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Statistical Theory of Collisional Energy Transfer in Molecular Collisions. *trans*-Stilbene Deactivation by Argon, Carbon Dioxide, and *n*-Heptane†

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Recent advances in experimental techniques have made it possible to measure the full conditional probability density $P(E, E')$ of the energy transfer between two colliding molecules in the gas phase, one of which is highly energized and the other in thermal equilibrium at a given temperature. Data have now become available for *trans*-stilbene deactivation by the three bath gas molecules Ar, CO_2, and *n*-heptane (C_7H_{16}). The initial energies of *trans*-stilbene are set to 10 000, 20 000, 30 000, and 40 000 cm^{-1}. The results show that exceptionally large amounts of energy are transferred in each collision. By application of our partially ergodic collision theory (PECT), we find that the energy transfer efficiency β_E ranges from a rather normal value of 0.15 for *n*-heptane at the highest excitation energy to 0.93—nearly in the ergodic collision limit—for the argon bath gas at high excitation energy. Generally, the PECT produces a good fit of the data except for the nearly elastic peak in the case of *n*-heptane, where PECT produces a rounded and downshifted peak in contrast to a sharply defined elastic maximum of the monoexponential functional fit produced from the original experimental data obtained by kinetically controlled selective ionization in the work of the group of Luther in Göttingen. This problem is analyzed and found to be related partly to the lack of treatment of glancing collisions in the theory with a remaining uncertainty due to the weak dependence of energy transfer efficiency on nearly elastic collisions. A summary of the present state of understanding shows that collisional activation and deactivation of reactant molecules is more efficient and more statistical than has been previously realized.

1. Introduction

Our understanding of chemical reactions can be traced back to contributions by Arrhenius[1] and Lindemann.[2] Arrhenius brought to us the realization that a chemical reaction nearly always proceeded over a potential barrier, because bonds had to be broken before new bonds were formed. Lindemann provided us with a mechanism by which we could understand the dependence on the medium pressure in gas-phase reactions. He showed how for unimolecular reactions the activation and deactivation of the reactant molecule could be treated as separable from the internal rearrangements at constant energy in the reaction mechanism. This insight led to an explanation of the pressure falloff of the unimolecular rate coefficient, i.e., the observation that the unimolecular reaction was of second order at low pressures when the activation step was the bottleneck, while at higher pressures, the reaction eventually "fell off" and became independent of gas pressure. Ever since, it has been a major goal to experimentally and theoretically resolve the collisional energy transfer between reactant molecules at elevated energies and medium molecules in thermal equilibrium. We want to know the conditional probability density $P(E', E)$ of finding the reactant molecule at energy E' after a collision which found it initially at energy E. The first steps were taken by Lindemann himself—who thought this probability density ought to be proportional to the Boltzmann factor $\exp(-E'/k_BT)$ and Hinshelwood[3] who introduced the so-called strong collision assumption (SCA), which meant that the reactant was assumed to be thermalized by the collision. This meant that the frequency of collisions became an empirical parameter far smaller than the collision frequencies generally used in gas kinetics.

About 40 years ago, Rabinovitch,[4−6] and a decade later, Troe,[7,8] and their co-workers ushered in the modern era in the unimolecular reaction field when they constructed and applied master equation theories based on microcanonical transition state theory[9,10] for the internal decay of the reactant molecule, but mathematical forms for the energy transfer kernel $P(E', E)$ recognized the general inefficiency of collisions in transferring energy. Thus, the weak collision master equations were developed and used with stepladder, exponential, or Gaussian forms of $P(E', E)$ depending on one or a few parameters determined empirically. The parameters were either used to fit the observed reaction rate coefficients or determined by fitting the energy transfer moments $\langle \Delta E \rangle$ and $\langle (\Delta E)^2 \rangle$ as determined in UV[11−13] and IR[14] experiments. The data were, however, of limited extent and accuracy and therefore unable to distinguish the true and detailed behavior of the energy transfer kernel. Apart from the general acceptance that collisions were weak, there was little understanding of how the energy transfer efficiency depended on the character of the two colliding molecules. The challenge of providing understanding and predictive capability in this important field of collisional energy transfer attracted theoretical analysis.[15−21] The ergodic collision theory (ECT)[22,23] was proposed as a more realistic strong collision limit where the colliding pair of reactant and medium molecule were assumed to end up in microcanonical equilibrium after the collision. It was apparent that the ECT still greatly overestimated the energy transfer efficiency, but it yielded results which correlated well with the trends seen in experimental data.[24] A series of extensions of the ECT was developed to account for the

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“nonergodicity” of the collisions and tested against experimental data and also against classical simulations of molecular collisions, which started to appear about 30 years ago.[25−28] While the documented weakness of the collisions and the presumed large quantum effects on the collision efficiency generally dampened interest in this early theoretical work, some revival arose when it was found that there were in both experiments[29−31] and simulations[32,33] evidence of tails in $P(E', E)$ of highly efficient collisions, which were called supercollisions. It became clear that the behavior of the energy transfer kernel was richer even than anticipated.

In the last years of the 20th century, a new method directly measuring the energy transfer kernel $P(E', E)$ for selected initial energies was developed in Göttingen by Luther and his collaborators,[34] and in 2000, the first publications appeared describing the KCSI (kinetically controlled selective ionization) method[35] and the results obtained for toluene colliding with one of a range of medium molecules.[36] The data were fitted to an energy transfer kernel of energy-dependent monoexponential form. For the first time, detailed and reliable information became available on the full form of $P(E', E)$. It thereby became possible to determine which of the many models employed could best capture the observed form of the energy transfer kernel. It was immediately clear that the simple exponential and Gaussian models previously favored in weak collision master equation calculations were unable to capture both the near elasticity and the tails of efficient collisions seen in experiments. We tested the PECT and found it to work remarkably well with only a minor disagreement around the elastic peak appearing for highly efficient reactant−medium pairs of molecules where the PECT predicts a peak shifted slightly but noticeably to lower final state energies.[37] A similar agreement between KCSI[38] and PECT results was found for azulene in collisions with a range of medium molecules.[39] Detailed analysis shows that the PECT form of the energy transfer kernel not only agrees with the KCSI-established long tails of efficient collisions smoothly attached to a dominant central peak, but also the shapes of peaks and tails are in reasonable agreement.[40] Thus, the supercollisions appear now to be a standard feature rather than an oddity, and the collisions—despite their significant inefficiency—are largely of a statistical nature responding to the complexities of the two colliding molecules, as if subsets of active degrees of freedom achieved microcanonical equilibrium. Interestingly, it also appears as if the collisions are not quite so inefficient as was generally assumed. In the case of biphenylene, we recently found that UV data on the average transfer collision indicate that the collision efficiency can reach well over one-half of the limiting ECT value.[40]

In the present study, we shall take advantage of new KCSI data on collisional energy transfer between *trans*-stilbene and the bath gases argon, carbon dioxide, and *n*-heptane.[41] These are by far the largest reactant molecules studied by the KCSI method so far, and we shall be able to see whether the high efficiency of biphenylene−argon collisions recurs for the even larger *trans*-stilbene reactant. This will indeed be verified. Since the amount of energy transferred per collision is very large when *trans*-stilbene is deactivated by *n*-heptane, we shall also analyze and attempt to solve the “downshifted peak problem” which is particularly prominent in these collisions. Although we shall be able to make it plausible that this disagreement is largely a result of a simple either hit or miss assumption in the PECT, which ignores the presence of glancing collisions, we emphasize that this problem requires deeper study which we hope to return to in the future. In the meantime, we shall show that from a practical point of view it is not difficult to cure this defect in the PECT representation of the energy transfer kernel.

2. The Partially Ergodic Collision Theory

The theory we have employed here is a member of a sequence of statistical theories which we shall briefly review. The original strong collision assumption introduced by Hinshelwood[3] amounted to the assumption—although not expressed in this way at the time—that the energy transfer kernel takes the form of a thermal final state energy distribution at the temperature of the bath gas, i.e.,

$$P(E', E) = \rho(E') \exp(-E'/k_BT)/Q(T) \tag{1}$$

where $Q(T)$ is the partition function

$$Q(T) = \int_0^\infty dE\rho(E) \exp(-E/k_BT) \tag{2}$$

and $\rho(E)$ is the density of interior (rotational and vibrational) states of the reactant molecule. This is, of course, generally a gross overestimate of the relaxation that occurs when a highly excited reactant molecule collides with a bath gas molecule at some temperature T. More reasonable but still a strong collision assumption is the idea that the two molecules, including their relative translation after the collision, are in microcanonical equilibrium with each other at the total energy defined by the sum of the initial energies E and E_M. This we will call the ergodic collision assumption, and the corresponding energy transfer theory is called the ergodic collision theory (ECT). This theory is based on the fact that, for the two noninteracting molecules in microcanonical equilibrium at the energy $E_{tot} = E + E_M$, the probability of finding the molecules with energies E' and $E_{tot} - E'$ is proportional to the product of their densities of states ρ and ρ_M at these energies

$$p(E_{tot}; E') = \rho(E')\rho_M(E_{tot} - E')/\rho_{tot}(E_{tot}) \tag{3}$$

and the total density of states is

$$\rho_{tot}(E_{tot}) = \int_0^{E_{tot}} dE\rho(E)\rho_M(E_{tot} - E) \tag{4}$$

Note that here we shall include the relative translational degrees of freedom in the medium molecule. The ECT prediction for $P(E', E)$ now follows by noting that the initial energy of the medium molecule is thermally distributed according to the probability density $p_M(T; E_M)$

$$p_M(T; E_M) = \rho_M(E_M) \exp(-E_M/k_BT)/Q_M(T) \tag{5}$$

We get the ECT prediction

$$P(E', E) = \int_{\max(E' - E, 0)} dE_M\, p(E + E_M; E')\, p_M(T; E_M) \tag{6}$$

The implementation requires densities of states to be evaluated for both the reactant and the medium molecule. This can be done within the assumption of quantized harmonic vibrations by exact count methods[42] or by our convenient thermodynamic method[43] which yields simple functional forms of type

$$\rho(E) = a(E + b)^c \tag{7}$$

with parameters a, b, and c determined from fits of thermodynamic properties.

As noted above, the ECT is a strong collision limit, so any realistic model of experimental data must include some form of nonergodicity, i.e., some limitation on the energy transfer leading to only partial redistribution of the energy in the collision. In the partially ergodic collision theory, we assume that there are subsets of active modes in both the reactant and the medium molecule, which relax microcanonically in the collision, while other modes are passive and unaffected by the collision. We take these active modes, for simplicity, to behave like classical rotational−vibrational modes. Thus, their densities of states take the forms

$$\rho_a(E) = C_a E^{(n_a-2)/2}$$

$$\rho_m(E) = C_m E^{(n_m-2)/2} \qquad (8)$$

Since the nature and precise density of states of these active modes are very much unknown at the moment, it is reasonable to use the simplest plausible form of density of states which measures the number of active modes and captures the corresponding rise in density of states with energy. In principle, we should now have developed the theory by first finding the probability density of active reactant energy given a fixed total energy E, $p_a(E; E_a)$, and then obtained the energy transfer kernel as

$$P(E', E) = \int dE_a \, p_a(E; E_a) \, P_a(E_a + E' - E, E_a) \qquad (9)$$

where $P_a(E'_a, E_a)$ is the ECT energy transfer kernel for the active degrees of freedom, which becomes

$$P_a(E'_a, E_a) = \int_{\max(E'_a - E_a,\, 0)} dE_m \frac{(E'_a)^{(n_a-2)/2}(E_a + E_m - E'_a)^{(n_m-2)/2}}{(E_a + E_m)^{(n_a+n_m-2)/2}} p_m(T; E_m) \qquad (10)$$

Here, the thermal probability density of active medium energy is

$$p_m(T; E_m) = E_m^{(n_m-2)/2} \exp(-E_m/k_BT) / \int_0^\infty dE E^{(n_m-2)/2} \exp(-E/k_BT) \qquad (11)$$

The probability density $p_a(E; E_a)$ is a result of the microcanonical equilibrium in the reactant molecule at energy E and can be recovered from the densities of states ρ and ρ_a at all energies up to E. We shall, however, use a simplified form valid if the passive modes can be regarded as a heat reservoir of much larger capacity than the active modes. This will normally be the case, but in the case of collisions approaching the ergodic limit of collision efficiency, as we shall see in some cases below, some significant error can be expected. In this "thermal reservoir" treatment of the reactant, the energy probability density for the active modes takes on canonical (i.e., thermal) form, but at a temperature $T(E)$ corresponding to the energy of the entire molecule as given by the equality

$$E = \langle E \rangle_{T(E)} = \int dE \rho(E) E \exp[-E/k_BT(E)]/Q[T(E)] \qquad (12)$$

For the high initial energies studied below, this temperature will be shifted far toward higher temperatures than that of the medium. The thermal approximation then yields the result

$$p_a(E; E_a) = p_a[T(E); E_a] = E_a^{(n_a-2)/2} \exp(-E_a/k_BT) / \int_0^\infty dE E^{(n_a-2)/2} \exp(-E/k_BT) \qquad (13)$$

The integral can be simplified as

$$\int_0^\infty dE E^{(n_a-2)/2} \exp(-E/k_BT) = (k_BT)^{n_2/2} \int_0^\infty dx x^{(n_a-2)/2} \exp(-x) = (k_BT)^{n_2/2} \chi(n_a) \qquad (14)$$

For even integers $n_a = 2, 4, ...$, we have $\chi(n_a) = (n_a/2)!$

Finally, we shall introduce an approximation to the parametrization of the active modes in terms of n_a and n_m. It is far easier to handle the determination of one rather than two parameters, so we shall let n_m be determined by n_a. This can be done with some physical justification, since it makes sense that the number of modes making contact in the collision is roughly the same for both molecules. We must, however, recall that the relative motion between the two molecules is taken as belonging to the medium molecule which thereby becomes more able to receive energy in the collision. It is generally found that energy transfer to translations is more efficient than to rotations which in turn are more active in energy transfer than vibrations. Thus, we have used the parameter reduction

$$n_m = n_a + 1 \qquad (15)$$

in our first two papers,[37,39] except for the inert gas medium molecules, for which we set $n_m = 1$. The parameter n_a, the "number of active reactant modes", has been fitted to the average energy transferred per collision $\langle \Delta E \rangle$, as observed in the experiments. An important measure of collision efficiency β_E is defined as the ratio of the experimentally observed to the ECT predicted values of $\langle \Delta E \rangle$, i.e.,

$$\beta_E = \langle \Delta E \rangle^{(obs)} / \langle \Delta E \rangle^{(ECT)} \qquad (16)$$

In the early application, this measure of collision efficiency was about 0.1 in most cases, indicating that the collisions were—as generally believed—quite weak. As we extended the applications to include biphenylene, we found, however, that β_E for inert gas bath gases approached and often exceeded 0.5. For such efficient collisions, the assumption $n_m = 1$, i.e., the assumption that only one of the three translational degrees of freedom of the relative motion between the colliding molecules was active, was too restrictive, and the same applies to the present studies of the reactant *trans*-stilbene. Thus, we have developed a more appropriate parameter reduction in the form

$$n_m = \min(n_a + 1, n_M) \qquad (17)$$

This reduction agrees with that previously used in most cases, except for efficient reactant−inert gas atom collisions when n_m can approach 3. We have recalculated our fits to the KCSI data for toluene and azulene using this new parameter reduction and found very similar results. Thus, we will use the new determination of n_m here. In fact, the previous value of n_m for inert gas atoms would not work at all in the case of *trans*-stilbene−argon collisions as studied here. It is, of course, possible that improved fits could be obtained by optimizing both n_a and n_m. However, we do not wish to increase the empirical content of the theory.

2.1. Correction for Glancing Collisions to *P*(*E*′, *E*). The analysis above does not explicitly account for the obvious fact that the colliding molecules approach each other at different impact parameters b. The energy transfer kernel is constructed as if the approaching molecules either collide, in which case their effects are incorporated in $P(E', E)$, or pass without collision, i.e., the encounter events are divided into "hits or misses". In reality, a head-on collision cannot be expected to produce the same result, on average, as a glancing collision of an impact parameter on the borderline between collision and noncollision. It is clear then that a better way to analyze the experimental data would be to consider the energy transfer kernel to be a function of b, $P(b; E', E)$, and the experimental observation to reflect an appropriate collision average of this function. We expect the collision efficiency to fall off with increasing impact parameter as indeed observed in simulations of collisional energy transfer.[44] It is, in fact, not possible to uniquely determine a cutoff of the impact parameter, which would yield a correspondingly unique collision frequency and form of averaged energy transfer kernel $P(E', E)$. Thus, an analysis resolving the b dependence would be the most satisfying solution to this dilemma. In the present work, we shall, however, take a more pragmatic approach to this problem. We shall explore the possibility of composing our energy transfer kernel as a linear superposition of two such kernels as developed above

$$P(E', E) = (1 - X)P(E', E; n_a) + XP(E', E; n_{ag}) \quad (18)$$

Here, the first term shall represent essentially "head-on" collisions and the second term "glancing" collisions. With this physical picture in mind, we expect the number of active reactant degrees of freedom n_a to be relatively large, and the corresponding number for the glancing collisions n_{ag} to be relatively small. The factor X is simply a weighting factor for the glancing collisions reflecting their relative frequency among all collisions. This composite form of $P(E', E)$ shall allow us to obtain a wider range of shapes of the distribution, and we shall use this flexibility to seek closer agreement with the shape of $P(E', E)$ found in the direct interpretation of the KCSI data.

The proper treatment of the effect of glancing collisions would be to extend the analysis to account for the detailed interactions of the colliding molecules. At this early stage, we shall be satisfied with a phenomenological treatment, given the uncertainty of the precision with which features of $P(E', E)$ for nearly elastic collisions are determined by the KCSI experiments and the need for good information on the nature of the interactions to resolve the effects theoretically from first principles. It may appear as if the empirical content of the PECT is then significantly increased, since instead of one parameter, there will now typically be three. This is not so, however, given that the process of going from one to three parameters can be carried out essentially within the PECT without the explicit use of the experimental data in the fitting process. We can simply observe the shift and rounding of the peak disappearing and the characteristic elastic peak of the monoexponential $P(E', E)$ appearing. There is no significant advantage to be gained by going beyond such a simple "visual optimization" to a three-parameter fit to experimental data. Note that our simple visual optimization can also be carried out for collider pairs not yet studied by the KCSI technique.

3. Calculations and Results

Applying the PECT analysis to the KCSI data for the deactivation of *trans*-stilbene[41] by the bath gas molecules Ar, CO_2, and *n*-heptane, we have further extended our previous studies[37,39,40] to include another reactant molecule. The collisional energy transfer is investigated at initial *trans*-stilbene excitation energies of 10 000, 20 000, 30 000, and 40 000 cm^{-1} with the bath gas at room temperature (300 K). The average energy transferred per collision, $\langle \Delta E \rangle$, determined in the KCSI experiments is given in Table 1.

When determining the measure of collision efficiency β_E, the densities of states for the reactant and the corresponding medium molecule need to be calculated. As mentioned earlier, the thermodynamic method is used. The vibrational frequencies used for *trans*-stilbene are reported in ref 41, and the frequencies for the three different bath gas molecules can be found in our earlier report.[37] Given the densities of states, the ECT limiting value of the first energy transfer moment is determined, and the ratio between the KCSI (Table 1) and ECT $\langle \Delta E \rangle$ yields the energy transfer efficiency. In Table 2, we present the β_E values for *trans*-stilbene at the different initial excitation energies. Comparing the energy transfer efficiency of *trans*-stilbene with corresponding results for the previous reactants toluene and azulene, we notice that *trans*-stilbene is much more efficient, with β_E values ranging from 0.15 (with *n*-heptane) to 0.93, indicating almost microcanonical equilibration between *trans*-stilbene and Ar at 40 000 cm^{-1}. The difference in β_E between the heavy atomic collider and the polyatomic colliders is mainly due to the particular efficiency of the translational degrees of freedom for Ar. Table 2 shows that the β_E values for CO_2 and *n*-heptane as colliders decrease, whereas in the case of Ar, the corresponding transfer efficiency increases as the initial energy of *trans*-stilbene increases. Similar trends are also present in our previous studies. The relatively slow vibrational−vibrational energy transfer is favored by complex formation and long lifetimes, leading to larger energy redistribution between the reactant and the medium molecule, resulting in larger β_E. For lower excitation energies, complex formation is more likely to happen, whereas for higher energies, the probability to form complexes and their lifetimes decrease. The energy transfer into the translational degrees of freedom on the other hand is not to the same extent dependent on complex formation; hence, β_E increases with increasing excitation energy.

TABLE 1: $\langle \Delta E \rangle$ Values Calculated from Optimized KCSI $P(E', E)$ Monoexponential Form with a Parametric Exponent[a]

	$\langle \Delta E \rangle$ (cm^{-1}) at			
bath gas	10 000 cm^{-1}	20 000 cm^{-1}	30 000 cm^{-1}	40 000 cm^{-1}
Ar	176	346	521	700
CO_2	264	460	652	845
n-heptane	953	1484	1990	2489

[a] ΔE is the energy transfer from the *trans*-stilbene molecule at the energy shown to the bath molecule at room temperature.

TABLE 2: Energy Transfer Efficiency β_E Values for *trans*-Stilbene Determined by Comparison of ECT Calculations with KSCI Experimental Results

	β_E at			
bath gas	10 000 cm^{-1}	20 000 cm^{-1}	30 000 cm^{-1}	40 000 cm^{-1}
Ar	0.83	0.83	0.88	0.93
CO_2	0.42	0.35	0.33	0.32
n-heptane	0.30	0.20	0.17	0.15

In the PECT model calculations, we have reduced our empirical parameters according to the parametrization in eq 17, leaving us with only one parameter n_a. We have varied the number of active reactant degrees of freedom, n_a, with a step size of 0.05 so that the resulting PECT form of $P(E', E)$ reproduces the observed $\langle \Delta E \rangle$ value from the KCSI measurements. The values of n_a obtained are shown in Table 3. We see that the numbers of active degrees of freedom in *trans*-stilbene participating in the energy redistribution are greater than for both toluene and azulene, which further supports the statement that *trans*-stilbene is a more efficient reactant molecule then the two previously studied. In Figures 1−6, we present

TABLE 3: The Number of Active Degrees of Freedom, n_a, for *trans*-Stilbene Used in the PECT Calculations of $P(E', E)$

	n_a at			
bath gas	10 000 cm^{-1}	20 000 cm^{-1}	30 000 cm^{-1}	40 000 cm^{-1}
Ar	3.70	3.75	4.35	4.95
CO_2	4.55	4.00	4.00	4.05
n-heptane	17.50	13.90	13.10	12.85

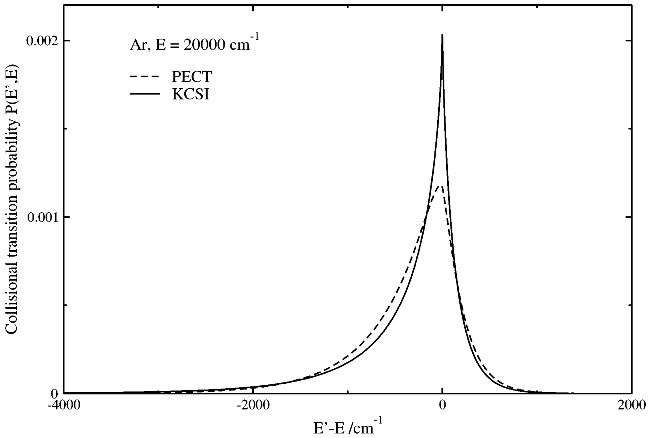

Figure 1. The energy transfer kernel $P(E', E)$ as a function of the final *trans*-stilbene energy E' colliding with Ar at the initial excitation $E = 20\,000\ cm^{-1}$ of *trans*-stilbene. Direct comparison between the PECT and KCSI forms.

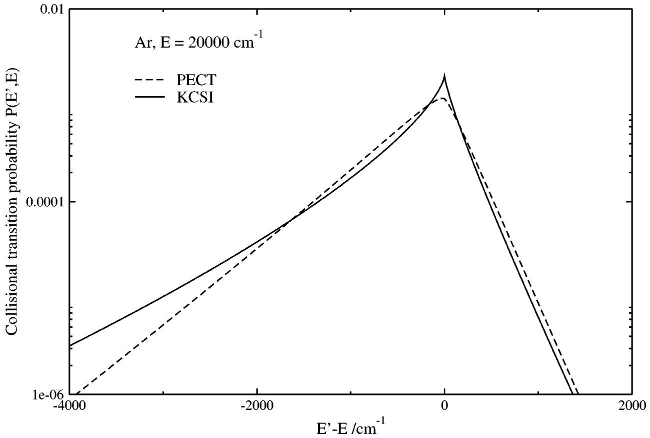

Figure 2. Same as in Figure 1, but with the collisional transition probability $P(E', E)$ on a logarithmic scale.

comparisons between the shapes of the PECT and KCSI forms[36] of the collisional transition probability function $P(E', E)$. Linear and log−linear plots are shown to capture the similarities and/or differences at both small and large values of $\Delta E = E' - E$, i.e, where little or much energy is being transferred in the collision. Comparisons are shown for the deactivation of *trans*-stilbene at an initial energy $E = 20\,000\ cm^{-1}$ for the three different medium molecules. For the *trans*-stilbene−Ar and *trans*-stilbene−CO_2 collider pairs (Figure 1 and Figure 3), we see that, for nearly elastic collisions, $\Delta E \approx 0$, PECT predicts a somewhat broader distribution than KCSI. Looking at the corresponding log−linear plots, we see that PECT reproduces the long tails of $P(E', E)$ to a reasonable accuracy. For the largest collider, *n*-heptane (Figure 5), we see that the PECT form of $P(E', E)$ shifts toward the deactivation direction and thus does not exhibit its maximum probability near the elastic peak, $\Delta E = 0$. We have experienced this elastic peak problem, involving larger medium molecules such as *n*-heptane, in all of our studied collision pairs so far.

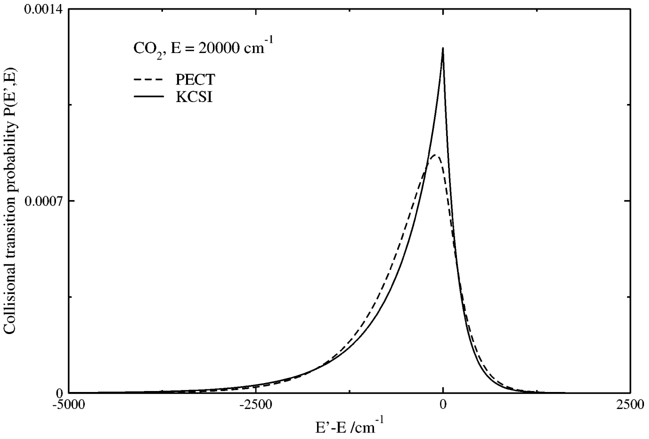

Figure 3. Same as in Figure 1, but for *trans*-stilbene colliding with CO_2.

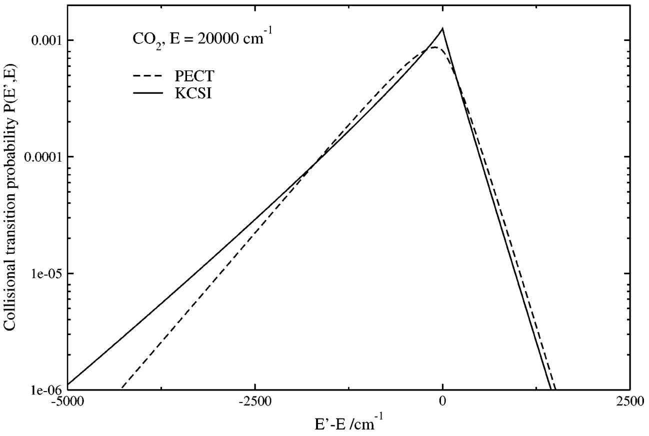

Figure 4. Same as in Figure 3, but with the collisional transition probability $P(E', E)$ on a logarithmic scale.

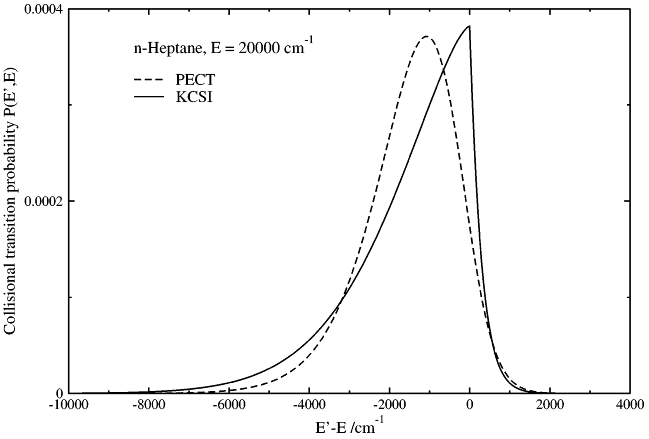

Figure 5. Same as in Figure 1, but for *trans*-stilbene colliding with *n*-heptane.

We now turn to the ability of the PECT model to predict the second moment of the energy transfer kernel, $\langle(\Delta E)^2\rangle$. Remember that we only use the first energy transfer moment when fitting our empirical parameter in PECT. Listed in Table 4 is the square root of the second energy transfer moment calculated using the PECT model and in parentheses the corresponding KCSI value. Figure 7 shows the difference in $\langle(\Delta E)^2\rangle^{1/2}$ between PECT and KCSI for all different initial energies and medium molecules. It is clearly shown the PECT predicts slightly smaller values of $\langle(\Delta E)^2\rangle$, and narrower distributions, than the KCSI form of $P(E', E)$.

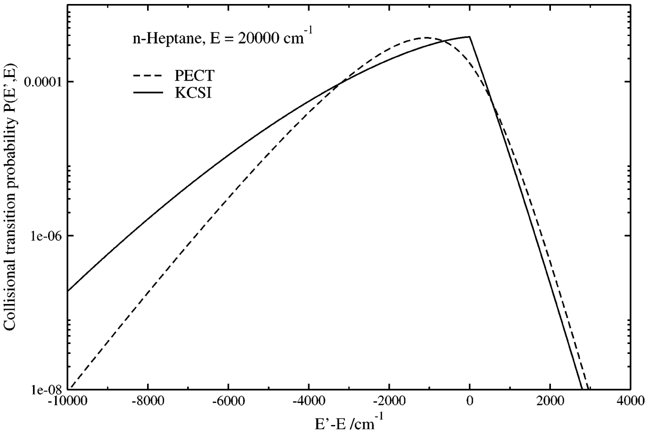

Figure 6. Same as in Figure 5, but with the collisional transition probability $P(E', E)$ on a logarithmic scale.

TABLE 4: PECT Values of the Square Root of the Second Energy Transfer Moment $\langle\Delta E^2\rangle^{1/2}$ [a]

bath gas	$\langle\Delta E^2\rangle^{1/2}$ (cm^{-1}) at 10 000 cm^{-1}	20 000 cm^{-1}	30 000 cm^{-1}	40 000 cm^{-1}
Ar	454 (481)	670 (748)	902 (1028)	1134 (1313)
CO_2	578 (599)	806 (863)	1048 (1136)	1288 (1413)
n-heptane	1360 (1454)	1898 (2098)	2448 (2739)	2996 (3380)

[a] ΔE is the energy transfer from the *trans*-stilbene molecule at the energy shown to the medium molecule at room temperature. The values in parenthesis are the corresponding values obtained in the KCSI measurements (KCSI).

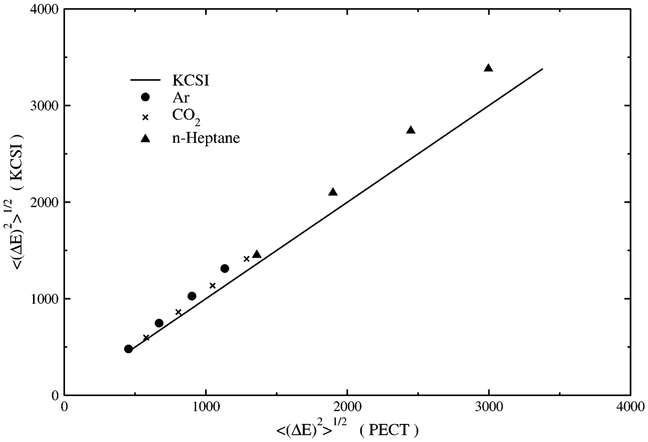

Figure 7. Square root of the second energy transfer moments $\langle(\Delta E)^2\rangle^{1/2}$, at the initial energies $E = 10\,000$, 20 000, 30 000, and 40 000 cm^{-1} for all of the *trans*-stilbene medium pairs studied. Comparison between prediction made with the PECT and the KCSI measurements (solid line). The PECT and KCSI data are shown in Table 4.

When performing the calculations containing the correction for the downshifting of the "elastic peak" using eq 18, the additional parameters, the active degrees of freedom accounting for the glancing collisions, n_{ag}, and the weighting factor, X, were held fixed, while n_a was varied as in the original implementation of PECT. We applied this corrected form of PECT to *trans*-stilbene in *n*-heptane and to two previously studied systems where the same shifted peak problem has been seen, toluene and azulene colliding with *n*-heptane. In two cases, for toluene at 40 000 cm^{-1} and *trans*-stilbene at 10 000 cm^{-1}, additional adjustments were needed with respect to X in order to avoid an unphysical shape due to the "bimodal" form of $P(E', E)$ in eq 18. Table 5 shows the parameters used in the corrected PECT calculations. As is shown, the number of active degrees of freedom involved in the energy exchange through the glancing collisions, n_{ag}, increases as the complexity of the reactant increases. Figures 8−10 contain the comparisons between the PECT, the KCSI, and the corrected PECT form of $P(E', E)$ for the deactivation of *trans*-stilbene, azulene, and toluene at initial excitation energy $E = 30\,000$ cm^{-1} in *n*-heptane. The fit between the corrected PECT and KCSI improves from the *trans*-stilbene case to azulene and becomes nearly perfect for toluene as the reactant.

TABLE 5: Parameters Used in the PECT Calculations with Correction for Glancing Collisions[a]

reactant		10 000 cm^{-1}	20 000 cm^{-1}	30 000 cm^{-1}	40 000 cm^{-1}
toluene	n_a	8.35	8.60	9.00	8.90
	n_{ag}	3.00	3.00	3.00	3.00
	X	0.45	0.45	0.45	0.40
azulene	n_a	14.25	12.30	12.10	
	n_{ag}	4.00	4.00	4.00	
	X	0.50	0.50	0.50	
stilbene	n_a	23.90	20.40	18.90	18.45
	n_{ag}	6.00	6.00	6.00	6.00
	X	0.35	0.45	0.45	0.45

[a] Here, n_a and n_{ag} are the active degrees of freedom for the direct and glancing collisions, respectively, and X is the weighting factor.

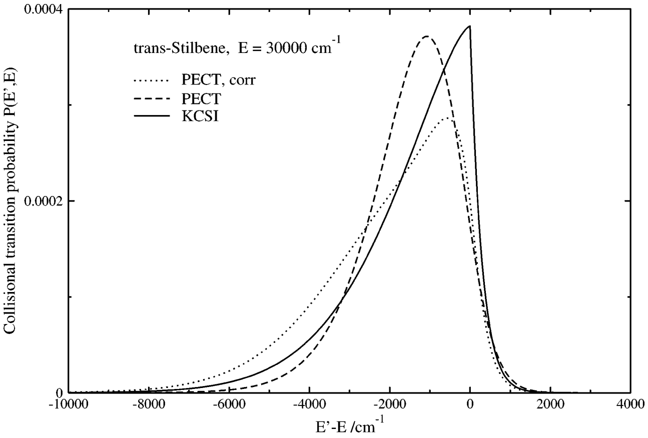

Figure 8. The energy transfer kernel $P(E', E)$ as a function of the final *trans*-stilbene energy E' colliding with *n*-heptane at the initial excitation $E = 30\,000$ cm^{-1} of *trans*-stilbene. Direct comparison between the PECT, KCSI, and the PECT form with correction made toward glancing collisions.

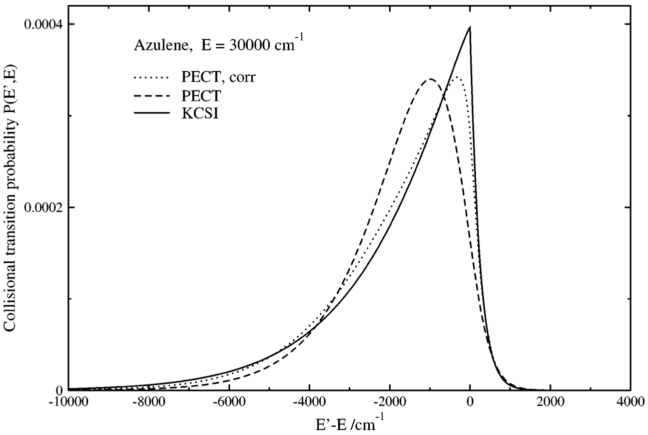

Figure 9. Same as in Figure 8, but for azulene colliding with *n*-heptane.

4. Discussion and Conclusion

trans-Stilbene is the largest reactant molecule for which we have been able to test our partially ergodic theory (PECT)

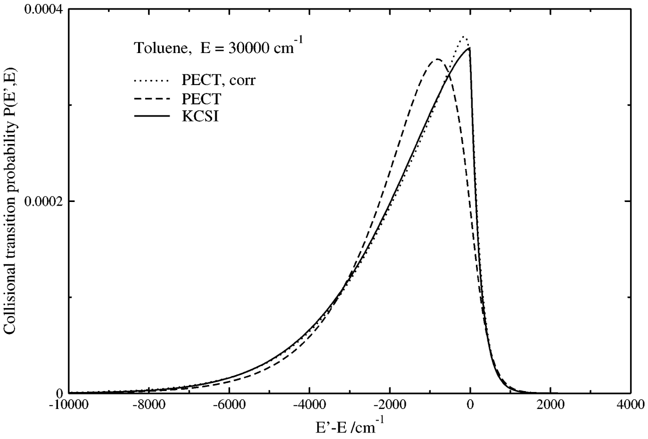

Figure 10. Same as in Figure 8, but for toluene colliding with *n*-heptane.

against reliable KCSI data. It is also by far the most efficient reactant molecule among toluene, azulene, and *trans*-stilbene. The collision efficiency β_E that we have found here falls between 0.15 (with *n*-heptane at 40 000 cm^{-1}) and 0.93 (with argon at 40 000 cm^{-1}), while for toluene and azulene, they are typically in the range from 0.1 to 0.3. We also found high collision efficiencies in our recent comparison[40] with UVA data on $\langle \Delta E \rangle$ for biphenylene where the β_E values were in the range from 0.1 to 0.8. There would appear to be a trend in which larger reactant molecules produce higher collision efficiencies, but there is a need to extend the small set of reactant molecules studied before more firm conclusions can be drawn. At least, we can say that, contrary to common perception before this work comparing ECT and PECT predictions with KCSI data was done, the collision efficiency is not always very low but very variable, sometimes reaching within 10% of the ergodic collision limit.

Despite the widely varying collision efficiency, the form of the PECT energy transfer kernel $P(E', E)$ continues to fit the KCSI-determined shape quite well. For the largest bath gas molecule *n*-heptane, the deviation for small ΔE due to the downshift of the PECT peak becomes more prominent. As we have shown above, the leading cause is likely to be the lack of specific treatment of glancing collisions by the statistical PECT, which considers the collision events as either “hits or misses”. Recognizing that there are nearly elastic “glancing” collisions and representing them by a separate contribution to $P(E', E)$ with a small n_a value readily recovers most of the agreement with the energy-dependent monoexponential form of the KCSI fit to $P(E', E)$. We should carefully note, however, that this issue is not definitively settled. The effect on energy transfer of small ΔE collisions is correspondingly small, which means that it is harder to determine the function $P(E', E)$ in the vicinity of $\Delta E = 0$. More experimental and also MD simulation studies of this region would be needed to clarify the contributions of nearly elastic collisions. Thereafter, we can propose a more fundamental theoretical solution. Until then, the present procedure of using a “bimodal” energy transfer kernel—one with a relatively high n_a value representing more efficient “head-on” collisions and another with a low n_a value representing glancing collisions—can be used to plausibly resolve the discrepancy. The remaining uncertainty concerning nearly elastic contributions to $P(E', E)$ is unlikely to have much effect on applications concerned with energy transfer, which is dominated by the contributions of stronger collisions in the ensemble.

In conclusion, we note that a fortunate convergence of experiment and theory has occurred such that reliable and detailed data on the transfer of energy between a highly excited reactant and a thermal medium molecule can now be reproduced by a simple theoretical model. This has thrown considerable new light on the nature of the energy transfer mechanism. It clearly responds to the complexity of the molecules in a basically statistical manner as described in the PECT model. There is a weakness of the collisions, a limit of the number of modes that can be relaxed in the collision. This weakness is very variable, often reducing the collision efficiency by a full order of magnitude, but there is now clear evidence that, at least for larger reactant molecules, the weakness is only minor, causing a loss of collision efficiency by less than 10% in some instances. It remains to understand and predict this variation in collision efficiency, but in the meantime, the ensemble of reactant—bath gas pairs that have been studied can be used to estimate the collision efficiency by a kind of chemical interpolation. In this way, it would now be possible to use the PECT model to provide a representation of the collisional activation and deactivation mechanism as needed in reaction rate theory.

The great simplicity of the PECT model may well strain its credibility as a representation of such an apparently complex dynamical process as the collisional energy transfer between a reactant and a medium molecule. One should recall then that the PECT is basically a statistical mechanical theory which provides a means of understanding and summarizing the main features without accounting for the detailed dynamics. There are many examples of such successes. One close at hand in this connection is the assumption of microcanonical equilibrium in the reactant molecule within the RRKM theory of unimolecular reactions. Thers is no doubt that the detailed dynamics is far more complex than the presumed fully ergodic and rapid internal vibrational energy redistribution in the RRKM analysis. Nevertheless, there is no doubt that this simple assumption is a very good summary of the main features in most cases and the appropriate starting point for a deeper and more detailed analysis. Similarly, one should not expect the PECT analysis to be accurate in detail. Clearly, the modes of the colliding molecules will be neither fully active nor fully inactive. They will have some fractional degree of activity that will sum to something like the parameters we find in the present PECT model, and the end result will be a partially ergodic energy redistribution like the one we have produced here. The fact that we are able to capture the main features of the collisional energy transfer in a simple statistical theory does not alter the fact that for a full understanding we still need to know how the detailed dynamics produces the observed result. It therefore still remains to explore the dynamical details of bimolecular collisions, which leads to a given degree of nonergodicity as measured by the collision efficiency β_E and the corresponding PECT parameters. Fortunately, we can expect β_E to vary systematically so that even a small set of experimental values can allow estimation of β_E for a much larger set of reactant—collider pairs. Molecular dynamics simulations may also provide complementary evidence to that obtained by experiment. There appears to be a good foundation for further progress in the unraveling of collisional activation and deactivation in reaction rate theory.

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