# Supporting Information for Structure and Desorption Kinetics of Acetonitrile Thin Films on Pt(111) and on Graphene on Pt(111)

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This supporting information contains the calculation of acetonitrile vapor pressure, the calculation of low coverage desorption energies for acetonitrile on Pt(111) with different prefactors, the effect of isotope on acetonitrile desorption kinetics, and the effect of  $T_{deposition}$  and  $T_{anneal}$  on the acetonitrile structure on Pt(111).

#### **1.** Calculation of acetonitrile vapor pressure:

Acetonitrile is a molecule of astrophysical interest as it has been found in various extraterrestrial environments. The vapor pressure data for the solid would be useful for modeling the atmospheres of other planets and moons, but this data has not been reported.<sup>1,2</sup> We can estimate the vapor pressure from the desorption rate measured in TPD experiments. For zero-order multilayer desorption the rate is determined by the equilibrium between the solid and gas phases. Molecules leave the film in attempt to establish the equilibrium vapor pressure. In a system at equilibrium, the rate of molecules leaving and impinging on the surface is equal. Since our TPD experiments occur in a large vacuum chamber with a high pumping speed, acetonitrile molecules desorb from the surface but don't re-adsorb. Therefore, the measured desorption rate is equal to the collision flux of the vapor at equilibrium. The desorption rate (d $\theta$ /dt) in ML/s can be transformed into a collision flux (Z) with units of molecules m<sup>2</sup> s<sup>-1</sup>:

$$Z = \frac{d\theta}{dt} \left(\frac{n}{V_{cell}}\right)^{2/3}$$

Where n is the number of molecules in a unit cell, and  $V_{cell}$  is the unit cell volume. We have used the temperature dependent volume data from neutron diffraction experiments by Torrie and Powell.<sup>3</sup> The collision flux and pressure can be related by using the kinetic theory of gases:

$$Z = \frac{P}{(2\pi m kT)^{1/2}}$$

Where P is pressure, m is the molecular mass, k is the Boltzmann constant, and  $N_a$  is Avogadro's number. A substitution and rearrangement give the following equation that yields pressure in Pa when using SI units:

$$P = \frac{d\theta}{dt} \left(\frac{n}{V_{cell}}\right)^{2/3} (2\pi m kT)^{1/2}$$

The results of this calculation are shown in Figure S1 along with the literature values of acetonitrile's triple point and boiling point.<sup>4,5</sup> The results of our calculation using TPD data is well fit by the empirical equation,  $\ln(P) = A + B/T + C/T^2$ ; this form has been shown to provide a good fit P vs T data.<sup>1</sup> The parameters are A = -0.09, B = 2800, and C = -541,000 for the range 123.7  $\leq$  T  $\leq$  150.1 K. This equation is represented as a red line in Figure S1. We also plot the results of a fit that includes the triple point at 229.3 K and boiling point at 354.8 K. The fit is represented by a grey line and the parameters are A = 20.8, B = -2860, C = -156000. These vapor pressure calculations are only estimates, but in lieu of direct measurements of the vapor pressure for acetonitrile solid, these results may be useful for astrophysical calculations.



**Figure S1:** Vapor pressure as a function of temperature. **Top plot:** The black solid line is the calculation of the vapor pressure using 50 ML crystalline TPD data and the kinetic theory of gases. The circles are the triple point and boiling point of acetonitrile.<sup>4,5</sup> The dashed lines are fits to the data with the form  $\ln(P) = A + B/T + C/T^2$ . The red dashed line is a fit to the TPD data only with A = -0.09, B = 2800, and C = -541,000. The grey dashed line is a fit to the TPD, triple point, and boiling point data with A = 20.8, B = -2860 and C = -156000. **Bottom Plot:** Comparison of the two fits for the temperature and pressure range of the TPD data.

#### 2. Calculation of low coverage desorption energies from Pt(111):

We calculated the coverage dependent desorption energies for acetonitrile desorbing from Pt(111) using the Polanyi-Wigner equation,  $d\theta/dt = -\nu * \theta^n * \exp(E_{des}(\theta)/RT)$ .<sup>6</sup> In this equation  $\theta$  is the coverage,  $\nu$  is the prefactor, n is the order of the desorption process, and R is the

gas constant. We inverted the equation and used the TPD data to calculate  $E_{des}(\theta)$  following a procedure that has been discussed in detail in prior publicaitons.<sup>7,8</sup> As explained in the main paper text, we did not use the variational method to determine the prefactor as it would not be sensitive for our broad TPD spectra.<sup>9</sup> In Figure S2 we plot the results of the calculation using many TPD coverages and a range of prefactor values. We observe the best qualitative agreement between individual TPDs for a prefactor of  $10^{16}$  s<sup>-1</sup>. For lower prefactors, we see that the high coverage "tails" from each TPD curve upwards and don't align with the desorption energy calculated from a higher coverage TPD spectra. For prefactors much larger than  $10^{16}$  s<sup>-1</sup> we observe the reverse behavior where the "tails" curve downwards. We observed qualitatively similar agreement between TPDs for prefactors of  $10^{15}$  s<sup>-1</sup>,  $10^{16}$  s<sup>-1</sup>, and  $10^{17}$  s<sup>-1</sup>, and therefore we estimate the prefactor to be  $10^{16 \pm 1}$  s<sup>-1</sup>. This value is consistent with the  $10^{16}$  ML/s value obtained from the Arrhenius fit of the multilayer desorption.



**Figure S2:** Plots of the desorption energy for 0.01 to 2 ML films on Pt(111) calculated from the Polanyi-Wigner equation using n = 1 and prefactor values of  $10^{12} \text{ s}^{-1}$ ,  $10^{16} \text{ s}^{-1}$  and  $10^{20} \text{ s}^{-1}$  for the top, middle, and bottom panel. We observe the best qualitative agreement for energies calculated for different TPD experiments for  $v = 10^{16 \pm 1} \text{ s}^{-1}$ . For clarity we show a wide range of prefactors.

## 3. Effect of isotope on acetonitrile desorption kinetics:

We performed TPD experiments for films of acetonitrile-d<sub>3</sub> on both Pt(111) and graphene. Select TPD spectra are plotted in Figure S3 for comparison. For desorption from both surfaces, we observe minimal difference in the kinetics for CH<sub>3</sub>CN and CD<sub>3</sub>CN isotopes over the entire range coverages investigated (0.01 to 10 ML). We only plotted the 3 ML coverages in Figure S3 for clarity.



**Figure S3:** TPD spectra of 3 ML acetonitrile films desorbing from Pt(111) (top plot) and from graphene (bottom plot). Black solid lines are the desorption of  $CH_3CN$ , and red dashed lines are the desorption of  $CD_3CN$ . We observe no change in the desorption kinetics for these isotopes. We have plotted a single coverage for clarity. For the range of 0.01 to 10 ML we observe no isotope effect.

## 4. Effect of T<sub>deposition</sub> and T<sub>anneal</sub> on the acetonitrile structure on Pt(111):

In Figure S4 we plot the RAIRS spectra for 0.9 ML of acetonitrile on Pt(111) for different preparation conditions. In the top panels the spectra are offset in order of increasing  $T_{deposition}$  from 60 to 140 K. The films in the bottom panels were all deposited at 60 K and then annealed for 1 second at a variety of annealing temperatures. The spectra in the bottom panels are offset in order of increasing annealing temperature. As temperature increases in both experiments, we observe the appearance of the CH<sub>3</sub> antisymmetric stretch peak, an increase in the CH<sub>3</sub> symmetric stretch intensity, and a decrease in C=N stretch intensity. The data show that at low deposition temperatures acetonitrile molecules adopt the N-top configuration. At higher deposition temperatures the molecules change to the  $\mu$  configuration. Also, when the substrate temperature is increased, molecules that were initially in the N-top configuration change to the  $\mu$  configuration.



**Figure S4:** RAIRS spectra of acetonitrile on Pt(111) for  $T_{deposition} = 60$  to 140 K (top panels) and  $T_{anneal} = 60$  to 140 K (bottom panels). There is a 10 K step size for both sets of experiments. The films for the annealing experiments were deposited at 60 K and then annealed to various temperatures. The C=N stretch peak decreases with increasing temperature when molecules switch from N-top configuration to a  $\mu$  configuration. The  $\mu$  orientation increases the CH<sub>3</sub> symmetric stretching peak and tilts the methyl group so that the CH<sub>3</sub> asymmetric stretch is an observed mode. Spectra are vertically shifted in order of increasing temperature for clarity.

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