational energy E_{av}

$$t_c=(2\mu)^{1/2}\int_d^{r_0} \mathrm{d}r\left[E_{\mathrm{av}}-V_{\mathrm{av}}(r)-E_{\mathrm{av}}\left(\frac{b_{\mathrm{av}}}{r}\right)^2\right]^{-1/2}. \tag{33}$$

Here μ is the substrate/bath gas reduced mass ($\mu^{-1}=m_{\mathrm{subs}}^{-1}+m_{\mathrm{bg}}^{-1}$, where the terms on the right-hand side are the molecular weights of substrate and bath gas respectively), $b_{\mathrm{av}}=\frac{2}{3}d$ is an average impact parameter, and r_0 is the classical turning point (i.e. where the quantity in square braces in (33) is zero). E_{av} in 'Model B' is taken as the average substrate molecule/bath gas translational energy

$$E_{\mathrm{av}}=2k_{\mathrm{B}}T, \tag{34}$$

(recall that this is $2k_{\mathrm{B}}T$ rather than the usual $1{\cdot}5k_{\mathrm{B}}T$).

The next step is to specify D, which starts with (22). We utilize the standard theoretical treatment of Brownian motion, to assume that the time evolution of E_i during a collision is given by a generalized Langevin equation

$$\frac{\mathrm{d}^2E_i}{\mathrm{d}t^2}=-a-\int_{-\infty}^{t} K(\tau)\dot{E}_i(t-\tau)\,\mathrm{d}\tau+X(t), \tag{35}$$

where a is a quantity related to z, $X(t)$ is a randomly fluctuating 'force', and $K(t)$ a memory kernel. The next supposition is that $K(t)$ is exponential

$$K(t)=(A^2+C^2)\exp(-2At). \tag{36}$$

Solution of (35) then yields

$$\langle \dot{E}_i(t)\dot{E}_i(0)\rangle=\langle \dot{E}_i^2\rangle\exp(-At)\left(\cos(Ct)+\frac{A}{C}\sin(Ct)\right). \tag{37}$$

After substituting (37) into (22), and then using (26), one has

$$s^2=\langle \dot{E}_i^2\rangle t_c\frac{2A}{A^2+C^2}. \tag{38}$$

The quantities then to be determined to yield the parameter s are $\langle \dot{E}_i^2\rangle$, t_c, A and C. C, which determines the rate of oscillations in the autocorrelation function (figure 6), is taken to be given by the highest vibrational frequency, ν_h, of the substrate molecule (this is usually a C–H stretch)

$$C=2\pi\nu_h. \tag{39}$$

A, which gives reciprocal of the decay time of the autocorrelation function, is estimated by noting that it is impulsive interactions which dominate the energy transfer, and that these impulsive interactions are strongest at the classical turning point of an atom/atom interaction. The decay time is therefore approximated as that occurring when a constant average force F acts on an average or 'local' atom/atom harmonic oscillator. If the energy involved is denoted $E(t)$, then the reciprocal of the decay time is given by the short-time limit of $E^{-1}\,\mathrm{d}E/\mathrm{d}t$ (this is found simply by treating the energy as *that of a harmonic oscillator under the influence of an external constant force). If the* initial energy is E_{av}, and the mass of the oscillator denoted m_b, then one finds

$$A=F\left(\frac{2}{m_b E_{\mathrm{av}}}\right)^{1/2}. \tag{40}$$

We take m_b as that appropriate for interaction between an average substrate atom and all the rest of the substrate, i.e. the reduced mass of a substrate atom, $\bar{m}=m_{\mathrm{subs}}/n_{\mathrm{atoms}}$ (where the substrate molecule contains n_{atoms} atoms), and the difference between m_{subs} and $\bar{m}$

$$\frac{1}{m_b}=\frac{1}{m_{\mathrm{subs}}-\bar{m}}+\frac{1}{\bar{m}}, \tag{41}$$

(note that (40) corrects an error in (34 *b*) of Gilbert and Lim 1990c). F is estimated by noting that it is the changes at the classical turning point of each local atom/atom interaction that contribute most to the energy transfer, and thus hypothesizing that F is the absolute value of the force due to a local atom/atom effective potential at the turning point

$$F=\left|\frac{\mathrm{d}V_{\mathrm{loc}}^{\mathrm{eff}}(r)}{\mathrm{d}r}\right|_{r=r_0}. \tag{42}$$

Here $V_{\mathrm{loc}}^{\mathrm{eff}}(r)=V_{\mathrm{loc}}(r)+E_{\mathrm{av}}(b_{\mathrm{loc}}/r)^2$, where the average 'local' impact parameter $b_{\mathrm{loc}}=\frac{2}{3}\sigma_{\mathrm{loc}}(\Omega_{2,2}^{*})^{1/2}$, and (assuming for simplicity that the interaction is Lennard-Jones) σ_{loc} is the 'local' Lennard-Jones radius, i.e. $V_{\mathrm{loc}}(r)=4\varepsilon_{\mathrm{loc}}[(\sigma_{\mathrm{loc}}/r)^{12}-(\sigma_{\mathrm{loc}}/r)^6]$. The parameters σ_{loc} and $\varepsilon_{\mathrm{loc}}$ are taken as the averages of those of the substrate atoms (see Gilbert and Smith 1990 for examples).

The mean-squared rate of substrate energy change, $\langle \dot{E}_i^2\rangle$, is estimated as the product of the frequency ν_h and some average energy. This average energy is in turn approximated as the average kinetic energy E_{av} minus an average energy change per oscillation period, ΔV, with the restriction that ΔV not be less than $\frac{1}{2}E_{\mathrm{av}}$. This gives

$$\langle \dot{E}_i^2\rangle=\{\nu_h[E_{\mathrm{av}}-\min(|\Delta V|,\ \tfrac{1}{2}E_{\mathrm{av}}])\}^2. \tag{43}$$

ΔV is found as follows. Let $\Delta x=(2E_{\mathrm{av}}/k)^{1/2}$ be the distance moved by the oscillator, where k is an appropriate force constant. The diminution ΔV can be approximated as $\Delta x\,\mathrm{d}V_{\mathrm{loc}}/\mathrm{d}x$, evaluated at an average atom–atom distance x. The force constant can be approximated as $k=4\pi^2 m_{\mathrm{light}}\nu_h^2$, where m_{light} is the mass of the lightest atom (it is the lightest atoms that are responsible for the rapid oscillations). The average atom–atom distance x can be approximated as the mean of an outer value ($x/\sigma_{\mathrm{loc}}=\frac{2}{3}$, again assuming a Lennard-Jones local interaction and using the average impact parameter as above) and an inner one ($x/\sigma_{\mathrm{loc}}=1$): thus the average x is given by $x/\sigma_{\mathrm{loc}}=\frac{5}{6}$. One thus has

$$\Delta V=4\varepsilon_{\mathrm{loc}}\frac{\Delta x}{x}\left[-12\left(\frac{\sigma_{\mathrm{loc}}}{x}\right)^{12}+\left(\frac{\sigma_{\mathrm{loc}}}{x}\right)^{6}\right]=-34{\cdot}0\,\frac{\varepsilon_{\mathrm{loc}}}{\sigma_{\mathrm{loc}}\nu_h}\left(\frac{E_{\mathrm{av}}}{m_{\mathrm{light}}}\right)^{2}. \tag{44}$$

Equations (38)–(44), (33) and (34) furnish the complete expressions required to evaluate the parameter s (and hence other energy transfer parameters such as $\langle \Delta E \rangle$ and $\langle \Delta E^2 \rangle^{1/2}$); a program to evaluate this quantity is included in the UNIMOL suite (Gilbert, Jordan and Smith 1991).

While easy to evaluate numerically (requiring only a quadrature), these expressions are not physically transparent. It is useful to consider some approximations which lead to simpler order-of-magnitude expressions. First, in (38), one notes that usually $A^2 \ll C^2$, and so the former term may be ignored in the numerator. Next, one ignores the terms involving ΔV in (43). One then obtains simply

$$s^2 \approx \frac{t_c F}{2\pi^2}(k_B T)^{3/2}\sqrt{\frac{1}{m_b}}. \tag{45}$$

This simplified and approximate expression does indeed lead to physical insight. It states that the energy transfer is dominated by the force at the turning point of a local atom/atom repulsion. Using typical values $t_c \approx 10^{-12}$ s, $F \approx (5\text{–}10) \times 10^{-11}$ N, the latter derived from a Lennard-Jones potential using $E_{av} = 2k_B T$, etc., immediately gives a value of s of about $10^2\,\text{cm}^{-1}$ at $T = 300$ K. This simple estimate immediately explains the typical size of the energy transferred per collisions observed experimentally with monatomic bath gases: something no other approximate model is able to do. The dominant energy transfer process in a collision between a highly excited substrate and a bath gas consists of many atom/atom interactions, which are dominated by the ('local') repulsive wall of the interaction between the individual substrate and bath gas atoms. The 'energy leak' that constitutes the energy transfer process is caused by the force at this repulsive wall, the energy involved being the mean kinetic energy of the bath gas.

The *impulsive ergodic collision theory* model of (32) also leads to an explicit expression for the energy transfer. Evaluation of the partition functions yields

$$\langle \Delta E \rangle = [\alpha E' - \tfrac{1}{2}(n_2 + 2)k_B T]\frac{n_1 + 2}{n_1 + n_2 + 4}, \tag{46}$$

where $\alpha = (3n-3)/(6n-8)$ for linear substrates and $\alpha = (3n-3)/(6n-9)$ for nonlinear ones (n being the number of atoms in the substrate; $n_1 = 3n-5$; and, for a monatomic bath gas, $n_2 = 1$, while for a polyatomic bath gas, n_2 has the same form as n_1, n now being the number of atoms in the bath gas). Comparisons of the predictions of the IECT with experiment show agreement for large bath gases (say, ones containing more than ten atoms), but poor accord for monatomic and diatomic bath gases: the predicted values of $\langle \Delta E \rangle$ are typically an order of magnitude too high in this case. The reason for this behaviour is that the collisions involving large polyatomic bath gases are probably of sufficient duration for significant energy randomization to occur, but this is not the case with a mon- or diatomic bath gas.

With both the BRW and the IECT, evaluation of the expressions for the average energy transfer can be easily carried out using readily available parameters of the substrate and bath gas: a major advantage of the models.

6. Comparison of experiment, simulations and models

In the present article, we do not give any overview of experimental data on collisional energy transfer of highly excited molecules, a subject which has been extensively reviewed elsewhere (Gordon 1988, Tardy and Rabinovitch 1977, Quack and Troe 1977 and 1981, Holbrook 1983, Barker 1984, Oref and Tardy 1990, Hippler and Troe 1989). We here compare experimental data, classical trajectory simulations, and results from approximate models, (1) to test the adequacy of the assumed potential functions and the possibility of quantum effects (comparing trajectories and experiments) and (2) to test the dynamical assumptions involved in approximate models, by comparing them with trajectory data obtained using the same potential function.

It is essential to note that the latter comparison is a more valid test of the models than are direct comparison of their predictions with experiment. This is because there are three assumptions in comparing models with experiment: (1) the potential function is correct; (2) the dynamical approximations are correct; and (3) quantum effects are unimportant (assuming that the model is a classical one). If there is accord between a model and experiment it could imply either that all approximations are justified, or that there are self-cancelling errors present (an illustration of this will be presented below). However, by model/simulation comparison with the same potential function, it is possible to test the dynamical approximations in a proper fashion that can lead to improved understanding.

Prior to making such comparisons, some consideration should be given to the quantities to be compared. For example, 'direct' experiments give a measure (after calibration!) of the value of the first moment $\langle \Delta E \rangle$, whereas (as explained above) the second moment $\langle \Delta E^2 \rangle$ is more readily obtained from trajectories. However, the various measures can be readily interconverted if one assumes a functional form for $R(E, E')$. The interconversion is through direct numerical evaluation of the defining equations, (4); in implementing this, it is essential to take account of microscopic reversibility, (7), and normalization, (2), which means that interconversion involves the solution to a nonlinear integral equation (Gilbert and King 1980). Numerical methods for carrying out this solution are easily implemented (Gilbert and King 1980), and available as part of a public-domain computer package (Gilbert *et al.* 1991).

It is found that this interconversion does not depend strongly on the assumed functional form, as illustrated in figure 7. If one chooses to make such comparison with per-collision quantities (e.g. $\langle \Delta E^2 \rangle^{1/2}$) rather than the rate (e.g. $R_{E',2}$) which constitutes the true observable, it is essential (e.g. Lim and Gilbert 1990a) that comparison be made using the same collision number. Which measure one chooses is virtually a matter of taste (*de gustibus non disputandem*); because the second moment expresses the average absolute energy transferred per collision, and because it arises naturally in the BRW model, we here choose $\langle \Delta E^2 \rangle^{1/2}$ to make our comparisons.

In the same context, it is pertinent to note (Clarke *et al.* 1991) that experimental data on the variation of $\langle \Delta E \rangle$ with E', about which there has been considerable debate (e.g. Barker 1984), are consistent (when converted to corresponding values of the second moment) with values of $\langle \Delta E^2 \rangle^{1/2}$ that have only a slight variation with E'. If $\langle \Delta E^2 \rangle$ shows no (or little) variation with E', then the variation of $\langle \Delta E \rangle$ with energy is dictated entirely by the density of states of substrate, through (4) and (7) (see also figure 7 and accompanying discussion).

It is also noteworthy that energy transfer quantities measured in any experiment are in fact an *ensemble* average of quantities which are functions of the initial energy E' (Penner and Forst 1977). These ensemble averages are denoted $\langle\langle \Delta E^n \rangle\rangle$, etc.

$$\langle\langle \Delta E^n \rangle\rangle = \int_0^\infty \langle \Delta E^n(E') \rangle G(E')\,\mathrm{d}E', \tag{47}$$

where $G(E')$ is a normalized population distribution appropriate to the experiment under consideration. As discussed above (see Clarke *et al.* 1991), trajectory data

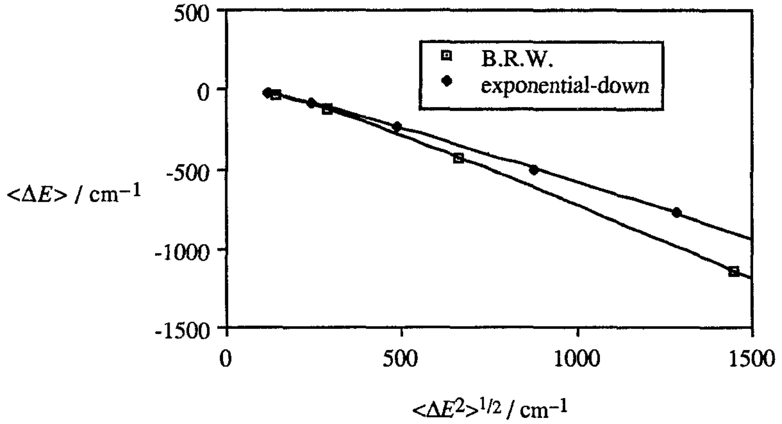

Figure 7. Comparison of mean and root-mean-square energy transferred per collision for azulene at 300 K, calculated with exponential-down and biased-random-walk forms for $P(E, E')$.

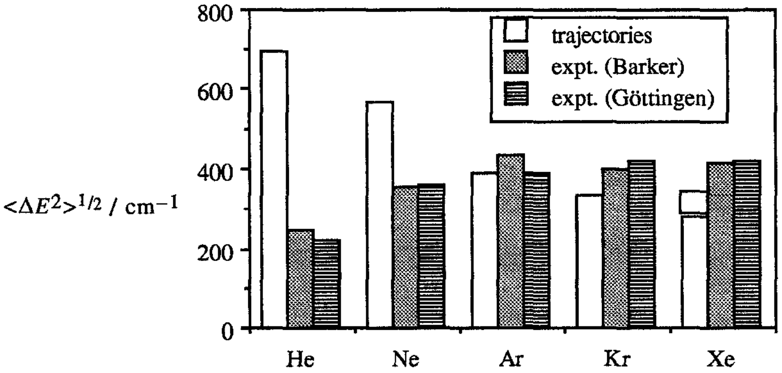

Figure 8. Trajectory (Lim and Gilbert 1990b, using 120 trajectories) and experimental (see text) values of $\langle \Delta E^2 \rangle^{1/2}$ (converted from rates using Lennard-Jones collision numbers of Hippler *et al.* 1989) for azulene/rare gas collisions at 300 K; initial azulene energy $= 30\,664\,\mathrm{cm}^{-1}$. Additional square on Xe trajectory results is component due to supercollisions found from running larger number of trajectories (Clarke *et al.* 1991).

indicate that the second moments ($R_{E',2}$ or $\langle \Delta E^2 \rangle$) are only weakly dependent on E'; hence the experimental ensemble averages for these quantities can be accurately taken as the values of the E'-dependent moments over a wide range of E'. However, the first moments, $\langle \Delta E \rangle$ or $R_{E',1}$, can depend strongly on E', and an experimental $\langle\langle \Delta E \rangle\rangle$ can only be equated to $\langle \Delta E(E') \rangle$ over a (possibly narrow) range of E'.

Figure 8 shows comparison of the results of trajectory simulations (Lim and Gilbert 1990b, originally carried out with 120 trajectories per bath gas) and experimental values (Yerram *et al.* 1990 and references therein, denoted Barker, which constitute the group of Barker and co-workers; Hippler, Otto and Troe 1989, and references therein, which constitute the Göttingen group). Results show $\langle \Delta E^2 \rangle^{1/2}$ for azulene initially at $E' = 30\,664\,\mathrm{cm}^{-1}$. The experimental data, which strictly refer to $\langle\langle \Delta E^2 \rangle\rangle$, actually refer to somewhat different energy distributions, but as stated it appears from trajectory data that the variation of the *second* (but not the first) moment with E' is small. The trajectory results for Xe include the increase of about 20% found when a very large number of trjectories is run, this increase being due to 'supercollisions' as discussed above (Thompson *et al.* 1991). These supercollision corrections to the original work of Lim and Gilbert (1990b) for gases other than Xe are as yet unavailable. It is seen that the accord between trajectory results and experiment is quite acceptable for the heavier bath gases, but poor for the lightest ones. It has been found (Lim and Gilbert 1990b) that making the assumed interaction potential significantly softer than Lennard-Jones can bring the trajectory results closer to experiment for the lightest bath gases, while making insignificant changes to the results for the heavier ones. These results suggest that the true bath gas/substrate potential function may be of a softer (e.g. exp-6) form (similar effects are found in rotational energy transfer, e.g. Evans *et al.* 1990). However, the comparison is also strongly suggestive that trajectory results for the heavier bath gases are a quantitative, and those for the lightest bath gases qualitative, reflection of the actual collision dynamics. This conclusion is supported by the observation of supercollisions in both experiment and trajectories, as discussed above.

Next, we consider the comparison with the predictions of the BRW model B, using the highly simplified description of the interaction dynamics embodied in (38)–(44), (33) and (34). The comparison is shown in figure 9. The BRW evaluations were carried out using the same interaction potential as was used for the full trajectory calculations, so the predictions of the simple model should be compared with 'exact' trajectory results rather than with experiment. It is seen that the BRW model gives quite good accord with the trajectory data for the same potential functions, for all except the lightest bath gases. This suggests that the parameterized form of the BRW model given in these equations should be of acceptable validity. The large underestimate for the lightest bath gases is ascribed to the substrate/bath gas interaction potential being too repulsive. Equation (45) suggests that the average energy transfer is extremely sensitive to the form of the repulsive wall, through the quantity F in that equation, which is the slope of the average atom/atom potential at the classical turning point.

While the underestimate of the amount of energy transfer for the lightest bath gases by the model B BRW is a cause for concern, by a coincidence it is in the opposite direction to the *over*estimate of the energy transfer when the trajectory results are compared to experiment. There is thus a cancellation of errors when the model is compared to experiment, as in figure 10. It is apparent that the approximate model is in surprisingly good accord with experiment! It is however emphasized that this is due to a fortunate cancellation of errors, and such accord cannot be relied upon to hold in all cases. Nevertheless, the BRW model B has now been tested in a wide variety of situations, and seems to give quite good results, as illustrated in table 1; the examples here are all those appearing in an illustrative compilation (Gilbert and Smith 1990). The BRW results are essentially of sufficient accuracy for falloff calculations.

7. Quantum effects

The theory discussed up to this point has been entirely classical. It is vital to assess the importance of quantum effects, since if these are significant the foregoing theoretical approach may be invalid. It will emerge that all current evidence suggests that quantum effects are in fact unimportant for most cases of interest involving collisions of a highly excited polyatomic: a conclusion which is of some relief, since it is evident that even a classical approach is a difficult one.

The basic reason for being able to ignore quantum effects arises from the enormous density of states of a highly excited polyatomic substrate, together with the strong

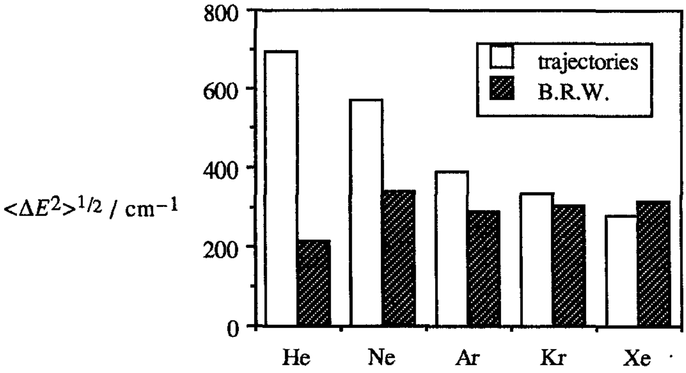

Figure 9. Trajectory and BRW model B$\langle \Delta E^2 \rangle^{1/2}$ for azulene/rare gas collisions at 300 K; initial azulene energy = 30 664 cm^{-1}. Supercollision corrections not included.

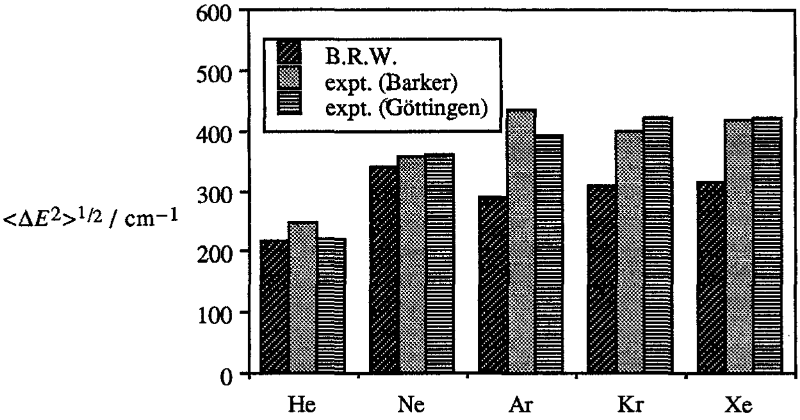

Figure 10. BRW model B and experimental $\langle \Delta E^2 \rangle^{1/2}$ (converted from rates using Lennard-Jones collision numbers of Hippler *et al.* 1989) for azulene/rare gas collisions at 300 K; initial azulene energy = 30 664 cm^{-1}.

Table 1. $\langle \Delta E^2 \rangle^{1/2}$ values (cm^{-1}) from experiment and BRW model B; bath gas is Ar. Experimental references and parameters from Table 5.2 of Gilbert and Smith (1990).

Molecule	$\langle \Delta E^2 \rangle^{1/2}$ (experiment)	$\langle \Delta E^2 \rangle^{1/2}$ (BRW)
Azulene	300	290
Toluene	260	300
Ethyl acetate	650	1000
CF_3I	200	210
CH_3CF_3	420	240
CH_3CH_2NC	390	520

coupling between these states engendered both by intramolecular anharmonicities in the substrate and (more importantly) the relatively strong couplings brought about during the passage of the bath gas. A typical energy change because of a collision is *c.* 10^2 cm^{-1}; since substrate densities of states can be in the range 10^5–10^{20} states per cm^{-1}, the system might pass through 10^7–10^{22} quantum states between the initial and final energies. Such a large change in quantum numbers involving coupled states should be a sufficient condition for the validity of a classical approximation to the dynamics. Nevertheless, this argument is more a pious hope than a rigorous proof, and we now turn to various tests of the supposition. After all, quantum effects in energy transfer for collisions involving *small* molecules are important, especially for low excitation energies, where the density of states is very small. These effects are known and relatively well understood (Orr and Smith 1987). In large molecules at low excitation energies (up to a few thousand cm^{-1}, much less than energies at which such molecules react) both experiment and theory indicate significant quantum effects (Hippler and Troe 1989); the observed trends can be explained semi-quantitatively in terms of quantum 'propensity rules' (Tang and Parmenter 1983, Kable, Thoman and Knight 1988). Could there also be significant quantum effects for collisions involving *large, highly excited* molecules?

Some quantification of the qualitative arguments for the unimportance of quantum effects is found in the calculations of Cochrane and Truhlar (1990), who compared quantum and classical calculations of $\langle \Delta E^2 \rangle$ for the collinear He/H_2 and He/Cl_2 systems. Any quantum effects would be expected to be very large in such systems, because of the light masses of one or more partners, and the low density of states arising from the small number of atoms and the collinearity. However, except in the case of extremely low energy transfer values, the quantum and classical results were typically within 30% of each other (the quantum result always being lower). Thus from the results of what might be described as a cruel test, it would appear that quantum effects are relatively unimportant in the systems forming the subject of this review, with their much higher dimensionality and density of states. Nevertheless, further evidence is certainly desirable, for the following reason.

In the comparison between the results of trajectory calculations and experiment for highly-excited azulene/rare gas collisions, there was good accord between trajectory and experimental results for all except the lightest bath gases: Ne and especially He. This was ascribed to the inaccuracy of the He/azulene interaction potential function employed (and indeed softening the repulsive wall brings about much better accord, as indeed is expected from (45)). However, quantum effects may play a role with a very light bath gas such as He. We now consider various possibilities.

(1) Quantum effects might arise from zero-point energy. An ordinary classical calculation takes no account of the zero-point energy of the polyatomic, which in the case of azulene is very large: about half the total substrate energy in the systems studied. Classically, there is no constraint for the energy in a particular mode not to go below its zero-point energy, whereas some quantum constraint exists, at least after the collision. Now, the energy transferred in a collision in these systems turns out to be only a small fraction of the total zero-point energy, so this contra-indicates a significant quantum effect due to this cause. Another argument is that experimental and trajectory results are in good agreement for the heavier bath gases: any azulene zero-point energy constraint should be equally operative for heavy and light bath gases. Finally, in

experimental studies (Brown, King and Gilbert 1988) of energy transfer differences between deuterated and undeuterated systems (e.g. *tert*-butyl bromide and *tert*-butyl bromide-d_9), only small differences were seen in the $\langle \Delta E^2 \rangle^{1/2}$ values of deuterated and undeuterated species, despite the very large differences in zero-point energy. The sum of these separate pieces of evidence strongly suggests that substrate zero-point energy cannot play any significant role in any quantum effect.

(2) Another possibility (Gilbert and Zare 1990) is that quantum effects could arise because of the interference involving the two matter waves giving zero angle of deflection; it is this interference that gives rise to a finite quantum total elastic cross section (Bernstein 1966). It is seen in figure 5 that a significant contribution to the energy transfer comes from impact parameters close to the Lennard-Jones radius, which is also close to the impact parameter at which a balancing between attractive and repulsive parts of the interaction potential gives zero angle of deflection. The same interference effects might be important in *inelastic* scattering. One means of answering this question would be through quantum calculations on the energy transfer. The only calculations to date of reasonable accuracy for such systems have been for *p*-difluorobenzene as substrate (Clary 1987), but here the substrate energy was very low. This is an important field for future work. An alternative test of quantum effects (Gilbert and Zare 1990) is to examine the behaviour when the mass of the bath gas is changed by isotopic substitution, i.e. the bath gas analogue of deuterating the substrate. Experimental studies of the effect of changing the bath gas from ^{4}He to ^{3}He (Toselli and Barker 1990) show only a small effect. However, any quantum interference phenomenon involving the bath gas would be expected to show a large change on such isotopic substitution. These experimental results strongly suggest that quantum interference effects can be discounted in the systems under consideration.

(3) Another possibility (Toselli and Barker 1990) is that quantum effects arise from the very different distribution functions in classical and quantum mechanics (e.g. a quantum oscillator in the lowest state is most likely to be found in the centre, while the corresponding classical one is most likely to be found at the ends). However, the experimental data on the effects of deuteration (which would significantly change the initial distribution), and the fact that corresponding trajectory studies (Clarke and Gilbert, to be published) mirror the small changes on isotopic substitution observed experimentally, again suggest that this effect does not significantly alter the energy transfer.

(4) Another suggestion (J. R. Barker, private communication) is that neither C–H nor C–D participate much in the actual (quantum) energy transfer process in these systems, because the average energy in these modes is very small, and hence the foregoing lack of effect on deuteration cannot be used to discount the importance of quantum effects. While this is an interesting possibility, the accord between experiment and trajectory results with heavier bath gases, when such an effect would also be operative, suggests that this may not be the case.

In summary, the sum of the evidence appears to indicate that quantum effects are unimportant in collisions between a highly excited polyatomic and a bath gas, and that the discrepancy between trajectory results and experiment for the lightest bath gases can be ascribed to the bath gas/substrate interaction potential being significantly softer than the Lennard-Jones r^{-12} atom/atom repulsion often used.

7. Summary

In this review, we have shown how the distribution function for the rate coefficient for energy transfer, $R(E, E')$, and its moments, can be obtained from classical trajectory simulations, and examined the physical insight to be gained from such calculations and from comparison with experiment. It is important to realise that one is calculating a *rate coefficient*, not an average energy transfer per collision, so that there is no need ever to try to define a 'collision'. The collision dynamics are best described as 'chattering': multiple interactions during a short ($c.\,10^{-12}$ s) collision between a bath gas and substrate, dominated by the repulsive part of the mutual interaction potential. There is also a small fraction (of the order of 1%) of supercollisions, which occur when a substrate atom is squashed between bath gas and substrate framework and which transfer a large amount of energy. Because the collisions are short-lived, there is no significant randomization of the energy distribution between the two entities (unless the bath is a very large polyatomic). Except for the lightest bath gases, trajectory data seem to be in accord with experiment, and the discrepancy observed for light bath gases can be ascribed to the bath gas/substrate interaction being softer than is commonly assumed.

The trajectory data can be used to develop and test approximate models for the energy transfer process. The most successful of these for collisions with a monatomic bath gas is the biased random walk model, which assumes that the energy transfer during the collision is random, subject to the constraint of microscopic reversibility. This leads to a Gaussian form for the probability of energy transfer. For large polyatomic bath gases, the impulsive ergodic collision theory model seems quantiatively applicable. The BRW model can be developed to yield a comparatively simple expression for the average energy transfer, with an accuracy that can be used to predict average energy transfer quantities of sufficient accuracy to be used in falloff calculations (although this is due to a fortunate cancellation of errors for the lightest bath gases). This model can also be used qualitatively to explain the magnitudes of experimental results.

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References

Barker, J. R., 1984, *J. phys. Chem.*, **88**, 11.
Bernstein, R. B., 1966, *Adv. chem. Phys.*, **10**, 75.
Brown, T. C., King, K. D., and Gilbert, R. G., 1988, *Int. J. Chem. Kinet.*, **20**, 549.
Bruehl, M., and Schatz, G. C., 1988, *J. chem. Phys.*, **89**, 770; *J. phys. Chem.*, **92**, 7223.
Bunker, D. L., and Hase, W. L., 1973, *J. chem. Phys.*, **59**, 4621.
Child, M. S., 1974, *Molecular Collision Theory* (London: Academic Press).
Clarke, D. L., Oref, I., Gilbert, R. G., and Lim, K. F., 1991, submitted to *J. chem. Phys.*
Clary, D. C., 1987, *J. chem. Phys.*, **86**, 813.
Cochrane, D. L., and Truhlar, D. G., 1990, *J. chem. Phys.*, **92**, 7716.
Evans, D. R., Evans, G. T., and Hoffman, D. K., 1990, *J. chem. Phys.*, **93**, 8816.

FORST, W., 1973, *Theory of Unimolecular Reactions* (New York: Acadmic Press).
GILBERT, R. G., 1984, *J. chem. Phys.*, **80,** 5501.
GILBERT, R. G., and KING, K. D., 1980, *Chem. Phys.*, **49,** 367.
GILBERT, R. G., and OREF, I., 1991, *J. phys. Chem.*, **95** (to be published).
GILBERT, R. G., and SMITH, S. C., 1990, *Theory of Unimolecular and Recombination Reactions* (Oxford and Cambridge, Mass.: Blackwell Scientific).
GILBERT, R. G., and ZARE, R. N., 1990, *Chem. Phys. Lett.*, **167,** 407.
GILBERT, R. G., JORDAN, M. J. T., and SMITH, S. C., 1991, Program UNIMOL (available from the first author).
GORDON, R. J., 1988, *Comments At. Mol. Phys.*, **21,** 123.
HIPPLER, H., and TROE, J., 1989, in *Gas Phase Bimolecular Processes*, edited by J. E. Baggott and M. N. Ashfold (London: Royal Society of Chemistry), p. 209.
HIPPLER, H., LINDEMANN, L., and TROE, J., 1985, *J. chem. Phys.*, **83,** 3906.
HIPPLER, H., OTTO, B., and TROE, J., 1989, *Ber. Bunsenges. Phys. Chem.*, **93,** 428.
HOLBROOK, K. A., 1983, *Chem. Soc. Rev.*, **12,** 163.
KABLE, S. H., THOMAN, J. W., and KNIGHT, A. E. W. K., 1988, *J. chem. Phys.*, **88,** 4748.
KECK, J. C., and CARRIER, G., 1965, *J. chem. Phys.*, **43,** 2284.
KING, K. D., NGUYEN, T. T., and GILBERT, R. G., 1981, *Chem. Phys.*, **61,** 223.
KOHLMAIER, G. H., and RABINOVITCH, B. S., 1962, *J. chem. Phys.*, **38,** 1692.
LAWRANCE, W. D., and KNIGHT, A. E. W., 1983, *J. chem. Phys.*, **79,** 6030.
LENDVAY, G., and SCHATZ, G. C., 1990, *J. phys. Chem.*, **94,** 8864.
LIM, K. F., and GILBERT, R. G., 1986, *J. chem. Phys.*, **84,** 6129.
LIM, K. F., and GILBERT, R. G., 1990c, *J. chem. Phys.*, **92,** 1819.
LIM, K. F., and GILBERT, R. G., 1990a, *J. phys. Chem.*, **94,** 72.
LIM, K. F., and GILBERT, R. G., 1990b, *J. phys. Chem.*, **94,** 77.
LIM, K. F., and HASE, W. L., 1990, *Program MARINER* (available through Q.C.P.E., or directly from K. F. Lim, Department of Chemistry, University of New England, Armidale, NSW 2351, Australia).
LÖHMANNRÖBEN, H. G., and LUTHER, K., 1988, *Chem. Phys. Lett.*, **144,** 473.
LUTHER, K., and REIHS, K., 1988, *Ber. Bunsenges. Phys. Chem.*, **92,** 442.
MCQUARRIE, D. A., 1976, *Statistical Mechanics* (New York: Harper and Rowe).
MORGULIS, I. M., SAPERS, S. S., STEEL, C., and OREF, I., 1989, *J. chem. Phys.*, **90,** 923.
NEUFELD, P. D., JANZEN, A. R., and AZIZ, R. A., 1972, *J. chem. Phys.*, **57,** 1100.
OREF, I., and TARDY, D. C., 1990, *Chem. Rev.*, **90,** 1407.
ORR, B. J., and SMITH, I. W. M., 1987, *J. phys. Chem.*, **91,** 6106.
PASHUTZKI, A., and OREF, I., 1988, *J. phys. Chem.*, **92,** 178.
PENNER, A. P., and FORST, W., 1977, *J. chem. Phys.*, **67,** 5296.
PORTER, R. N., and RAFF, L. M., 1976, in *Dynamics of Molecular Collisions, Vol. B*; edited by W. H. Miller (New York: Plenum).
PRESENT, R. D., 1958, *Kinetic Theory of Gases* (New York: McGraw-Hill).
QUACK, M., and TROE, J., 1977, *Specialist Periodical Reports Gas Kinetics and Energy Transfer, Vol. 2*, edited by P. G. Ashmore and R. J. Donovan (The Chemical Society: London).
QUACK, M., and TROE, J., 1981, *Int. Rev. Phys. Chem.*, **1,** 97.
SCHRANZ, H. W., and NORDHOLM, S., 1981, *Int. J. Chem. Kinet.*, **13,** 1051.
SHI, J., and BARKER, J. R., 1988, *J. chem. Phys.*, **88,** 6211, 6219.
SMITH, S. C., and GILBERT, R. G., 1988, *Int. J. Chem. Kinet.*, **20,** 307 and 979.
SMITH, S. C., MCEWAN, M. J., and GILBERT, R. G., 1989, *J. chem. Phys.*, **90,** 1630.
TANG, K. Y., and PARMENTER, C. S., 1983, *J. chem. Phys.*, **78,** 3922.
TARDY, D. C., and RABINOVITCH, B. S., 1977, *Chem. Rev.*, **77,** 369.
THOMSON, K. C., CLARKE, D. L., and GILBERT, R. G., 1991, *Chem. Phys. Letts.*, **182** (to be published).
TOSELLI, B. M., and BARKER, J. R., 1990, *Chem. Phys. Letts.*, **174,** 304.
TROE, J., 1977, *J. chem. Phys.*, **66,** 4745, 4758.
WHYTE, A. R., and GILBERT, R. G., 1989, *Aust. J. Chem.*, **42,** 1227.
YERRAM, M. L., BRENNER, J. D., KING, K. D., and BARKER, J. R., 1990, *J. phys. Chem.*, **94,** 6341.