

SUPPLEMENTARY MATERIAL

Tabulated microcanonical evaporation rates for cluster sizes from $n=2$ to $n=40$ are given between 0 and 20 eV at $J = 0$.

Tabulated canonical evaporation rates for cluster sizes from $n=2$ to $n=40$ are given between 50 and 400 K.

File with figures with the canonical evaporation rates calculated with the same conditions as in figure 10 for sizes $n=3$ and $n=20$.

APPENDIX: DERIVATION OF EVAPORATION RATES

We first recall the expression for the PST evaporation rate:

$$W(E, J) = \frac{(\alpha_f/\alpha_b)G(E_f, J)}{h(2J + 1)N(E)}$$

where J is the rotational state of the parent cluster, α_f and α_b are the forward and backward reaction path degeneracy respectively.

The density of state N and total number of states G are obtained by inverting the partition functions associated with the parent and products.

The version of PST used here contains the constraint that total angular momentum is conserved, and that in the reverse process the associating product must overcome the maximum of the centrifugal barrier which defines the position of the transition state (loose transition state).

The interaction between the products is represented by an effective central potential of the form:

$$V_{eff}(r) = -\frac{C_n}{r^n} + \frac{L^2 \hbar^2}{2\mu r^2}$$

and the minimum energy y_m required to clear the centrifugal barrier is:

$$y_m = \left(\frac{L^*}{b_n}\right)^{\frac{2n}{n-2}} + B_r(L^* - J)^2$$

$$b_n = \frac{1}{\hbar} \left(\frac{2n\mu}{n-2}\right)^{1/2} \left(\frac{(n-2)C_n}{2}\right)^{1/n}$$

with μ is the reduced mass of the fragments, $B_r = \frac{B_1 B_2}{B_1 + B_2}$, B_1 and B_2 being the rotational constants for the products. In other words, y_m is the energy sufficient to generate the combined translational-rotational energy corresponding to J .

For the considered ion polar interaction $n=4$, and the coefficient C_n is given as $C_4 = \frac{1}{2} \alpha \frac{e^2}{4\pi\epsilon_0}$, where $\alpha = 29.72 \text{ \AA}^3$ is the pyrene polarisability [81].

The interpolated partition function between low and high J for external (rotational) degrees of freedom that takes into account the minimum energy required to generate the given J is:

$$Q_{xi} = e^{-\frac{y_m(J)}{k_B T}} \frac{b}{\sigma} (k_B T)^{r/2} \text{erf}\left(J + \frac{1}{2}\right) \frac{a}{(k_B T)^{1/2}}$$

where σ is the product of the symmetric numbers for fragments 1 and 2. It is taken equal to 1 since we assume spherical symmetry for all products.

For two spherical fragments the parameters are:

$$a = \left(\frac{B_1 B_2}{B_1 + B_2}\right)^{\frac{1}{2}}$$

$$b = \frac{\pi}{(B_1 B_2)^{\frac{3}{2}}}$$

$$r = 6$$

The total number of states of the fragments $G(E, J)$ is obtained by inverting the combined vibrational and external partition function:

$$Q_{vx} = Q_v^f Q_{xi}$$

where Q_v^f is the vibrational partition function of the fragments.

$$G(E) = \mathcal{L}^{-1}\left(\frac{Q_{vx}(x)}{x}\right)$$

The inverse Laplace transform is obtained by the Steepest Descent method also called saddle-point method, which yields:

$$G(E) = \frac{\exp(\phi(x^*))}{(2\pi\phi''(x^*))^{1/2}}$$

with

$$\phi(x) = \ln(Q_v^f(x)) + (E - y_m(J)) + \ln\left(\frac{b}{\sigma}\right) - \left(1 + \frac{r}{2}\right)\ln(x) + \ln(\operatorname{erf}(a\sqrt{x}))$$

and x^* defined as :

$$\frac{\partial\phi(x)}{\partial x} = 0$$

The vibrational partition function is taken as:

$$Q_v^f = \prod_i^n \frac{1}{1 - \exp(-\hbar\omega_i/(k_b T))}$$

which is the one for an ensemble of n independent harmonic oscillators.

Similarly, the density of states of the parent is obtained with the same procedure by inverting the vibrational partition function of the parent:

$$N(E) = \mathcal{L}^{-1}(Q_v(x))$$

$$N(E) = \frac{\exp(\phi(x^*))}{(2\pi\phi''(x^*))^{1/2}}$$

with this time:

$$\phi(x) = \ln(Q_v(x))$$

We performed a Monte Carlo integration over the thermal distribution of internal energies E and angular momentum J . The internal energies are sampled by randomly picking up the occupation number n_i of mode i so that it follows the probability:

$$P(n_i) = (1 - e^{-\hbar\omega_i/k_B T})e^{-n_i\hbar\omega_i/k_B T}$$

and the internal energy is obtained as:

$$E = \sum_i n_i \hbar \omega_i$$

The occupations numbers n_i are obtained as :

$$n_i = \text{int} \left(-\frac{k_B T}{\omega_i} \ln(1 - \zeta) \right)$$

The probability of having an angular momentum J is taken in the low rotational constant limit (or equivalently high temperature limit):

$$P(J) = \frac{4}{\sqrt{\pi}} \left(\frac{B_0}{k_B T} \right)^{3/2} J^2 e^{-\frac{J^2 B_0}{k_B T}}$$

APPENDIX: ENERGY DISTRIBUTIONS

The probability of energy partition between internal vibrations and external translations and rotations is given by:

$$P(E_v, E_{rel}, E_r) dE_v dE_{rel} dE_r = \frac{N_1(E_v) N_2(E_f - E_v - E_{rel} - E_r) N_x(E_r, E_{rel}, J)}{G(E_f, J)} dE_v dE_{rel} dE_r$$

where N_1 and N_2 are the harmonic vibrational densities for the fragments and N_x is the density of states for external degrees of freedom, *i.e.* translational + rotational. The total fragments energy E_f is partitioned in E_v , the vibrational energy in the charged fragment, $E_f - E_v - E_{rel} - E_r$ the vibrational energy in the evaporated neutral pyrene molecule, E_{rel} the relative kinetic energy between fragments and E_r the total rotational energy of fragments. The normalization factor is the total number of states of the fragments that has already been encountered for the calculation of the evaporation rates.

The vibrational densities are obtained once again by the Laplace transform of the corresponding vibrational partition functions.

The density of external states depends on the relative values of J , J_r^* and L^* where:

$$L^* = b_n(E_t) \frac{n-2}{2n}$$

$$J_r^* = \frac{\sqrt{\frac{4E_r}{B_r} + 1} - 1}{2}$$

and is given by:

$$L^* < J, \quad J_r^* < J \quad N_x = R1$$

$$L^* \geq J, \quad J_r^* < J, \quad L^* < J + J_r^* \quad N_x = R1$$

$$L^* \geq J, \quad J_r^* < J, \quad L^* \geq J + J_r^* \quad N_x = 2R4$$

$$L^* < J, \quad J_r^* \geq J, \quad L^* \geq J_r^* - J \quad N_x = R2$$

$$L^* < J, \quad J_r^* \geq J, \quad L^* < J_r^* - J \quad N_x = R3$$

$$L^* \geq J, \quad J_r^* \geq J, \quad L^* \geq J_r^* + J \quad N_x = R5$$

$$L^* \geq J, \quad J_r^* \geq J, \quad L^* < J_r^* + J, \quad J_r^* \geq L^* + J \quad N_x = R3$$

$$L^* \geq J, \quad J_r^* \geq J, \quad L^* < J_r^* + J, \quad J_r^* < L^* + J \quad N_x = R2$$

where the expressions for R1 to R4 can be found in [74].

Finally the probability to have a rotational energy E_{r1} of the charged fragment, assuming spherical tops, is given by:

$$P(E_{r1})dE_{r1} = \frac{16}{\pi E_r^3} \sqrt{E_r} (E_r - E_{r1})^{3/2} dE_{r1}$$