

Supporting Information:

Water Attachment Onto Size-Selected Cationic Pyrene Clusters

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Abstract

We report measurements of the attachment rates of water molecules onto mass-selected cationic pyrene clusters for size from $n=4$ to 13 and for different collision energies. Comparison of the attachment rates with the collision rates measured in collision induced dissociation experiments provides access to the values of the sticking coefficient. The strong dependence of the attachment rates on size and collision energy is rationalized through a model in which we use a Langevin-type collision rate and adjust on experimental data the statistical dissociation rate of the water molecule from the cluster after attachment. This allows us to extrapolate our results to the conditions of isolation and long timescales encountered in astrophysical environments.

We provide here as supporting information expressions for the geometric and Average Dipole Orientation (ADO) collision rates, the details of the calculation of the average col-

lision energy for ADO cross sections and the details of the model used to reproduce the experimental data. We also provide a figure showing the influence of the dissociation energy value onto the temperature dependence of the attachment rate.

1 Geometric and ADO collision rates

For a purely geometric cross-section, the collision rate is given by:

$$K_{geo} = \int_0^{\infty} \sigma_0 v_{rel} f(v_{rel}) dv_{rel} \quad (1)$$

where the distribution of relative velocities is given by:

$$f(v_{rel}) = \left(\frac{2m}{\pi k_B T} \right)^{1/2} \frac{v_{rel}}{v_{cluster}} e^{-\frac{1}{2}m(v_{cluster}^2 + v_{rel}^2)/k_B T} \sinh \left(\frac{mv_{rel}v_{cluster}}{k_B T} \right) \quad (2)$$

The average relative velocity $\overline{v_{rel}}$ is:

$$\overline{v_{rel}} = v_{cluster} \left(\operatorname{erf}(\sqrt{a}) \left(1 + \frac{1}{2a} \right) + \frac{e^{-a}}{\sqrt{\pi a}} \right) \quad (3)$$

with $a = \frac{mv_{cluster}^2}{2k_B T}$.

The geometric collision rate is therefore given by:

$$K_{geo} = \sigma_0 \overline{v_{rel}} \quad (4)$$

The collision rate can also be estimated with the Langevin rate using the Average Dipole Orientation (ADO) approximation.^{S1-S4} For an interaction of an ion with a polar molecule, Su *et al* showed that the rate can be parametrized as:

$$K_{ADO} = \int_0^{\infty} \frac{q}{2\varepsilon_0 \sqrt{\mu}} \left(\sqrt{\alpha} + \frac{C\mu_D}{\sqrt{\mu}v_{rel}} \right) f(v_{rel}) dv_{rel} = \frac{q}{2\varepsilon_0 \sqrt{\mu}} \left(\sqrt{\alpha} + \frac{C\mu_D}{\sqrt{\mu}v_{cluster}} \operatorname{erf}(a) \right) \quad (5)$$

where C is the dipole locking constant.

2 Calculation of the average collision energy for ADO cross-section

Here we give the expression for the average collision rate and the average collision energy for an ion passing through a collision cell of length L_{cell} with velocity $v_{cluster}$. The temperature of the cell is T_{cell} and the density of molecules of mass m in the cell is ρ . The average collision rate is given by:

$$W_{col} = \int_0^{+\infty} f(v_{rel}) dv_{rel} \rho \sigma_{ADO} v_{rel} \quad (6)$$

$$= \frac{q\rho}{2\varepsilon_0} \left(\frac{C_l \mu_D \operatorname{erf}(\sqrt{a})}{\mu v_{cluster}} + \sqrt{\frac{\alpha}{\mu}} \right) \quad (7)$$

The rate of deposited energy per collision is:

$$W_{imp} = \int_0^{+\infty} f(v_{rel}) dv_{rel} \rho \sigma_{ADO} v_{rel} \times \frac{1}{2} \mu v_{rel}^2 \quad (8)$$

$$= \frac{q\rho}{4\varepsilon_0} \left(C_l \mu_D \overline{v_{rel}} + 2 \sqrt{\frac{\alpha}{\mu}} \overline{E_{rel}} \right) \quad (9)$$

with

$$\overline{E_{rel}} = \frac{m}{M+m} E_k + \frac{3}{2} \frac{M}{M+m} k_B T_{cel} \quad (10)$$

And therefore the average collision energy is:

$$E_{col} = \frac{W_{imp}}{W_{col}} \quad (11)$$

Similar expressions were recently given by Liang and Kresin for the case of a geometric cross-section.^{S5} For a purely polar molecule ($\mu_D = 0$), the average collision energy deposited upon attachment is simply the average relative velocity $\overline{E_{rel}}$. When the cluster velocity is

much larger than $k_B T_{cell}$ we have $a \gg 1$ which implies:

$$\text{erf}(\sqrt{a}) \approx 1 \quad (12)$$

$$\overline{v_{rel}} \approx v_{cluster} \quad (13)$$

$$\overline{E_{rel}} \approx \frac{1}{2} \mu v_{cluster}^2 \quad (14)$$

$$E_{col} \approx \frac{1}{2} \mu v_{cluster}^2 \quad (15)$$

In the present study, we have a ranging from 1.3 to about 10. In the worst case, i.e. for $n=13$ and a kinetic energy of 5 eV in the laboratory frame, the average collision energy is 84% of $\overline{E_{rel}}$.

3 Model

In order to fully account for the present results, the lifetime of the formed water-pyrene cluster complex must be considered. We must therefore consider the temporal evolution of the cluster population during the propagation in the collision cell and to the detector. At the entrance of the collision cell, the parent cluster population is I_0 . This I_0 population is made of clusters with well defined internal energies E_{ini} . The distribution of these internal energies is due to the initial thermalization at 25 K and is given by:

$$P(E_{ini}) = \frac{\Omega(E_{ini})}{Z(T)} e^{-E_i/(k_B T)} \quad (16)$$

where $\Omega(E_{ini})$ is the density of states at energy E_{ini} and $Z(T)$ the canonical partition function. We will restrict ourselves to the case of independent harmonic oscillators and therefore:

$$Z(T) = \prod_i \frac{1}{1 - e^{-\hbar\omega_i/k_B T}} \quad (17)$$

The average internal energy of the pyrene clusters is given by:

$$(18)$$

The harmonic frequencies ω_i are obtained for any pyrene cluster size by a simple extrapolation model.^{S6,S7} We give in Figure S1 the curves $E(T)/n$ as a function of the temperature for cluster sizes from $n=2$ to 15.

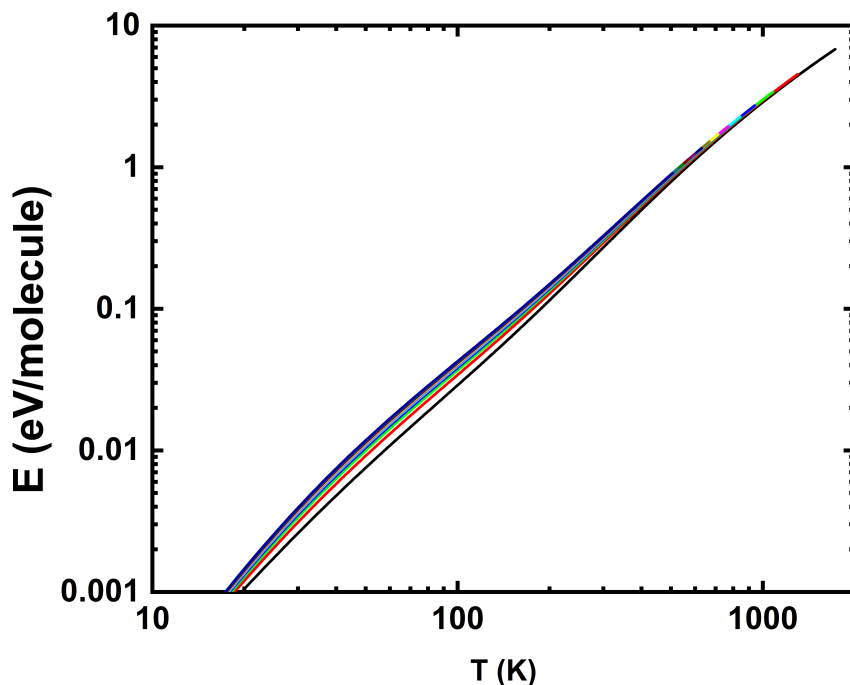


Figure S1: Average internal energy per molecule as calculated from eq.18 as a function of the temperature. The different colors correspond to cluster sizes from $n=2$ to $n=15$.

After the attachment of a water molecule, the internal energy of the water-pyrene cluster complex becomes:

$$E_f = E_{ini} + D + E_{COM} \quad (19)$$

where D is the dissociation energy of the water molecule from the cluster and E_{COM} the COM collision energy. In principle, the average of the initial internal energy distribution must be

taken into account. Similarly, the relative velocity distribution must be taken into account. In the first case, given the small amount of internal energy at 25 K, we will consider that all clusters initially have the corresponding average internal energy. For the second, integration over the relative velocity distribution will be performed.

The attachment of a water molecule may only last a short time compared to the experimental timescale if the internal energy after attachment is too high. To quantify this phenomenon, we will use a simple statistical dissociation model. In this model, we consider that the unimolecular dissociation rate k_{diss} of the attached water molecule is given by:

$$k_{diss}(T_f) = Ae^{-D/k_B T_f} \tag{20}$$

where the prefactor A is adjusted to reproduce the experimental results. The temperature T_f is obtained from the $E(T)$ curve by setting $E(T_f) = E_f$. In doing so, we do not take into account the additional degrees of freedom introduced by the attachment of the water molecule onto the cluster. We can assume that these additional vibrational degrees of freedom will be very similar for all sizes. Furthermore, the internal degrees of freedom of the water molecule can be considered frozen given the small amount of collision energies considered. Therefore, neglecting them in the determination of the temperature T_f may lead to a slight underestimation, which can anyway be compensated by adjusting the prefactor A . Again, given the rudimentary nature of the model, such subtleties should not play a major role.

In order to reproduce the experimental results, we have to consider three different populations of clusters:

1. Clusters that do not undergo attachment I_n
2. Clusters that undergo attachment $I_{n,a}$
3. Clusters resulting from the statistical dissociation of a water molecule after attachment $I_{n,a,e}$

The above partition of the cluster population amounts to neglecting events such as attachment-statistical dissociation-attachment. In other words, we consider that we are in the single collision regime. The population of clusters I_n at the exit of the collision cell, after the propagation time t required for the cluster to cross the collision cell, is given by:

$$I_n(t) = I_{n0}e^{-\rho\langle K\rangle t} \quad (21)$$

where ρ is the density in the collision cell and $\langle K \rangle$ is the averaged attachment rate over the relative velocity distribution:

$$\langle K \rangle = \int_0^{+\infty} dv_{rel} f(v_{rel}) K(v_{rel}) \quad (22)$$

The evolution of the cluster population having one water molecule attached leading to an internal energy E_f is:

$$\frac{dI_{n,a}(E_f)}{dt} = \rho K(v_{rel}) I_n - k_{diss}(T_f) I_{n,a}(E_f) \quad (23)$$

The solution of this differential equation is:

$$I_{n,a}(t) = I_{n0} \rho K(v_{rel}) \frac{e^{-k_{diss}(T_f)t} - e^{-\rho\langle K\rangle t}}{\rho\langle K\rangle - k_{diss}(T_f)} \quad (24)$$

Finally the evolution of the population of clusters that have undergone attachment followed by statistical dissociation is given by:

$$\frac{dI_{n,a,e}(E_f)}{dt} = k_{diss}(T_f) I_{n,a}(E_f) \quad (25)$$

and we have:

$$I_{n,a,e}(t) = I_{n0} \frac{K(v_{rel})}{\langle K \rangle} \frac{k_{diss}(T_f)(e^{-\rho\langle K\rangle t} - 1) - \rho\langle K\rangle(e^{-k_{diss}(T_f)t} - 1)}{\rho\langle K\rangle - k_{diss}(T_f)} \quad (26)$$

After the collision cell, the clusters must fly to the second acceleration stage, which takes a t' time. During this time, statistical dissociation can still occur and the populations are:

$$I_n(t + t') = I_{n0}e^{-\rho\langle K\rangle t} \quad (27)$$

$$I_{n,a}(t + t') = I_{n,a}(t)e^{-k_{diss}(T_f)t'} \quad (28)$$

$$I_{n,a,e}(t + t') = I_{n,a,e}(t) + I_{n,a}(t)(1 - e^{-k_{diss}(T_f)t'}) \quad (29)$$

After acceleration by the second Wiley-McLaren, if the statistical dissociation occurs before the reflectron entrance, the clusters are lost: their time of flight no longer belongs to the fitted regular peaks. Therefore, the populations are:

$$I_n(t + t' + t'') = I_{n0}e^{-\rho\langle K\rangle t} \quad (30)$$

$$I_{n,a}(t + t' + t'') = I_{n,a}(t)e^{-k_{diss}(T_f)(t+t'')} \quad (31)$$

$$I_{n,a,e}(t + t' + t'') = I_{n,a,e}(t) + I_{n,a}(t)(1 - e^{-k_{diss}(T_f)t''}) \quad (32)$$

where t'' is the time required to reach the reflectron entrance. The above expressions are then averaged over the distribution of relative velocities:

$$\langle I_n \rangle = \int_0^{+\infty} dv_{rel} f(v_{rel}) I_n(t + t' + t'') \quad (33)$$

$$\langle I_{n,a} \rangle = \int_0^{+\infty} dv_{rel} f(v_{rel}) I_{n,a}(t + t' + t'') \quad (34)$$

$$\langle I_{n,a,e} \rangle = \int_0^{+\infty} dv_{rel} f(v_{rel}) I_{n,a,e}(t + t' + t'') \quad (35)$$

and finally, we calculate the theoretical rate similarly to the experimental one:

$$k_{theo} = \frac{-v_{cluster}}{\rho L_{cell}} \ln \left(\frac{\langle I_n \rangle + \langle I_{n,a,e} \rangle}{\langle I_n \rangle + \langle I_{n,a,e} \rangle + \langle I_{n,a} \rangle} \right) \quad (36)$$

so that they can be directly compared.

The modeling is done with $K = K_{ADO}$ using the values of C given in Table S1.

Table S1: Dipole locking constant values that allows to best reproduce the experimental results.

E_k (eV)	5	10	15	20
C	0.35	0.30	0.25	0.17

The dissociation energy D is taken equal to 0.3 eV and the prefactor A has been taken equal to 10^{17} s⁻¹. This simple model allows to reproduce the experimental results in a satisfactory way.

4 Attachment rate temperature dependence

We have plotted in Figure S2 the attachment rate as a function of the temperature after collision. The temperature after collision is obtained as:

$$E_{th}(T) = E_{th}(25K) + D + E_{COM} \quad (37)$$

where E_{COM} is the center of mass collision energy, E_{th} is the thermal internal energy of the cluster and D the water-pyrene cluster dissociation energy. As the dissociation energy increases, we observe that the threshold for observing attachment shifts to higher temperatures. We also note that the points are less scattered around the threshold for dissociation energies of 0.2-0.3 eV.

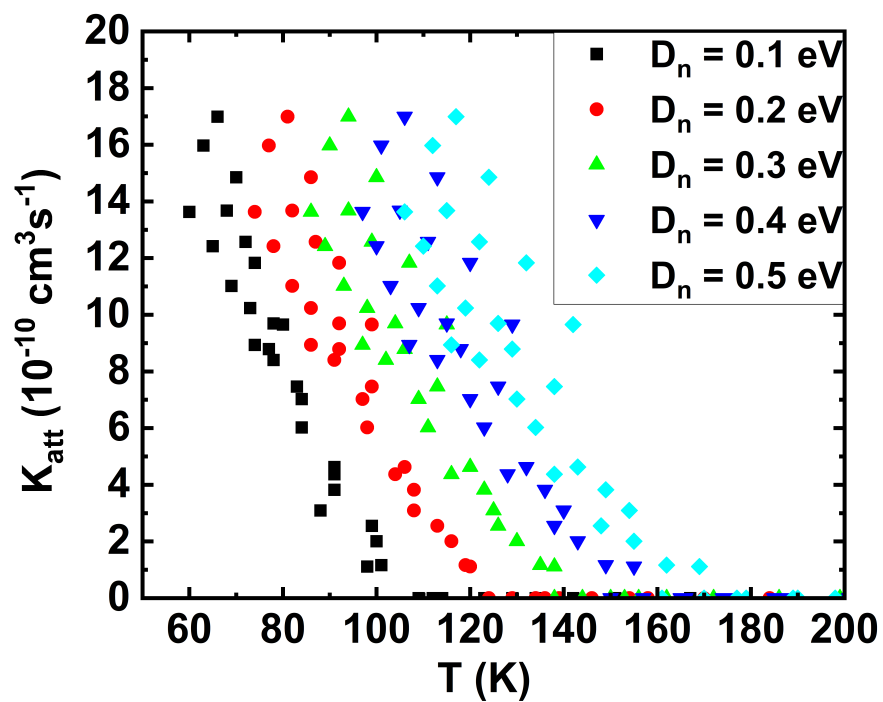


Figure S2: Water attachment rates onto mass-selected pyrene clusters as a function of cluster temperature after collision. The different colors correspond to different values of the dissociation energies.

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