PECT Model Analysis and Predictions of Experimental Collisional Energy Transfer Probabilities $P(E',E)$ and Moments $\langle \Delta E \rangle$ for Azulene and Biphenylene†

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Experimental collisional energy transfer data from kinetically controlled selective ionization (KCSI) and ultraviolet absorption (UVA) experiments are analyzed in the framework of the partially ergodic collision theory (PECT). Collisions of azulene and biphenylene with different colliders are investigated as case studies. The downward wings of the $P(E',E)$ energy transfer distributions obtained from the PECT model are fitted to the recently introduced "variable-shape"-exponential 3-parameter functional form of $P(E',E)$ obtained from KCSI experiments, $P(E',E) \propto \exp[-\{(E - E')/(C_0 + C_1E)\}^Y]$. The PECT model is able to reproduce the characteristic dependence of the KCSI "shape parameter" Y on the choice of collider, the energy dependent width of the KCSI $P(E',E)$ distributions, described by $\alpha(E) = C_0 + C_1E$, and the temperature dependence of the UVA data above room temperature. The statistical approach of PECT obviously captures the essence of large molecule energy transfer at chemically significant energies without the need of knowing specific features of the detailed collision dynamics. It therefore shows promise for predicting the shape of $P(E',E)$ in master equation kernels for larger molecules.

1. Introduction

Modeling reaction systems in combustion and related processes requires sufficient knowledge of the rate constants not only of the reactions involved but also of the competitive processes, especially collisional energy transfer (CET). As an example, at chemically relevant energies with their high densities of states, a simple system with only a single reaction channel can be described by the continuous master equation

$$\frac{\mathrm{d}g(E,t)}{\mathrm{d}(Z[\mathrm{M}]t)} = \int_0^\infty [P(E,E')\, g(E',t) - P(E',E)\, g(E,t)]\, \mathrm{d}E' - k(E)\, g(E,t) \quad (1)$$

where $g(E,t)$ is the population distribution of the reactive educt at energy E and time t, Z is a collision number, [M] is the bath gas concentration, $k(E)$ is the energy dependent rate constant of the reactive process, and $P(E',E)$ is the collisional transition probability density function ("energy transfer probability") for a collision-induced transition from energy E to E'.

Statistical approaches such as the statistical adiabatic channel model (SACM) or Rice−Ramsperger−Kassel−Marcus (RRKM) theory have been successful in providing reliable values for $k(E)$;[1] see, e.g., refs 2 and 3. Concerning the CET processes, the situation is however less advanced. Accurate experimental data on the shape of the full energy transfer kernel $P(E',E)$ for large systems such as toluene or azulene have now become available from measurements employing kinetically controlled selective ionization (KCSI).[4−7] In addition, the method of IR diode laser spectroscopy on bath gas colliders, originally developed by Flynn,[8−12] has provided absolute $P(E',E)$ values selectively on the high energy tails of very large ΔE, in several aromatic systems mainly for CO_2 as a collider.[13,14] A reliable theoretical model for a detailed description of CET is however still missing, which could be applied with some reasonable accuracy to polyatomic molecules at energies of chemical relevance. Very recently, a modified statistical approach, the partially ergodic collision theory (PECT), has emerged, which yields $P(E',E)$ distributions with main features in good agreement with the results from the KCSI experiments.[15,16] In the present paper, we provide a detailed systematic comparison of PECT data with results from KCSI and ultraviolet absorption (UVA) experiments, with respect to the shape, energy dependence, and temperature dependence of $P(E',E)$ and its moments to assess the performance of this model in predicting the CET behavior of larger highly excited molecules.

2. KCSI Experiments and PECT Calculations

The KCSI experiments and their application to highly vibrationally excited azulene (= "azulene*") and other molecules have already been described in detail.[4,5,6,7] Briefly, KCSI is the only experimental method available so far which can provide complete $P(E',E)$ distributions for larger molecules. This is achieved by employing a time-resolved two-photon ionization process to monitor the distributions $g(E,t)$ of highly vibrationally excited molecules, as they relax through experimentally defined "energy windows" during their collisional deactivation with a bath gas M. The KCSI data is typically analyzed using a master equation of the form

$$\frac{\mathrm{d}g(E,t)}{\mathrm{d}(Z[M]t)} = \int_0^\infty [P(E,E')\, g(E',t) - P(E',E)\, g(E,t)]\, \mathrm{d}E' \quad (2)$$

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For data evaluation, an empirical minimum parameter expression for $P(E',E)$ was found

$$P(E',E) = \frac{1}{c(E)}\exp\left[-\left(\frac{E-E'}{\alpha(E)}\right)^Y\right] = \frac{1}{c(E)}\exp\left[-\left(\frac{E-E'}{C_0+C_1E}\right)^Y\right], \quad (E' \le E) \quad (3)$$

which is of monoexponential type with a flexible shape determined by a parametric exponent Y in the argument. Y depends on the excited molecule, the collider, and the temperature, but not on the energy. The energy dependent parameter $\alpha(E) = C_0 + C_1E$ describes the width of the energy transfer probability and is thus related to the efficiency of the collisions. $c(E)$ is a normalization constant. With this functional form, it has been possible to consistently model all experimental KCSI signals obtained so far for colliders varying from atomic to large polyatomic ones. In systems such as toluene*[5,6] or azulene*,[4] the exponents Y vary smoothly with the "size" of the collider, yielding values between $Y = 0.65$ (toluene* + helium) and 1.5 (toluene* + *n*-heptane). The width parameter $\alpha(E)$ is linearly dependent on energy, which leads to an approximately linear energy dependence of the first moment of energy transfer $\langle\Delta E\rangle$, the average energy transferred per collision, and the square root of the second moment of energy transfer $\langle\Delta E^2\rangle^{1/2}$, where the moments $\langle\Delta E^n\rangle$ are defined as

$$\langle\Delta E(E)^n\rangle = \int_0^\infty (E'-E)^n P(E',E)\,\mathrm{d}E' \quad (4)$$

In contrast, experiments such as time-resolved UVA only yield information on the energy dependent first moment $\langle\Delta E\rangle(E)$. Their reliability depends sensitively on the accurate knowledge of the energy dependence of $\epsilon(E)$ [or $\epsilon(T)$], which relates measured changes of absorption with $\langle E\rangle$, the average energy of the relaxing molecules. Sufficiently precise calibration curves are required. They have to be measured by shock wave or laser excitation techniques.[17]

The methodology for obtaining collisional transition probabilities $P(E',E)$ from PECT has already been discussed in detail.[15,16] Therefore, only a brief outline will be given here. PECT is an extension of ergodic collision theory (ECT) which starts from the microcanonical strong collision assumption stating that after each collision the reactant molecule ends up in a microcanonical equilibrium with the bath gas molecule.[18] Typically, ECT overestimates experimental $\langle\Delta E\rangle$ values by up to 1 order of magnitude. This can be quantified by a collisional energy transfer efficiency parameter β_E

$$\beta_E = \langle\Delta E\rangle_{\mathrm{exp}}/\langle\Delta E\rangle_{\mathrm{ECT}} \quad (5)$$

To account for the weakness of the collisions, the PECT model has been developed.[19] In this modified version of ECT, a complete microcanonical equilibrium in the collision complex is assumed only for a subset of the degrees of freedom, the so-called "active degrees of freedom". One finally arrives at the following expression for $P(E',E)$:[15,16]

$$P(E',E) = c(E)\int_{\max[0,E-E']}^{E} \mathrm{d}E_a \exp\{-E_a/[k_BT(E)]\}E_a^{(n_a-2)/2} \int_{\max[0,E'_a-E_a]}^{\infty} \mathrm{d}E_m\left[\frac{E'_a{}^{(n_a-2)/2}(E'_mE_m)^{(n_m-2)/2}}{(E_a+E_m)^{(n_a+n_m-2)/2}}\exp(-E_m/(k_BT))\right] \quad (6)$$

where $T(E)$ is the canonical temperature at the internal energy E of the excited molecule and T is the temperature of the bath gas. E_a and E_m are the energies in the active degrees of freedom of the excited molecule and the collider, respectively; n_a and n_m represent the number of active degrees of freedom of the excited molecule and the bath gas. Note that the final state active energies are defined by $E_a' = E_a + E' - E = E_a + \Delta E$ and $E_m' = E_m + E - E' = E_m - \Delta E$ (also note that the sign for ΔE here is changed from that in refs 15 and 16). It follows that $E_a + E_m = E_a' + E_m'$ as required by energy conservation. The constant $c(E)$ ensures that the integral of $P(E',E)$ over all final energies E' yields unity as it must; that is, it is a normalization constant. As a further simplification of the model, one assumes $n_m = n_a + 1$ for polyatomic colliders (where the translational degree of freedom is associated with the bath gas) and $n_m = 1$ for rare gases, leaving n_a as the only adjustable parameter. This is varied to reproduce a single experimental observable, typically $\langle\Delta E\rangle$. In the present work, PECT $P(E',E)$ distributions for biphenylene were calculated via eq 6 using the following 54 vibrational frequencies for biphenylene (in cm^{-1}): 3074, 3072, 3072, 3057, 3057, 3030, 3022, 3010, 1840, 1666, 1638, 1602, 1598, 1462, 1449, 1444, 1426, 1399, 1288, 1267, 1260, 1194, 1166, 1151, 1128, 1105, 1105, 1076, 1053, 1019, 992, 989, 975, 962, 928, 915, 765, 751, 736, 735, 733, 655, 628, 612, 600, 567, 437, 395, 380, 366, 339, 212, 175, 120.[20,21] Note that these frequencies are needed to obtain the "internal temperature" for this reactant molecule within the so-called "canonical approximation", which is discussed in more detail in the earlier PECT papers. For azulene, toluene, and the whole set of colliders, normal-mode frequencies were used as tabulated in the same references.[15,16]

3. Comparison of KCSI and PECT Data

3.1. *P*(*E*′,*E*) Shape and Energy Dependence for Azulene. Figure 1 shows a comparison of $P(E',E)$ obtained from KCSI and PECT for collisions of azulene* with CO_2 (a) and *cis*-2-butene (b) at $E = 10\,000\ \mathrm{cm}^{-1}$, in a semilogarithmic representation. The PECT model (dashed lines) describes the shape and width of the experimental KCSI transition probabilities (solid lines) very well. It is remarkable that PECT does reproduce the "concave" curvature (in a logarithmic plot) for smaller colliders (like CO_2 and argon) as well as the change into a "convex" curvature for larger colliders (like *cis*-2-butene), as it was observed in the KCSI experiments. In other words, the PECT model finds a clear relationship between the efficiency of the collisions (determined by the number of active degrees of freedom n_a) and the shape and width of $P(E',E)$ in agreement with the experimental KCSI data.

The comparison in Figure 1 was carried out at a fixed excitation energy, so for a more general check, one would like to look at the energy dependence of $P(E',E)$. In all cases studied so far, the KCSI experiments feature a linear dependence of the collision parameter α in eq 3 on excess energy.[4,6] A comparison of PECT and KCSI can be most conveniently done by fitting the downward wings of the energy dependent PECT $P(E',E)$ distributions by the empirical KCSI fitting function (eq 3), as shown in Figures 2a, 3a, and 4a for azulene* collisions with the colliders CO_2, argon, and *n*-heptane, respectively. The PECT distributions given in Figures 2a, 3a, and 4a, calculated via eq 6 at different energies E, were fitted *simultaneously* for each bath gas using eq 3 by applying a Levenberg−Marquardt χ^2 minimization algorithm, as implemented in the ORIGIN 6.1 program package.[22] For a consistent comparison with the existing KCSI parametrization [eq 3 in section 2],[4] the additional condition was imposed that Y is energy independent for each

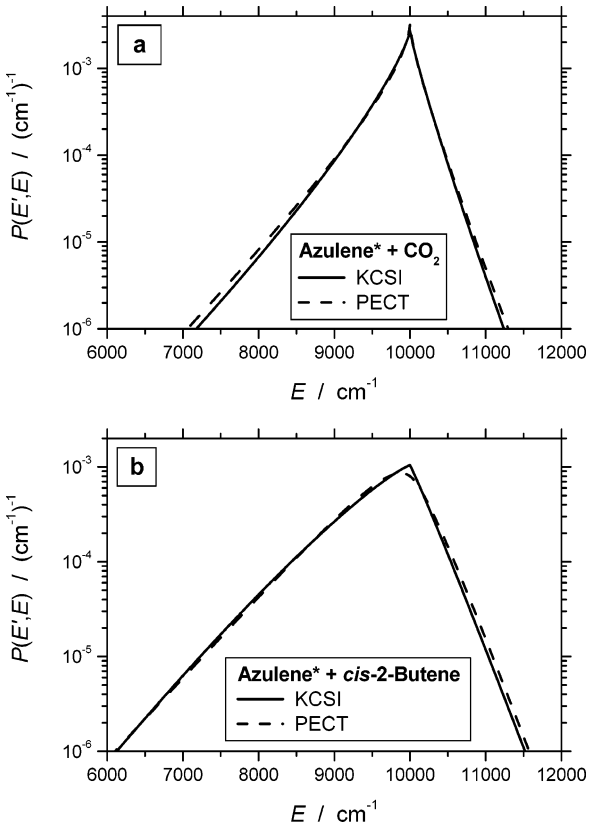

Figure 1. Comparison of $P(E',E)$ distributions from PECT calculations (dashed lines) and KCSI experiments (solid lines)[4] at $E = 10\,000$ cm^{-1}. (a) azulene* + CO_2 and (b) azulene* + *cis*-2-butene.

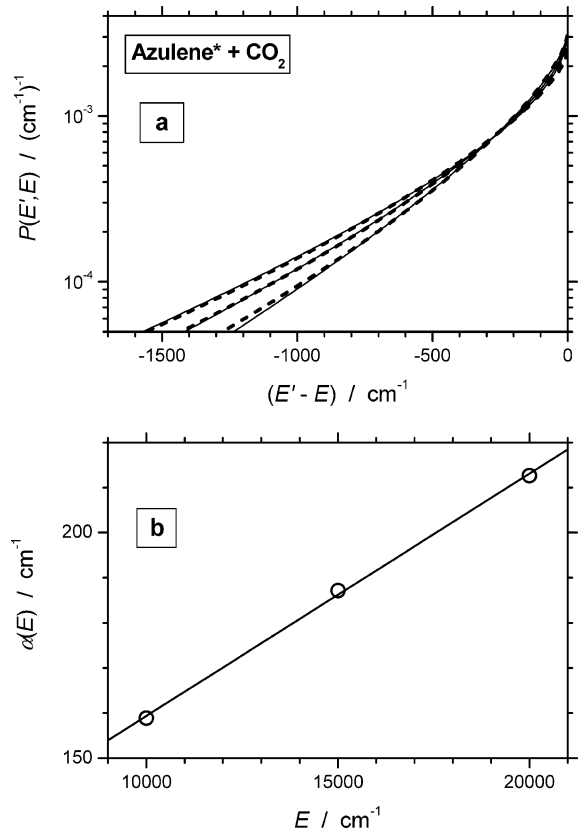

Figure 2. (a) $P(E',E)$ distributions (deactivating collisions) from PECT (solid lines) compared to fits using the empirical expression eq 3 from KCSI (dashed lines),[4] (b) linear fit $C_0 + C_1E$ to the $\alpha(E)$ values obtained in (a), see also Table 1. System: azulene* + CO_2 at $E = 10\,000$, 15 000, and 20 000 cm^{-1} [respective lines in (a) from right to left]. The resulting fit parameters can be found in Table 1.

bath gas. As a representative fitting example, in the argon case (Figure 3a), this results in an optimized energy independent $Y = 0.453 \pm 0.001$ and energy dependent $\alpha(E) = 23.5 \pm 0.3$, 30.2 ± 0.4, 36.7 ± 0.5, 43.4 ± 0.6, and 49.5 ± 0.6 cm^{-1} for the energies 10 000, 15 000, 20 000, 25 000, and 30 000 cm^{-1}, respectively. The $\alpha(E)$ values for each bath gas obtained from this procedure are plotted in Figures 2b, 3b, and 4b as open circles. Note that in the fits for CO_2 and argon the downward wings with amplitudes $\geq 10^{-5}$ (cm^{-1})$^{-1}$ were considered up to $(E' - E) = -100$ cm^{-1}. The downward portion of $P(E',E)$ with smaller amplitudes only negligibly contributes to the overall energy transfer, as demonstrated in our most recent KCSI paper and can therefore be discarded without a significant loss of accuracy.[4] Values close to the elastic peak region were omitted in the fitting procedure because it is well-known that the PECT model in the current simple form has systematic deficiencies in describing the amplitude of $P(E',E)$ in this region.[15,16] This is particularly clear in the *n*-heptane case (Figure 4a), where one observes a turnover region for $(E' - E) < 0$. As eq 3 is clearly not able to describe such a turnover behavior, in the *n*-heptane case, the fit was restricted to the region left of the maximum up to $(E' - E) = -2000$ cm^{-1}. The cutoff procedure near the elastic peak unavoidably results in uncertainties of the fitted parameters. For the argon case mentioned above, we estimate a variation of ± 0.10 in Y, accompanied by a corresponding systematic change of the α values by $\pm 30\%$. In any case, this is good enough to obtain satisfactory estimates of sufficient accuracy for Y and α.

In general, reasonable fits of the $P(E',E)$ distributions were obtained, as seen in Figure 2a for CO_2, and also in Figures 3a and 4a for the bath gases argon and *n*-heptane, respectively. It is remarkable, and was not to be expected a priori, that the fitted α values in Figures 2b, 3b, and 4b also exhibit a linear dependence on energy. Fitting these to the expression $C_0 + C_1E$ [as in the denominator of eq 3], one obtains positive values for C_0 and C_1. A comparison of the PECT fit values with the KCSI data is shown in Table 1. The agreement of the Y values is satisfactory: values much smaller than 1 are obtained for the smaller colliders Ar and CO_2 [corresponding to a "concave" shape in the semilogarithmic representation of $P(E',E)$], whereas for *n*-heptane, $Y > 1$ is found ("convex" shape), i.e., reduced probabilities for large $\Delta E = |E' - E|$ relative to a simple exponential ($Y = 1$) shape.

Thus, in essence, the PECT model features wings of $P(E',E)$ consistent with eq 3, which was originally introduced as a successful, yet simple mathematical form to consistently represent $P(E',E)$ measured by KCSI, chosen within a physically meaningful framework of exponential type decays, as e.g. found in trajectory calculations for molecules such as benzenes.[23] Note that such a behavior is not expected a priori, as the model could have found that also the shape of $P(E',E)$ (i.e, the type of exponential decay, and not the width) would be energy dependent. It is a remarkable fact that the statistical PECT model in even such a simplified form shows the same central systematic features of the experimentally determined $P(E',E)$, although it does not account for *any* dynamical details of the collision process. One might stress the similarity of the situation with the established one in reactive processes where theories of purely statistical nature or with minimum of additional insight on the dynamics can well describe the rate constants of a wide range of "normal" reactions without the need to perform calculations of the full dynamics on accurate potential energy surfaces. The fact that even a simple statistical model can

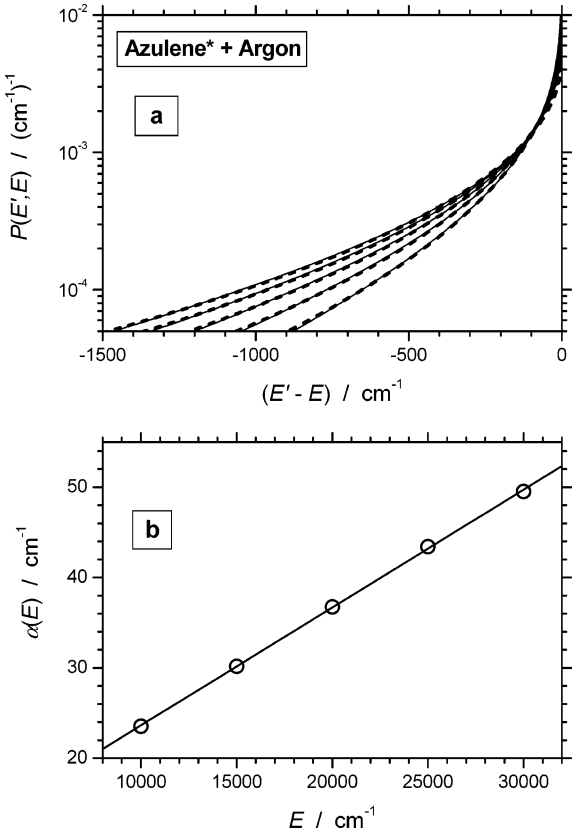

Figure 3. Same as in Figure 2, but for azulene* + Ar at $E = 10\,000$, 15 000, 20 000, 25 000, and 30 000 cm^{-1}.

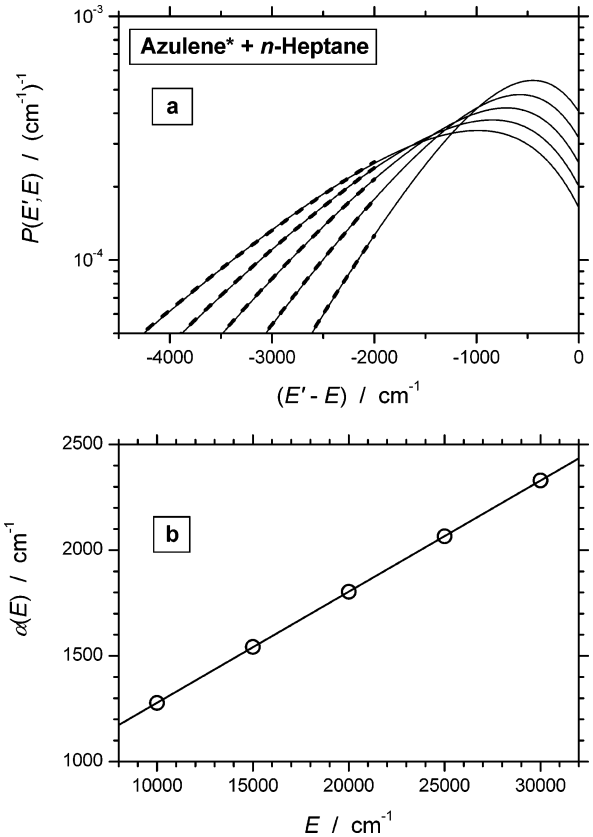

Figure 4. Same as in Figure 2, but for azulene* + *n*-heptane at $E =$ 10 000, 15 000, 20 000, 25 000, and 30 000 cm^{-1}.

reproduce the systematic variation between $Y < 1$ ["extended tail" of $P(E',E)$ distribution] for small colliders and $Y > 1$ ["reduced tail" of $P(E',E)$; all relative to a straight monoexponential, $Y = 1$] even proposes new types of "border-lines" in the discussion of CET dynamics. As in reactive processes, limits of statistical behavior and dynamics beyond it will be the issues of special interest, but no longer the fact alone, that a $P(E',E)$ has a distribution with a "longer tail" than a straight monoexponential.

TABLE 1: Optimized $P(E',E)$ Parameters from KCSI Measurements for Azulene Colliding with Different Bath Gases Compared to Those Obtained by Fitting the Downward Wing of the Energy Dependent PECT $P(E',E)$ Using the Empirical Minimum Parameter Expression from KCSI [Eq 3] as Described in the Text[a]

bath gas	method	C_0/cm^{-1}	C_1/10^{-3}	Y
Ar	KCSI	33	4.20	0.65
	PECT	11	1.31	0.45
CO_2	KCSI	130	8.30	0.80
	PECT	106	5.38	0.68
n-heptane	KCSI	645	59.5	1.20
	PECT	753	52.5	1.46

[a] See also Figures 2−4.

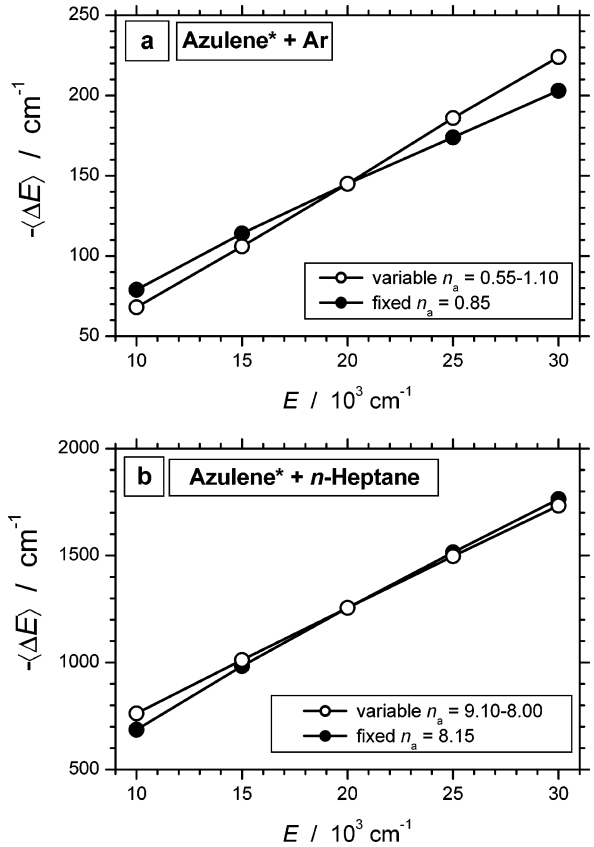

Figure 5. Energy dependence of $\langle\Delta E\rangle$ from PECT for the collisional deactivation of azulene*. (○) By varying n_a in eq 6 to reproduce the $\langle\Delta E\rangle$ from KCSI at all energies; (●) with n_a fixed by fitting only the single value at $E = 20\,000$ cm^{-1}. (a) azulene* + Ar, $n_a = 0.55-1.10$ and $n_a = 0.85$, respectively; (b) azulene* + *n*-heptane, $n_a = 9.10-8.00$ and $n_a = 8.15$, respectively.

3.2. Energy Dependence of $\langle\Delta E\rangle$ in Azulene Collisions. In the following, we concentrate on the corresponding moments of energy transfer from PECT, specifically $\langle\Delta E\rangle$. These are shown in Figure 5 for collisions between azulene* and argon (a) and azulene* and *n*-heptane (b). As discussed in section 2, the parameter n_a was varied to reproduce the $\langle\Delta E\rangle$ values of the KCSI experiments. In Figure 5, this corresponds to the open circles. For systems where, e.g., only a single $\langle\Delta E\rangle$ value at one excitation energy is known from experiment, it would be

TABLE 2: Energy and Temperature Dependent $\langle\Delta E\rangle$ Values for the Deactivation of Biphenylene from UVA Measurements[17] [a]

	$-\langle\Delta E\rangle$/cm^{-1}											
	at 10 000 cm^{-1}				at 20 000 cm^{-1}				at 30 000 cm^{-1}			
T/K	300	333	413	523	300	333	413	523	300	333	413	523
He	53	52	51	49	107	105	101	98	159	157	152	147
Ne	89	88	86	86	179	177	172	171	268	265	258	257
Ar	132	128	119	112	266	257	238	224	399	385	357	335
Kr	123	121	117	110	245	241	233	220	368	362	350	330
Xe	127	121	108	102	254	242	217	203	382	363	325	304
N_2	151	145	133	125	300	289	267	250	451	434	400	375
CO_2	222	214	198	167	445	428	395	333	666	642	593	500
ethane	292	281	261	226	585	563	521	451	876	844	782	677
n-heptane	705	655	554	458	1410	1309	1108	916	2115	1964	1662	1374

[a] Values at 300 K extrapolated from the data at higher temperatures.

TABLE 3: Collisional Energy Transfer Efficiency Parameters β_E for Biphenylene at Different Initial Energies and Temperatures of the Bath Gas[a]

	β_E											
	at 10 000 cm^{-1}				at 20 000 cm^{-1}				at 30 000 cm^{-1}			
T/K	300	333	413	523	300	333	413	523	300	333	413	523
He	0.18	0.19	0.24	0.35	0.20	0.20	0.22	0.25	0.21	0.21	0.22	0.24
Ne	0.31	0.33	0.40	0.61	0.33	0.34	0.37	0.44	0.36	0.36	0.38	0.43
Ar	0.46	0.48	0.56	0.80	0.50	0.50	0.52	0.58	0.53	0.53	0.53	0.56
Kr	0.42	0.45	0.55	0.79	0.46	0.47	0.51	0.57	0.49	0.50	0.52	0.55
Xe	0.44	0.45	0.50	0.73	0.47	0.47	0.47	0.53	0.51	0.50	0.48	0.50
N_2	0.25	0.26	0.30	0.44	0.28	0.28	0.29	0.33	0.30	0.30	0.30	0.32
CO_2	0.25	0.26	0.30	0.38	0.25	0.25	0.26	0.25	0.26	0.25	0.25	0.23
ethane	0.16	0.16	0.18	0.23	0.14	0.14	0.14	0.14	0.14	0.13	0.13	0.12
n-heptane	0.17	0.17	0.17	0.20	0.15	0.15	0.13	0.12	0.15	0.14	0.12	0.11

[a] Ratio of results from UV absorption experiments[17] and the present ECT calculations. See also Figure 6.

desirable to reliably extrapolate $\langle\Delta E\rangle$ to other excess energies. We can easily explore how the PECT model would perform in such a situation. For this, we used a fixed value for the number of active degrees of freedom n_a for each system, which reproduced the respective $\langle\Delta E\rangle$ at 20 000 cm^{-1} correctly, and used this n_a afterward to determine first moments between 10 000 and 30 000 cm^{-1}. The corresponding results are shown in Figure 5 as black circles. Interestingly, the change in the energy dependence is only minor in both cases. One still obtains an almost linear relationship with a worst case deviation from the experimental value of about 20% for argon collisions and even much better for the *n*-heptane case. It is reasonable to assume that the number of active modes participating in CET will be at best only weakly dependent on the excess energy of the excited molecule (and also temperature, see the next section). If this is correct, the linear $\langle\Delta E\rangle$ dependence observed in the experiments can be easily explained on the basis of purely statistical arguments and without looking at the detailed dynamics of individual collisions.

3.3. Temperature and Energy Dependence of $\langle\Delta E\rangle$ in Biphenylene Collisions. An important field for predicting collisional energy transfer properties is temperature dependence: One often encounters the situation that $\langle\Delta E\rangle$ has been measured only at room temperature. However, one would, e.g., need the value at higher temperatures in a combustion system. As it is impossible to perform direct CET experiments under such conditions for each system of interest, a reliable extrapolation with a theoretical model is needed. Here we want to explore the performance of PECT in such a situation. For that purpose, we chose one of our systems, where temperature-dependent CET data is available for comparison: the collisional deactivation of biphenylene, as measured by the UV absorption technique.[17]

In the first step, we carried out ECT calculations for biphenylene. By relating $\langle\Delta E\rangle$ values from these calculations

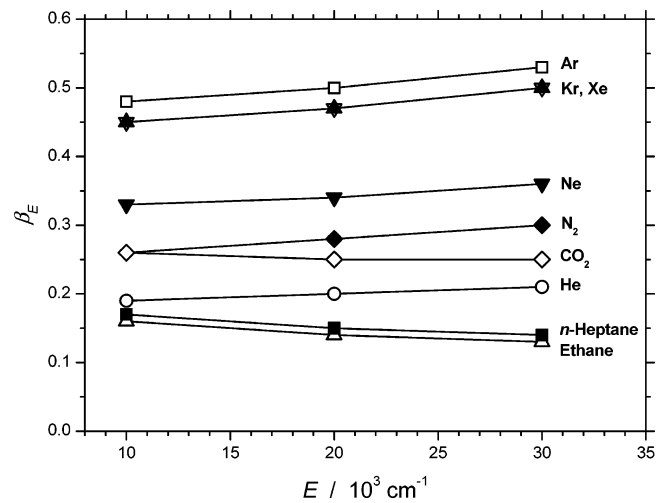

Figure 6. Collisional energy transfer efficiency parameter β_E as a function of excess vibrational energy for biphenylene* collisions with several bath gases at a temperature of 333 K.

with those from the UVA experiments (Table 2), one can obtain β_E via eq 5. In this case, the values at 300 K are extrapolated from the available UVA experiments to allow a comparison with the toluene and azulene data at 300 K given in the earlier PECT papers.[15,16] The results are summarized in Table 3. Figure 6 shows a plot of β_E as a function of energy for $T = 333$ K. Note that very similar results are obtained at the other temperatures. Depending on the bath gas, values between 0.13 and 0.53 are observed. As expected, ECT overestimates the experimental values, because it assumes complete energy redistribution in the collision complex. Interestingly, the β_E values obtained for biphenylene are, on average, much larger than for the previously studied systems azulene and toluene. This is not unexpected, because the statistical description should improve

TABLE 4: Number of Active Degrees of Freedom in the Reactant Molecule Biphenylene, n_a, Used in the PECT Calculations at Different Energies and Temperatures[a]

	n_a											
	at 10 000 cm^{-1}				at 20 000 cm^{-1}				at 30 000 cm^{-1}			
T/K	300	333	413	523	300	333	413	523	300	333	413	523
He	0.30	0.40	0.80		0.45	0.50	0.65	0.95	0.55	0.60	0.70	0.85
N_2	1.70	1.80	2.10	3.30	1.85	1.90	1.95	2.25	2.00	2.00	2.00	2.15
CO_2	2.65	2.80	3.35	4.50	2.90	2.95	3.05	3.10	3.15	3.10	3.10	2.95
ethane	3.60	3.80	4.55	6.25	3.95	4.00	4.15	4.35	4.25	4.20	4.25	4.15
n-heptane	9.30	9.40	10.10	13.10	10.15	9.80	9.30	9.25	10.85	10.40	9.50	8.85

[a] Note that $n_m = n_a + 1$ for polyatomic colliders and $n_m = 1$ for rare gases.

with increasing molecular size and correspondingly stronger interactions with the collider. The latter ones increase the interaction time during a collision and thus the degree of energy equilibration between the different degrees of freedom in the collision complex. In fact, the β_E values of biphenylene are so much higher than those found for toluene and azulene that the simplified PECT implementation used for the latter molecules cannot be applied for those biphenylene/collider pairs which show too high energy transfer efficiencies. Thus, we shall have to develop a generalization of the current model to include such highly efficient bath gases to which we shall return in a future report.

Nevertheless, as described in detail earlier, the restricted exchange of energy between the collision partners due to the limited interaction time must still be taken into account also for biphenylene.[15,16] With the proviso that our weak collision implementation ($\beta_E \leq 0.1$) may not be entirely plausible, we shall still apply it to the biphenylene data wherever the β_E values are not too large. The parameter n_a in eq 6 was varied until the best agreement with the UVA data for biphenylene was achieved. Values for the different bath gases can be found in Table 4. As expected, n_a is increasing with increasing size of the collider, and values between 0.30 (helium) and 13.10 (*n*-heptane) were found. These are similar to those obtained in the corresponding toluene and azulene calculations. Note, however, that we leave out the n_a parameters for one of the helium experiments and all of the experiments for neon, argon, krypton, and xenon. In these cases, the β_E values are too high for our standard weak collision implementation of the PECT.

To test the capabilities of PECT with respect to predicting the temperature dependence of biphenylene CET, we pursued a strategy similar to that in section 3.2. Assuming that only n_a data at 300 K were available, these were used as fixed values for temperature-dependent calculations. In Figure 7, plots of $\langle\Delta E\rangle$ as a function of T are presented for the colliders CO_2 and *n*-heptane as black circles. In both cases, a strictly linear and weakly negative temperature dependence is observed with relatively small deviations from calculations using variable n_a (open circles), the latter ones being identical to the $\langle\Delta E\rangle$ from the UVA experiments. This means that, even with knowing only a single value of $\langle\Delta E\rangle$ at room temperature, PECT is able to reproduce the experimentally observed negative temperature dependence quite well. We have also calculated $\langle\Delta E\rangle$ at a temperature of 200 K. However, there are unfortunately no biphenylene CET data to compare with. It is hard to say if the strictly linear dependence predicted by PECT persists at low temperatures. There are at least some indications from trajectory calculations for azulene that a steeper increase of $-\langle\Delta E\rangle$ for temperatures smaller than the effective well depth of the collision pair can be expected.[24] In this case, the complex interplay between the relative velocity of the collision partners and the well depth of the interaction potential seems to play a role, a dynamical aspect, which is of course not covered by the statistical approach.

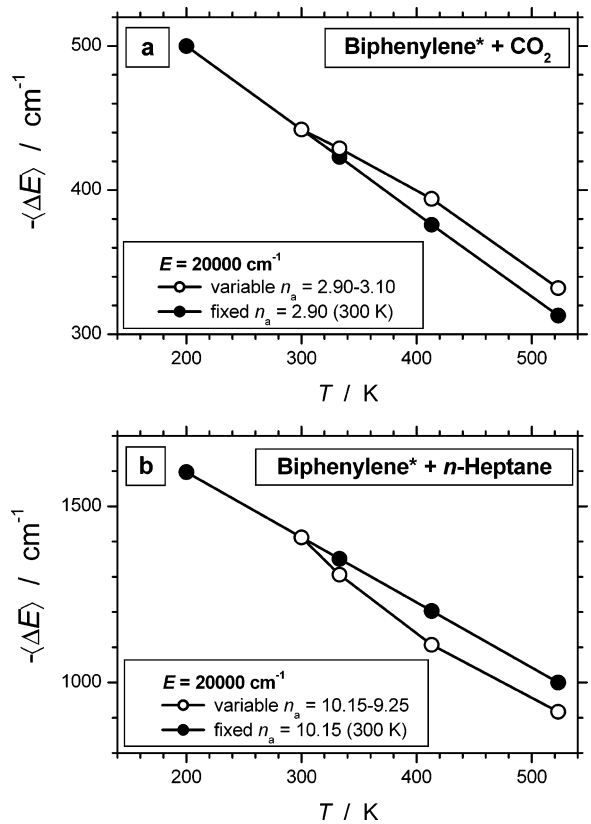

Figure 7. Temperature dependence of $\langle\Delta E\rangle$ from PECT for the collisional deactivation of biphenylene* at $E = 20\,000$ cm^{-1}. (○) By varying n_a in eq 6 to reproduce the $\langle\Delta E\rangle$ from the UVA measurements at all energies;[17] (●) with n_a fixed by fitting only the single value at $T = 300$ K. (a) biphenylene* + CO_2, $n_a = 2.90-3.10$ and $n_a = 2.90$, respectively; (b) biphenylene* + *n*-heptane, $n_a = 10.15-9.25$ and $n_a = 10.15$, respectively.

4. Conclusions

Despite its simplicity, the PECT model performs astonishingly well in decribing the gas-phase collisional energy transfer of the molecules azulene and biphenylene investigated in this study. The shape and energy dependence of $P(E',E)$ is well reproduced for CO_2 and argon, as is the wing region of $P(E',E)$ for *n*-heptane. The linear energy dependence found for $\langle\Delta E\rangle$ is consistent with the results from accurate KCSI measurements on azulene. The temperature dependence of the UVA data for biphenylene collisions with CO_2 and *n*-heptane is correctly reproduced. Obviously, the systematic variations in the shape of $P(E',E)$ as a function of "collider size" observed in the KCSI experiments have a general statistical justification. The model shows surprisingly good predictive capabilities for the energy

and temperature dependence, provided a single $\langle \Delta E \rangle$ determination is available from experiment. Once a database of PECT parameters has been accumulated for a wider range of experimental CET systems and conditions, even this referencing to measured values might no longer be necessary: One would be able to estimate numbers of active degrees of freedom, n_a, the single adjustable parameter needed in the PECT model, from known reference substances. Although the results presented in this paper appear to be a promising first step toward predicting $P(E',E)$ and related quantities, there is nevertheless still ample room for further refinements of the PECT model: Especially the description of the region around the elastic peak of $P(E',E)$ has to be improved (see, e.g., the *n*-heptane case in Figure 4a). We also note that the biphenylene data clearly show that the inherent ability to transfer energy also depends quite strongly on the nature of the reactant molecule and may approach the strong collision limit of the ECT model. For such strong collisions, the PECT implementation needs to be generalized to better reflect the efficient flow of energy among many, and perhaps most, of the degrees of freedom of the colliding molecules. Work along these lines is already in progress. Other limitations of the present form of PECT theory have been introduced to take advantage of simple approximations where more detailed treatments are unlikely to significantly alter the performance. Thus, we have neglected angular momentum conservation and used a classical representation of the active degrees of freedom in both reactant and medium molecule. To account for angular momentum conservation would complicate the algebra greatly but in most cases explain only a minor part of the collisional inefficiency. Similarly, we could use a quantum model of the active degrees of freedom but again at the cost of considerable added complexity with only minor gain in validity of the model. Rather, we propose to maintain the simplicity and broaden the set of investigated reactant−medium pairs in the hope of finding systematic variation in the single parameter n_a so that it can be predicted by "molecular interpolation". This would eliminate the need to have good data for $\langle \Delta E \rangle$ in order to calculate $P(E',E)$.

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