Supporting Information for Publication :

# **Exploring the Role of PAHs in the Formation of Soot:**

# **Pyrene Dimerization**

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### Description of experimental apparatus and methods

The apparatus was based on a CRESU<sup>S1</sup> reactor adapted for the study of the kinetics of condensable species and used to measure rate coefficients for the reactions of anthracene with CH and OH.<sup>S2,3</sup> The chamber was coupled to a time-of-flight mass spectrometer (R.M Jordan and CO, TOF-MS D-850 Reflectron) (Fig. S1) to investigate the dimerization of pyrene ( $C_{16}H_{10}$ ) which is difficult to probe by laser spectroscopic techniques. The basis of the CRESU technique and its adaptation to reactions involving PAHs have been presented in detail elsewhere.<sup>S4,5</sup> Only a brief description will be presented here, focusing on the combination of the CRESU apparatus with the TOF-MS and the procedure followed during the dimerization experiments.

The CRESU technique achieves low temperatures via the isentropic expansion of a gas through a convergent-divergent Laval nozzle. Each nozzle generates a radially and axially uniform supersonic flow at a particular temperature, density and velocity. Local thermodynamic equilibrium is ensured by collisions due to the relatively high density of the flow (10<sup>16</sup>-10<sup>17</sup> cm<sup>-3</sup>). All the properties of the flow are conserved in its core over a few tens of centimeters, corresponding to a hydrodynamic time of several hundreds of microseconds.

The PAHs are highly condensable species at room temperature with saturated vapor pressures lower than the partial pressure necessary for the experiment. In previous work, even small amount of these species (e.g. anthracene  $C_{14}H_{10}$ ) introduced into the reservoir at room temperature have caused the obstruction of the throat of the Laval nozzle. This problem was solved by heating both the reservoir and the Laval nozzle. During the present work the temperature of these two components was maintained at 470 K at which the saturated vapor pressures of mid-size PAHs are well above the required maximum partial pressure of a few tenths of a mbar in the reservoir.

The reservoir (see Fig. S1) comprises a triple-walled stainless steel cylinder. Heated silicone oil circulates in the outer layer ensuring a constant temperature. The oil was heated and its temperature was regulated by a thermostatic bath circulator (Lauda C20CS). The selected aluminum Laval nozzle was placed in a conical hollow aluminum support mounted on the reservoir and heated by thermal conduction. All Laval nozzles were characterized by impact-pressure measurements, each providing specific temperature and density for the selected buffer gas (He or  $N_2$ ). The reservoir and nozzle temperatures were measured by two *K*-type thermocouples.

At room temperature, pyrene ( $C_{16}H_{10}$ , Sigma Aldrich, 99% purity) is a yellow solid. It is placed in a stainless steel oven, heated electrically via a wire resistance wound around it, and its temperature is maintained constant by a PID regulator in the range 520-550 K with  $\pm$  3 K fluctuation. The vapor produced is mixed with a flow of around 500 sccm (cubic centimeters per minute at STP) of carrier gas, which is the same as the main buffer gas, and flushed into the heated reservoir. The flow rate of the condensable species,  $Q_{cond}$  is calculated via the relation:

$$Q_{cond} = Q_{carrier} \frac{P_{vap}(T)}{P_{oven} - P_{vap}(T)}$$
(1)

where  $Q_{carrier}$  is the volume flow rate of the carrier gas controlled by the mass flow controller (Tylan Corporation),  $P_{oven}$  the total pressure of the oven controlled using a downstream needle valve (Swagelok SS Bellows-Sealed), and  $P_{vap}(T)$  is the vapor pressure of the condensable species at the oven temperature. The temperature of the gas line between the oven and the heated reservoir was maintained constant at 50 K over the temperature of the oven to avoid the condensation of the species in the gas lines. Pyrene vapor (at a dilution of ~1 %) and the buffer

gas (in great excess) were warmed up during their circulation in the reservoir inner layer, and penetrated the reservoir through small holes present all around the third wall. Subsequently, they expanded into the chamber through the Laval nozzle. The resulting pressure in the main chamber was maintained in the range 0.3 - 0.9 mbar by a high capacity Roots/rotary pumping group regulated by means of a variable baffle valve.

The uniform supersonic flow exited the Laval nozzle, and after traveling a variable known distance (from which the reaction time could be deduced from knowledge of the flow velocity) was sampled by a first skimmer, leading into the intermediate chamber where a background pressure of 10<sup>-3</sup> mbar was maintained using a turbomolecular pump (Leybold Turbovac 450) with a capacity of 450 dm<sup>3</sup> s<sup>-1</sup>. This sampling resulted in a drastic reduction in density, effectively 'freezing' any further reactions owing to the lack of subsequent collisions. A commercial aerodynamic beam skimmer (Beam Dynamics, Inc) was used. This consists of a hollow conical body truncated at its apex to form a knife-edged circular aperture. The axial core of the uniform flow passes isentropically through the skimmer and out of the CRESU chamber, forming a molecular beam. The external apex angle of the skimmer is sufficiently acute (30°) that the oblique shock does not detach to form a standing shock wave upstream of the skimmer. At the same time, the internal angle is less acute (25°) so that the skimmed beam, still expanding, does not scatter from the internal wall of the skimmer. The leading edge of the skimmer is extremely sharp (10 µm), allowing oblique conical shock attachment at the brim and avoiding backscattering from the brim if in a more rarefied flow regime. The gas density in the expanding beam is very low, drastically limiting the number of collisions between molecules, thus ensuring that the cluster distribution in the beam remains essentially identical to that in the uniform flow.

The expanded gas was irradiated transversally by a pulsed  $F_2$  excimer laser (TuiLaser Excistar XS) operating at a wavelength of 157 nm with a 10 ns duration pulse. The laser beam entered the intermediate chamber via a MgF<sub>2</sub> window of thickness 1.5 mm, with an energy of ~1 mJ per pulse, corresponding to a fluence of ~1.5 mJ cm<sup>-2</sup> in the ionization zone. Typically, the repetition rate employed to study the kinetics of PAHs was 100 Hz. This laser is capable of ionizing mid size PAHs with a single photon energy ( $E_{photon} = 7.89 \text{ eV}$ ) just above the ionization threshold, thus minimizing excess energy deposited into the molecules, and reducing any subsequent fragmentation.

Sabbah et al.

A cylinder with a hole of 3mm diameter, aligned with the centerline of the expanded gas, was placed at the entry of the TOF-MS chamber (Fig. S1) where a background pressure of 10<sup>-6</sup> mbar was maintained by another turbomolecular pump (Leybold Turbovac 450). This cylinder was negatively polarized to attract the packet of ions produced in the ionization chamber, accelerating and injecting them into a time of flight mass spectrometer to be analyzed. When an accelerated packet of ions reached the MCP detector, the detector provided an analog output pulse whose amplitude was proportional to the number of the ions in the packet. This analog signal was amplified by a fast preamplifier (Ortec, 9326-P) and transferred to a digital signal averager (Ortec Fastflight). For each extraction pulse, the digital signal averager digitized the analog signal from the detector and added this digital record to the sum of the previous records with a regular sampling frequency (0.5 GHz). This process was repeated for a few hundred (~200) pulses to improve the signal-to-noise ratio by averaging, before the resulting data were transferred to a PC. The repetition rate of the digital signal averager (100 Hz, 10 µs width) was controlled by an external pulse generator. The ion peaks were identified according to their flight time in the drift tube, and converted to mass over charge ratio. The resulting mass spectrum depended on the delay between the ion generation and the extraction pulse. An ion of a packet produced in the ionization chamber at an instant  $t_0$  takes a specific time  $t_h$  (horizontal flight time), according to its mass and its position with respect to the cylinder, to reach the extraction zone. In order to detect the whole ion packet, the laser pulse, which defines the instant  $t_0$ , was synchronized with the pulse extraction via a delay generator (DG 535, Stanford Research Systems), enabling the scanning of a specified fixed time interval of  $t_h$  for each mass spectrum. An example of mass spectra resulting from a scan of several  $t_h$  is shown in Fig. S2. It shows pyrene monomer and cluster peaks at different  $t_h$ . For a given horizontal time of flight,  $t_h$ , the ion integrated signal,  $s_{Pv}$ was extracted. The total pyrene monomer signal,  $\sigma_{Pv}$ , was derived through the integration of  $s_{Pv}$ over an appropriate horizontal flight time interval.

The experimental procedure consisted of two steps. The first one was the identification of the temperature range over which the nucleation of pyrene was observed, by plotting  $\sigma_{Py}$  against the nominal pyrene concentration (see Fig. S3). These experiments showed that sudden nucleation of pyrene only occurred under the conditions of this experiment at 120 K and below. In this temperature range three different values (60, 80 and 120 K) were provided by the available Laval nozzles.

The second step was to determine the rate coefficients for dimerization of pyrene monomer at these temperatures. In order to achieve this objective, it was necessary to know the absolute concentration of pyrene molecules in the flow exiting the Laval nozzle because the rate equation for dimerization is second order and therefore requires knowledge of the absolute concentration of pyrene monomer. It was also necessary to perform the experiments under conditions such that the loss of monomer via the formation of oligomers higher than the dimer was minimized. The rate of loss of pyrene ( $C_{16}H_{10}$ ) monomer is given by equation (2), under conditions where the reverse reactions do not occur to any substantial extent.

$$-\frac{d\left[C_{16}H_{10}\right]}{dt} = 2k_2\left[C_{16}H_{10}\right]^2 + k_3\left[C_{16}H_{10}\right]\left[\left(C_{16}H_{10}\right)_2\right] + k_4\left[C_{16}H_{10}\right]\left[\left(C_{16}H_{10}\right)_3\right] + \cdots$$
(2)

where  $k_i$  is the rate coefficient for the formation of  $(C_{16}H_{10})_i$  by addition of monomer to the polymer containing *i*-1 molecules of pyrene. Obviously to measure the second-order rate coefficient for dimerization of pyrene  $k_2$ , it is necessary to operate under conditions where the first term of equation (2) is dominant; i.e.:

$$\sum_{i\geq 2} k_{i+1} \Big[ \big( C_{16} H_{10} \big)_i \Big] \ll 2k_2 \Big[ C_{16} H_{10} \Big]$$
(3)

Assuming that the rate coefficients have similar values, equation (3) can be reformulated as follows:

$$\sum_{i\geq 2} \left[ \left( C_{16} H_{10} \right)_i \right] << \left[ C_{16} H_{10} \right]$$
(4)

To satisfy this condition, the total concentration of pyrene oligomers that are formed should be significantly less than that of the monomers that remain. Consequently, a good approximation is to perform the experiments under conditions where there is a relatively small loss of monomer (< 20-30%). In the light of these assumptions the evolution of pyrene monomer concentration vs. distance in the flow exiting the Laval nozzle can be written as follows:

$$\frac{1}{\left[C_{16}H_{10}\right]_{d}} - \frac{1}{\left[C_{16}H_{10}\right]_{d_{0}}} = \frac{2k_{ba}d}{v}$$
(5)

Where  $k_{ba}$  is the apparent bimolecular rate coefficient, *d* is the distance between the exit of the Laval nozzle and the skimmer, *v* the velocity of the flow calculated when the Laval nozzle was characterized by the impact-pressure measurements and  $[C_{16}H_{10}]_d$  and  $[C_{16}H_{10}]_{x0}$  are respectively

Sabbah et al.

the concentration of pyrene at distances d and  $d_0 = 0$  from the exit of the Laval nozzle, which to a good approximation corresponds to the point at which the cold uniform supersonic flow is established and therefore to the start of the dimerization reaction.

At a specified temperature,  $\sigma_{Py}$  was measured for several different distances from the exit of the Laval nozzle as shown in Fig. 2(a). The values of  $\sigma_{Py}$  were then converted to the concentration of pyrene monomer in the flow. The inverse values of pyrene concentration  $1/[C_{16}H_{10}]_x$  are plotted against reaction time *t* to yield the  $k_{ba}$  for the reactions of dimerization of pyrene monomer at that temperature. The  $k_{ba}$  rate constants for the dimerization of pyrene were obtained for three temperatures 60, 80 and 120 K (Figs. 2(b) and S4(a) and (b)). The nucleation process was not observed at 235 K although it was still possible to measure a small (10%) loss of monomer signal with a very high initial concentration of pyrene (1.5% of the flow density) to give an approximate value for  $k_{ba}$  (Fig. S4(c)). The results of these experiments are listed in Table S1. The estimated error in the measurements of  $k_{ba}$  is a combination of a statistical contribution, corresponding to the standard error  $\sigma_{std}$  from the plots of  $1/[Py]_x$  vs. *x* multiplied by the appropriate value of the Student's *t* distribution for the 95% point ( $\sigma_{syst} = t \sigma_{std}$ ), and an estimate of the likely systematic error  $\sigma_{syst}$ .

#### **Description of theoretical methods**

The dimerization of PAHs generally involves only weak, non-chemical, bonding arising from electrostatic and dispersion interactions. Correspondingly, there is little change in the intramolecular vibrational frequencies of the two reacting PAHs during the dimerization process. In essence, these "conserved" vibrational modes are largely decoupled from the recombination kinetics and can be considered separately from the intermolecular dynamics. Thus, the present theoretical analysis focuses on the rigid body dynamics of the two reactant PAHs.

The kinetic analysis for this rigid body dynamics requires some description of the potential energy for the interaction between the two PAHs over a wide range of separations. The high pressure capture kinetics rely on an accurate description of these intermolecular interactions for large separations ( $\sim$ 8-20 Å). Meanwhile, the redissociation rates, which determine the pressure dependence of the recombination kinetics, depend on the density of states for the complex, which in turn is governed by the interaction energies for separations centered about the equilibrium geometry of the dimer ( $\sim$ 4 Å).

The present kinetics calculations require estimated interaction energies for a large number of geometries. In particular, on the order of 10<sup>4</sup> evaluations are required to converge the configurational integrals implicit in the transition state theory analyses for the capture and redissociation kinetics. The relatively large size of PAHs makes the accurate determination of these interaction energies directly from ab initio electronic structure calculations very computationally demanding. Thus, in this initial study of the kinetics, we have chosen to implement a simple model potential as in a number of previous studies of the binding of two or more PAHs.<sup>S6-11</sup> The parameters in this model potential are designed to reproduce both the long-range interaction energies and high level theoretical estimates of the binding energies for a range of PAHs.

The present model potential is written as the sum an electrostatic interaction and a dispersionrepulsion term. The electrostatic interaction is represented in terms of the Coulombic interactions between sets of partial changes  $\{q_i\}$  located at the nuclei of each of the atoms,

$$V_Q = \sum_{ij} \frac{q_i q_j}{r_{ij}} \quad , \tag{6}$$

where  $r_{ij}$  is the separation between atom *i* in one PAH and atom *j* in the other PAH. Meanwhile, the dispersion-repulsion interaction is represented with the Buckingham *exp-6* form

$$V_{disp-rep}^{\exp-6} = \sum_{ij} A_{ij} \exp\left(-B_{ij}r_{ij}\right) - \frac{C_{6,ij}}{r_{ij}^{6}} \quad ,$$
(7)

where  $A_{ij}$ ,  $B_{ij}$ , and  $C_{6,ij}$  are parameters specifying the interaction between atoms *i* and *j*.

The parameters for this potential are derived from those previously reported by Rapacioli et al..<sup>S9</sup> and by Miller et al.,<sup>S7</sup> with modifications based on the work of Wu and Yang<sup>S12</sup> and of Marques et al.<sup>S13</sup> In particular, in analogy with Rapacioli et al.,<sup>S9</sup> the atomic charges are derived from the electrostatic potential (ESP) fitting analysis as implemented in the GAUSSIAN electronic structure software package.<sup>S14</sup> We employ B3LYP/6-311++G\*\* geometries and wavefunctions

for this charge analysis. Initial values for the parameters  $A_{ij}$  and  $B_{ij}$  in the *exp-6* potential are taken from Miller et al..<sup>S7</sup> The absence of any dipoles in the PAHs considered here implies that the dispersion interaction  $(-C_{6,ij}/R_{ij}^{6})$  is the longest ranged term in the potential. Correspondingly, it is this interaction that determines the high pressure capture rate at low temperature. Thus, it is of some importance to the present analysis to have an accurate description of these coefficients.

Accurate molecular  $C_6$  coefficients have been determined by Meath and coworkers for a range of molecules from their measurements of dipole oscillator strength distributions (DOSD).<sup>S15</sup> Wu and Yang have used these molecular coefficients to derive atomic  $C_{6,ij}$  coefficients including values for  $C_6$  in an  $sp^2$  environment.<sup>S12</sup> Recently, Marques et al.<sup>S13</sup> used TDDFT (time-dependent DFT) to calculate the molecular  $C_6$  coefficients for a number of PAHs. For benzene, the TDDFT molecular  $C_6$  coefficient is in quantitative agreement with the DOSD value and similar accuracy is expected for the other PAHs studied in Marques et al.<sup>S13</sup> The atomic  $C_{6,ij}$  coefficients of Wu and Yang yield molecular  $C_6$  coefficients that on average are 20% lower than the TDDFT PAH values. Thus, in the present work, we employ the  $C_{6,ij}$  values of Wu and Yang<sup>S12</sup> multiplied by 1.25.

For pyrene the resulting molecular  $C_6$  coefficient of  $1.6 \times 10^5$  Å<sup>6</sup> kcal mol<sup>-1</sup> is identical to the TDDFT prediction.<sup>S13</sup> The present atomic  $C_6$  coefficient for the CC interaction is 470 Å<sup>6</sup> kcal mol<sup>-1</sup>. For comparison, typical values employed in the literature range from about 390 to about 740 Å<sup>6</sup> kcal mol<sup>-1</sup>,<sup>S16,17</sup> with the standard molecular mechanics force field CHARMM27 employing a value of 560 Å<sup>6</sup> kcal mol<sup>-1</sup>.<sup>S18</sup> According to long-range transition state theory,<sup>S19</sup> the low temperature capture rate is proportional to  $(C_6)^{I/3}$ . Thus, the apparent 40% uncertainty in this coefficient correlates with only a 12% uncertainty in the capture rate. Reasonable variations in other components of this potential have essentially no effect on the predicted capture rate but do strongly affect the binding energy, equilibrium constant and dissociation rates.

The combination of these revised  $C_{6,ij}$  parameters, the set of  $A_{ij}$  and  $B_{ij}$  parameters from Miller et al.,<sup>S7</sup> and the ESP charges yields dimer binding energies that are about 10 to 20% below the estimated CCSD(T)/CBS and SAPT(DFT) quantum chemical estimates for benzene and pyrene. To improve the agreement we have adjusted the  $A_{ij}$  values, with a uniform reduction (0.92) to uniformly increase the binding energies and a further specific reduction to  $A_{CH}$  (0.8) to

differentiate the effect on the benzene binding energy, where the C:H ratio is only 1:1, from the effect on the pyrene binding energy, where the C:H ratio is 1.6:1.

The optimized parameters  $A_{ij}$ ,  $B_{ij}$ , and  $C_{6,ij}$  employed in this work are reported in Table S2. The predicted binding energies from this model for benzene, naphthalene, anthracene, and pyrene are generally within 10% of those from corresponding high level ab initio predictions.<sup>S20-26</sup> The present theoretical predictions for the pyrene dimerization energies are contrasted with a variety of related predictions in Table S3. The density functional theory (DFT) based symmetry adapted perturbation theory (SAPT) results, which accurately reproduce the benchmark CCSD(T) calculations for benzene,<sup>S23</sup> should provide a valid benchmark for pyrene. Notably, the present model predictions remove the apparent overestimate that was present in earlier model potentials and should provide a reasonably accurate representation of the binding in pyrene and other PAH dimers.

The high pressure capture rate coefficients for the pyrene self-recombination were analyzed with both trajectory simulations and variable reaction coordinate (VRC) transition state theory (TST) employing the above described model potential. These calculations are performed in a reduced dimensional transitional mode space consisting of only the rotational and translational degrees of the freedom of the reactants. The VRC-TST approach<sup>S27,28</sup> has been shown to provide an effective means of accounting for the effect of short range interactions.<sup>S29,30</sup> It incorporates accurate phase space integral based anharmonic state counts at the total energy *E* and total angular momentum *J* resolved level for the full dimensional transitional mode space.

The present model potential was also employed in phase space integral based evaluations of the equilibrium constant. These evaluations again assumed a separation into the conserved internal vibrational modes and transitional intermolecular modes. The conserved mode vibrational frequencies of the dimers are assumed to be identical to those of the reactants. In this case, the contribution of the conserved mode vibrations to the dimer and monomer partition functions cancel.

To predict the kinetics at low pressure we have performed master equation simulations implementing the dynamically corrected VRC-TST E/J resolved rate constants. These master equation simulations employ an exponential down model for the collisional energy transfer process and Lennard Jones collision rates. Related studies of pressure dependent recombination

reactions have empirically suggested that the average downwards energy transfer,  $\langle \Delta E_{\text{down}} \rangle$ , decreases with temperature and is reasonably well represented by the form  $\alpha_0 (T/300 \text{ K})^{0.85} \text{ cm}^{-1}$ , where *T* is in K. The Lennard Jones parameters for He and N<sub>2</sub> are taken from Hirschfelder, Curtiss and Bird,<sup>S31</sup> and those for the pyrene dimer are taken to be  $\sigma = 9 \text{ Å}$  and  $\varepsilon = 500 \text{ K}$ .

The conserved mode vibrational frequencies, which are required for the generation of absolute state densities in the master equation simulations, are obtained from B3LYP density functional theory employing the 6-311++G\*\* basis set. For simplicity, the density of states for the complex simply employs a one-dimensional hindered rotor treatment of the lowest frequency transitional mode and harmonic oscillator treatments for the remaining ones, using the transitional mode frequencies from Rapacioli et al.<sup>S32</sup> The resulting canonical partition function for the complex agrees with the fully anharmonic phase space integral analysis to within 20% for temperatures ranging from 60 K to 235 K. This agreement suggests that the corresponding state density is at least accurate in some average sense.

The weakness of the bonding interactions for these  $\pi$ -complexes creates some complications for the analysis of the capture process. In particular, the application of variational TST to the process presumes some minimum in the plot of the flux versus fixed assumed separation between the two reactants, with the location of this minimum defining the transition state. As the separation is decreased from this transition state separation, the flux at fixed separation rises, usually quite dramatically, before it ultimately decays to zero as the separation decreases below that corresponding to the equilibrium of the complex. With weak bonding the flux minimum becomes quite shallow and even disappears at higher energies or temperatures and the location of the transition state becomes ill-defined.

The *R* dependent behavior of the VRC-TST calculated flux is illustrated in Fig. S5 for the dimerization of pyrene. At low temperature (e.g., 40 - 390 K) these plots show a clear flux minimum at  $R \sim 10$  to 20 Å. The flux minimum then gradually disappears over the 510 to 740 K range, and then for even higher temperature there is no minimum at all. To make predictions for these higher temperatures we simply restrict the separation to  $R \ge 6.3$  Å, which is the location of the remnant of the maximum in the flux as it disappears. This absence of a maximum in the reactive flux at high energies has an even greater effect on the final canonical rate when the TST

analysis is implemented at the proper E/J resolved level. As a result, the present predictions for the high-pressure capture rate can only be considered reliable for temperatures up to about 300 K. Related problems arise in the trajectory simulations. For such simulations there is generally a plateau in the calculated recrossing probability as a function of the value of the minimum potential taken to define the formation of the complex. At higher temperatures, i.e., above 200 K, the plateau in this recrossing probability disappears and it simply decreases with decreasing minimum potential value. In essence, the rate constant itself is ill-defined as the complex and the reactants are no longer dynamically distinct.

At temperatures of 200 K or lower, where the rate coefficients are well defined, the trajectory and VRC-TST rate predictions are in very good agreement, with discrepancies of 10% or less. As the temperature increases, the discrepancy gradually increases, but is still less than 20% for temperatures of 500 K or less.

At higher temperatures the equilibrium constant also becomes ill-defined for much the same reasons as discussed for the rate coefficients. In particular, at temperatures of 500 K and above the peak in the differential contribution to the partition function comes from pyrene-pyrene separations R that are greater than 6.3 Å. Correspondingly, the radial component of the integral cannot be converged. Nevertheless, we have evaluated the equilibrium constant by simply restricting the radial integral to R < 6.3 Å.

The VRC-TST predictions for the high pressure capture rate are contrasted in Fig. S6 with the present experimental results for the pyrene dimerization. The modest decrease in the predicted high pressure recombination rate coefficient for pyrene at the highest temperatures is an indication of the effect of the short range repulsions that reduce the flux at shorter separations. As the temperature rises, the transition state separation decreases and these repulsions become more effective in reducing the available flux. Notably, theory and experiment approach one another as the temperature decreases. The careful nature of the theoretical examination of the high pressure limit strongly suggests that the increasing discrepancy with increasing temperatures is due to significant fall-off in the rate constant for the experimentally studied pressures.

Illustrative results from master equation simulations of the pressure dependence for the recombination rate coefficient are provided in Fig. S7. Notably, the reference calculations (solid lines), which employ a representative  $\langle \Delta E_{\text{down}} \rangle$  of 400 (T / 300 K) cm<sup>-1</sup>, do not show nearly

enough falloff at low temperature. Fits to the experimental data would require  $\langle \Delta E_{\text{down}} \rangle$  values of a few cm<sup>-1</sup>; which is unphysically small. Other reasonable changes in physical parameters such as the dissociation energy or effect of anharmonicities on the state densities cannot yield the necessary dramatic change in  $\langle \Delta E_{\text{down}} \rangle$ .

The reference calculations presume rapid transfer of energy amongst all modes. In contrast, the dashed lines in Fig. S7 illustrate the predicted pressure dependence for a limiting case where we assume no transfer of energy between the transitional and conserved modes of the dimer. For this case, the rate coefficients are predicted to decrease too rapidly with decreasing pressure, suggesting that some partial but incomplete energy transfer occurs. As illustrated in Fig. 4, the experimental data can be fairly well reproduced by assuming that energy transfer from the transitional modes is rapid to only the lowest 3 conserved modes of the complex. Interestingly, for benzene, related master equation simulations to model the CRESU data of Hamon et al.,<sup>S33</sup> do not depend on the coupling of the conserved modes because, due to the low binding energy, there is not enough energy in the complex for them to be excited.

### Tables

**Table S1:** Rate coefficients for the dimerization of pyrene monomer at temperatures between 60 and 120 K. At 235 K the value of  $k_{ba}$  should be considered as an upper limit. Quoted errors correspond to 95% confidence limits.

		[M]/10 <sup>16</sup>	$[Py]/10^{12}$	No. Of	$k_{ba}$ / 10 <sup>-11</sup> cm		<sup>1</sup> cm <sup>3</sup>
<i>T</i> /K	М	molecules cm <sup>-3</sup>	molecules cm <sup>-3</sup>	Points	molecules <sup>-1</sup> s <sup>-1</sup>		$s^{-1} s^{-1}$
60	He	4.01	40	9	3.28	±	1.4
60	Не	4.01	65	9	4.05	±	1.0
80	$N_2$	9.04	60	8	1.87	±	0.35
80	$N_2$	5.43	50	9	1.6	±	0.48
120	$N_2$	1.96	65	11	0.42	±	0.1
120	$N_2$	1.96	125	9	0.56	±	0.16
235	$N_2$	2.06	350	9	0.044	±	0.025
470	$N_2$	5.17	1567	16		-	

**Table S2**: *Exp-6* parameters for the model potential.

Parameter	Pair of Atoms					
	CC	СН	HH			
$A_{ij}{}^a$	7.69x10 <sup>4</sup>	$6.45 \times 10^3$	$2.44 \times 10^3$			
$B_{ij}{}^b$	3.60	3.67	3.74			
$C_{6ij}{}^c$	470	116	48.8			

<sup>a</sup> Parameter  $A_{ij}$  in Å<sup>6</sup> kcal mol<sup>-1</sup>.

<sup>b</sup> Parameter  $B_{ij}$  in Å<sup>-1</sup>.

<sup>c</sup> Parameter  $C_{6,ij}$  in Å<sup>6</sup> kcal mol<sup>-1</sup>.

**Table S3**: Pyrene-pyrene interaction energies (kcal mol<sup>-1</sup>).

Method		G				
	Gr		SP-L	Х	SP-S	S
Ab Initio						
SAPT(DFT) <sup>a S26</sup>	-9.87	-9.90	-9.44		-9.75	
c-DFTB-D <sup>b,S32</sup>		-10.02	-9	.94	-10.22	-8.93
DFT-D <sup>c,S32</sup>		-8.12			-7.88	
vdW-DF <sup>d,S34</sup>						-6.50
DFT-D <sup>c,S16</sup>						-11.82
MP2/6-31G* <sup>S35</sup>					-12.35	
MP2/6-		-17.8				
$31G^{*}(0.25)^{e,S36}$						
MP2/6-31G <sup>S37</sup>	-12.91	-13.11	-1(	).42	-12.90	
HFD/6-31G <sup>f S37</sup>	-11.97	-12.19	-11.70		-11.97	
<b>Empirical Models</b>						
Present	-10.01	-10.14	-9	.88	-9.93	-9.45
Herdman et al. <sup>S11</sup>			-14	4.24		
Rapacioli et al. <sup>89</sup>			-12	2.72		

<sup>&</sup>lt;sup>a</sup> Symmetry adapted perturbation theory based on DFT treatment of the monomers.
<sup>b</sup> Electrostatic charge and dispersion correction density functional tight binding calculations.
<sup>c</sup> Dispersion corrected DFT.
<sup>d</sup> van der Waals DFT.
<sup>e</sup> MP2 calculations with a modified 6-31G\* basis set.

<sup>&</sup>lt;sup>f</sup> Dispersion corrected Hartree-Fock theory.

## Figures



**Fig. S1:** CRESU apparatus dedicated to kinetics studies of reactions involving condensable species combined with a time of flight mass spectrometer for detection of the reactants and products. See text for details.



**Fig. S2:** Experimental mass spectra of a 60 K,  $4.01 \times 10^{16}$  molecules cm<sup>-3</sup> helium supersonic flow containing  $1.35 \times 10^{14}$  molecules cm<sup>-3</sup> pyrene at a reaction time of 48.5 µs, recorded for different  $t_h$ , indicated on the right. The horizontal arrival time corresponding to the maximum ion signal consistently increases with cluster size.



**Fig. S3:** Plots of pyrene monomer signal  $\sigma_{py}$  as a function of nominal pyrene density (as calculated from pyrene flow rate, mixing ratio and total flow density). The upper panel (a) demonstrates the linear dependence of  $\sigma_{py}$  on pyrene density at 470 K in a subsonic flow at a total density of  $7.97 \times 10^{16}$  molecules cm<sup>-3</sup>. In the lower panel (b), nucleation at a temperature of 60 K is evidenced by the collapse of the pyrene monomer signal above a nominal pyrene density of  $\sim 10^{14}$  molecules cm<sup>-3</sup> for a reaction time of 48 µs and a total density of  $4.01 \times 10^{16}$  molecules cm<sup>-3</sup>.



Page 19 of 25

**Fig. S4:** Plots of 1/[py] as a function of time at (a) 60 K with an initial concentration of pyrene  $[py]_0 = 6.5 \times 10^{13}$  molecules cm<sup>-3</sup> – an apparent bimolecular rate coefficient  $k_{ba} = (4.05 \pm 1.0) \times 10^{-11}$  cm<sup>3</sup> molecules<sup>-1</sup> s<sup>-1</sup> is deduced from the slope of the plot; (b) 120 K with an initial concentration of pyrene  $[py]_0 = 12.5 \times 10^{13}$  molecules cm<sup>-3</sup> – an apparent bimolecular rate coefficient  $k_{ba} = (0.56 \pm 0.16) \times 10^{-11}$  cm<sup>3</sup> molecules<sup>-1</sup> s<sup>-1</sup> is deduced from the slope of the plot; and (c) 235K with an initial concentration of pyrene  $[py]_0 = 3.5 \times 10^{14}$  molecules cm<sup>-3</sup>. An upper limit of  $k_{ba} = (0.044 \pm 0.025) \times 10^{-11}$  cm<sup>3</sup> molecules<sup>-1</sup> s<sup>-1</sup> is deduced from the slope of the plot.



**Fig. S5:** Plot of the TST capture rate coefficient as a function of fixed intermolecular separation R for the TS dividing surface in pyrene + pyrene at a variety of temperatures.



**Fig. S6:** Comparison of the VRC-TST predictions for the high pressure capture rates for pyrene + pyrene with the experimental measurements for the capture rate at a pressure of  $\sim 1$  mbar.



**Fig. S7:** Pressure dependent rate coefficients for pyrene dimerization at temperatures of 60, 80, 120, and 235 K (color-coded as indicated on the plot). The lines denote master equation simulations that assume either rapid IVR amongst all the modes (solid lines) or amongst only the transitional modes (dashed lines). The symbols denote the present experimental measurements, where the point at T = 235 K represents an upper limit.

### References

- S1 The acronym CRESU stands for Cinétique de Réaction en Ecoulement Supersonique Uniforme, or Reaction Kinetics in Uniform Supersonic Flow. The technique was originally developed by Rowe and his co-workers for the study of ion-molecule reactions: see Dupeyrat, G.; Marquette, J. B.; Rowe, B. R. Design and Testing of Axisymmetric Nozzles for Ion-Molecule Reaction Studies between 20-Degrees K and 160-Degrees K. *Phys. Fluids* **1985**, *28*, 1273-1279.
- S2 Goulay, F.; Rebrion-Rowe, C.; Biennier, L.; Le Picard, S. D.; Canosa, A.; Rowe, B. R. Reaction of Anthracene with CH Radicals: An Experimental Study of the Kinetics between 58 and 470 K. J. Phys. Chem. A 2006, 110, 3132-3137.
- S3 Goulay, F.; Rebrion-Rowe, C.; Le Garrec, J. L.; Le Picard, S. D.; Canosa, A.; Rowe, B. R. The Reaction of Anthracene with OH Radicals: An Experimental Study of the Kinetics between 58 and 470 K. J. Chem. Phys. 2005, 122, 104307.
- S4 Rowe, B. R.; Dupeyrat, G.; Marquette, J. B.; Gaucherel, P. Study of the Reactions N-2+ + 2n2-]N-4+ + N2 and O-2+ + 2o2-]O-4+ + O2 from 20 to 160 K by the Cresu Technique. J. Chem. Phys. **1984**, 80, 4915-4921.
- Sims, I. R.; Queffelec, J. L.; Defrance, A.; Rebrion-Rowe, C.; Travers, D.; Bocherel, P.; Rowe, B. R.; Smith, I. W. M. Ultralow Temperature Kinetics of Neutral-Neutral Reactions the Technique and Results for the Reactions Cn+O-2 Down to 13 K and Cn+Nh3 Down to 25 K. J. Chem. Phys. 1994, 100, 4229-4241.
- S6 van de Waal, B. W. Calculated Ground-State Structures of 13-Molecule Clusters of Carbon Dioxide, Methane, Benzene, Cyclohexane, and Naphthalene. J. Chem. Phys. **1983**, 79, 3948-3961.
- S7 Miller, J. H.; Mallard, W. G.; Smyth, K. C. Intermolecular Potential Calculations for Polycyclic Aromatic-Hydrocarbons. J. Phys. Chem. **1984**, 88, 4963-4970.
- S8 Rubio, M.; Orti, E.; Sanchez-Marin, J. A Study of Coronene-Coronene Association Using Atom-Atom Pair Potentials. *Int. J. Quantum Chem.* 1996, 57, 567-573.
- S9 Rapacioli, M.; Calvo, F.; Spiegelman, F.; Joblin, C.; Wales, D. J. Stacked Clusters of Polycyclic Aromatic Hydrocarbon Molecules. J. Phys. Chem. A 2005, 109, 2487-2497.
- S10 Obolensky, O. I.; Semenikhina, V. V.; Solov'yov, A. V.; Greiner, W. Interplay of Electrostatic and Van Der Waals Forces in Coronene Dimer. *Int. J. Quantum Chem.* 2007, 107, 1335-1343.
- S11 Herdman, J. D.; Miller, J. H. Intermolecular Potential Calculations for Polynuclear Aromatic Hydrocarbon Clusters. J. Phys. Chem. A 2008, 112, 6249-6256.
- S12 Wu, Q.; Yang, W. T. Empirical Correction to Density Functional Theory for Van Der Waals Interactions. J. Chem. Phys. 2002, 116, 515-524.
- S13 Marques, M. A. L.; Castro, A.; Malloci, G.; Mulas, G.; Botti, S. Efficient Calculation of Van Der Waals Dispersion Coefficients with Time-Dependent Density Functional Theory in Real Time: Application to Polycyclic Aromatic Hydrocarbons. J. Chem. Phys. 2007, 127, 014107.
- S14 Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Stratmann, R. E.; Burant, J. C.; Dapprich, S. et al. *Gaussian 98* (Gaussian, Inc., Pittsburgh, PA 1998).
- S15 Kumar, A.; Meath, W. J. Dipole Oscillator Strength Properties and Dispersion Energies for Acetylene and Benzene. *Mol. Phys.* **1992**, *75*, 311-324.
- S16 Grimme, S. Accurate Description of Van Der Waals Complexes by Density Functional Theory Including Empirical Corrections. J. Comput. Chem. 2004, 25, 1463-1473.
- S17 Kaminski, G. A.; Stern, H. A.; Berne, B. J.; Friesner, R. A. Development of an Accurate and Robust Polarizable Molecular Mechanics Force Field from Ab Initio Quantum Chemistry. J. Phys. Chem. A 2004, 108, 621-627.
- S18 MacKerell, A. D.; Bashford, D.; Bellott, M.; Dunbrack, R. L.; Evanseck, J. D.; Field, M. J.; Fischer, S.; Gao, J.; Guo, H.; Ha, S. et al. All-Atom Empirical Potential for Molecular Modeling and Dynamics Studies of Proteins. J. Phys. Chem. B 1998, 102, 3586-3616.
- S19 Georgievskii, Y.; Klippenstein, S. J. Long-Range Transition State Theory. J. Chem. Phys. 2005, 122, 194103.
- S20 Sherrill, C. D.; Takatani, T.; Hohenstein, E. G. An Assessment of Theoretical Methods for Nonbonded Interactions: Comparison to Complete Basis Set Limit Coupled-Cluster Potential Energy Curves for the Benzene Dimer, the Methane Dimer, Benzene-Methane, and Benzene-H2s. J. Phys. Chem. A 2009, 113, 10146-10159.
- S21 Tsuzuki, S.; Honda, K.; Uchimaru, T.; Mikami, M. High-Level Ab Initio Computations of Structures and Interaction Energies of Naphthalene Dimers: Origin of Attraction and Its Directionality. J. Chem. Phys. 2004, 120, 647-659.

- S22 Tsuzuki, S.; Honda, K.; Uchimaru, T.; Mikami, M. Ab Initio Calculations of Structures and Interaction Energies of Toluene Dimers Including Ccsd(T) Level Electron Correlation Correction. J. Chem. Phys. 2005, 122, 144323.
- S23 Podeszwa, R.; Bukowski, R.; Szalewicz, K. Potential Energy Surface for the Benzene Dimer and Perturbational Analysis of Pi-Pi Interactions. J. Phys. Chem. A 2006, 110, 10345-10354.
- S24 Krause, H.; Ernstberger, B.; Neusser, H. J. Binding-Energies of Small Benzene Clusters. Chem. Phys. Lett. 1991, 184, 411-417.
- S25 Grover, J. R.; Walters, E. A.; Hui, E. T. Dissociation-Energies of the Benzene Dimer and Dimer Cation. J. *Phys. Chem.* **1987**, *91*, 3233-3237.
- S26 Podeszwa, R.; Szalewicz, K. Physical Origins of Interactions in Dimers of Polycyclic Aromatic Hydrocarbons. *Phys. Chem. Chem. Phys.* **2008**, *10*, 2735-2746.
- S27 Klippenstein, S. J. Variational Optimizations in the Rice-Ramsberger-Kassel-Marcus Theory Calculations for Unimolecular Dissociations with No Reverse Barrier. J. Chem. Phys. **1992**, *96*, 367-371.
- S28 Georgievskii, Y.; Klippenstein, S. J. Transition State Theory for Multichannel Addition Reactions: Multifaceted Dividing Surfaces. J. Phys. Chem. A 2003, 107, 9776-9781.
- S29 Harding, L. B.; Klippenstein, S. J.; Georgievskii, Y. Reactions of Oxygen Atoms with Hydrocarbon Radicals: A Priori Kinetic Predictions for the CH3+O, C2H5+O, and C2H3+O Reactions. *Proc. Combust. Inst.* 2005, 30, 985-993.
- S30 Klippenstein, S. J.; Georgievskii, Y.; Harding, L. B. Predictive Theory for the Combination Kinetics of Two Alkyl Radicals. *Phys. Chem. Chem. Phys.* 2006, *8*, 1133-1147.
- S31 Hirschfelder, J. O.; Curtiss, C. F.; Bird, R. B. Molecular Theory of Gases and Liquids; John Wiley & Sons: New York, 1954.
- S32 Rapacioli, M.; Spiegelman, F.; Talbi, D.; Mineva, T.; Goursot, A.; Heine, T.; Seifert, G. Correction for Dispersion and Coulombic Interactions in Molecular Clusters with Density Functional Derived Methods: Application to Polycyclic Aromatic Hydrocarbon Clusters. J. Chem. Phys. 2009, 130, 244304-244310.
- S33 Hamon, S.; Le Picard, S. D.; Canosa, A.; Rowe, B. R.; Smith, I. W. M. Low Temperature Measurements of the Rate of Association to Benzene Dimers in Helium. J. Chem. Phys. 2000, 112, 4506-4516.
- S34 Chakarova, S. D.; Schroder, E. Van Der Waals Interactions of Polycyclic Aromatic Hydrocarbon Dimers. J. Chem. Phys. 2005, 122, 054102.
- S35 Yurtsever, E. Pi-Stack Dimers of Small Polyaromatic Hydrocarbons: A Path to the Packing of Graphenes. J. *Phys. Chem. A* **2009**, *113*, 924-930.
- S36 Lee, N. K.; Kim, S. K. Ab Initio-Based Intermolecular Carbon-Carbon Pair Potentials for Polycyclic Aromatic Hydrocarbon Clusters. J. Chem. Phys. 2005, 122, 031102.
- S37 Gonzalez, C.; Lim, E. C. Evaluation of the Hartree-Fock Dispersion (Hfd) Model as a Practical Tool for Probing Intermolecular Potentials of Small Aromatic Clusters: Comparison of the HFD and MP2 Intermolecular Potentials. J. Phys. Chem. A 2003, 107, 10105-10110.