

Supporting information: Acetone adsorption on ice investigated by X-ray spectroscopy and density functional theory

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Additional adsorption structures considered in DFT calculations

Here we report some information on the results for additional adsorption structures considered. In Fig. S1 the seven different Class IV adsorption structures are shown. Table S1 summarizes the adsorption energies and some bond lengths between the acetone molecule and ice surface for all the structures discussed in the paper.

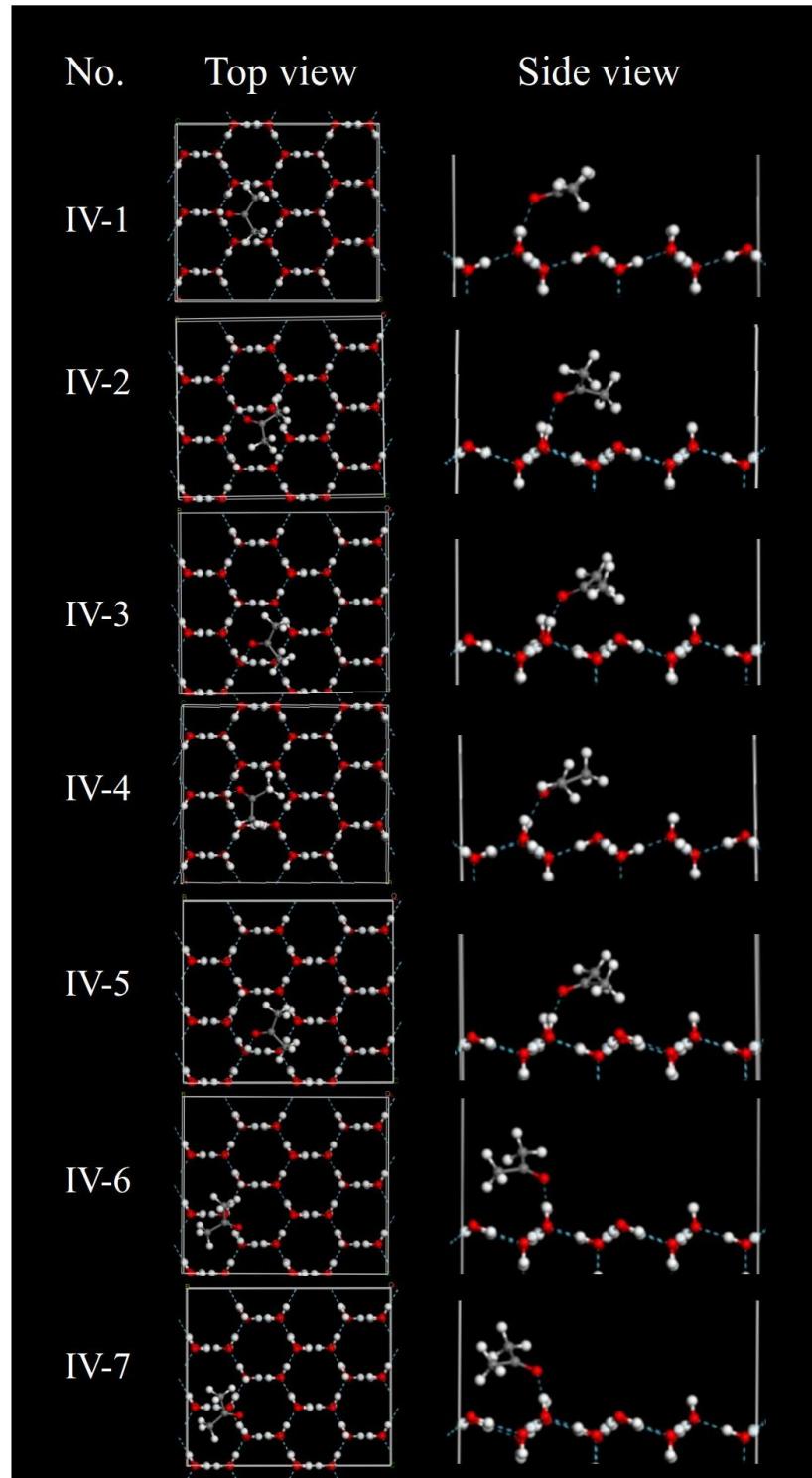


Fig. S1: Seven Class IV adsorption structures similar to Class IV in Fig. 9. They all have essentially the same adsorption energy (see Table S1).

Table S1: Adsorption energies and selected structural parameters for the four classes of acetone/ice adsorption configurations. The third column refers to the stronger hydrogen bond between a carbonyl oxygen atom and a dangling OH bond on the ice surface. The fourth column shows the two shortest distances between H in the methyl groups and water without a dangling OH group on the ice surface. The bracket means the H atoms comes from the same CH₃ group.

No.	Adsorption energy [eV]	C=O---H(ice) [Angstrom]	CH ₃ ---O(ice) [Angstrom]
I	-0.271	-	-
II	-0.126	-	-
III	-0.178	-	-
IV-1	-0.446	1.85	2.44, 2.39
IV-2	-0.446	1.87	(2.49; 2.81)
IV-3	-0.457	1.86	(2.74, 2.74)
IV-4	-0.446	1.82	2.37, 3.20
IV-5	-0.451	1.91	(2.98, 2.60)
IV-6	-0.442	1.82	(2.28, 3.53)
IV-7	-0.451	1.91	(2.34, 3.52)

Van der Waals and finite temperature effects

As discussed in the main manuscript our zero Kelvin adsorption energies have been obtained with the semi-local PBE functional and neglect zero point energy and thermal effects. We show below that whilst accounting for van der Waals forces increases the computed adsorption energy adding in thermal and zero point energy effects decreases it.

A. Van der Waals: In order to obtain a qualitative estimate of the role of van der Waals forces, we calculated the adsorption energy of acetone on ice with the PBE-D3ⁱ approach. With this particular scheme for accounting for van der Waals the adsorption energy increases from 0.43 eV to 0.66 eV.

B. Thermal and zero point energy effects: For the thermal effects, we simply estimated this by accounting for the phonon contribution to the adsorption energy. Within the Einstein approximation, the thermal energy at temperature T is written asⁱⁱ

$$u = u^{eq} + \sum_i \frac{\hbar\omega_i}{2} + \sum_i \frac{\hbar\omega_i}{e^{\beta\hbar\omega_i} - 1}, \quad \beta = \frac{1}{k_B T},$$

Where u^{eq} is the energy of the equilibrium adsorption configuration, \hbar is the reduced Planck's constant, ω_i is the i th phonon angular frequency, and k_B is the Boltzmann constant. The second term in the equation above is the zero point energy, and the third term accounts for the temperature dependence. Hence the adsorption energy at temperature T is estimated by

$$E_{ad}(T) = E_{ad}^{geo-opt} - \left(\sum_i \frac{\hbar\omega_i^{acetone/ice}}{2} - \sum_i \frac{\hbar\omega_i^{acetone}}{2} - \sum_i \frac{\hbar\omega_i^{ice}}{2} \right) - \\ \left(\sum_i \frac{\hbar\omega_i^{acetone/ice}}{e^{\beta\hbar\omega_i^{acetone/ice}} - 1} - \sum_i \frac{\hbar\omega_i^{acetone}}{e^{\beta\hbar\omega_i^{acetone}} - 1} - \sum_i \frac{\hbar\omega_i^{ice}}{e^{\beta\hbar\omega_i^{ice}} - 1} \right),$$

where $E_{ad}^{geo-opt}$ is the calculated adsorption energy in the main text, $\omega_i^{acetone/ice}$, $\omega_i^{acetone}$ and ω_i^{ice} are the phonon frequencies of the adsorption system, isolated acetone molecule and ice slab, respectively.

As a further approximation, the change of the vibrational contribution of the ice slab is neglected, so $E_{ad}(T)$ is rewritten as

$$E_{ad}(T) = E_{ad}^{geo-opt} - \left(\sum_i \frac{\hbar\omega_i^{ad-acetone}}{2} - \sum_i \frac{\hbar\omega_i^{acetone}}{2} \right) - \\ \left(\sum_i \frac{\hbar\omega_i^{ad-acetone}}{e^{\beta\hbar\omega_i^{ad-acetone}} - 1} - \sum_i \frac{\hbar\omega_i^{acetone}}{e^{\beta\hbar\omega_i^{acetone}} - 1} \right),$$

where $\omega_i^{ad-acetone}$ comes from vibrational modes of the acetone molecule adsorbed on the ice surface including its translational and rotational modes on the ice surface. The finite displacement method is used to calculate the vibrational frequencies for the acetone molecule. Within the protocol as described the resulting temperature dependence of the adsorption energy is shown in Fig. S2. Taking in to account the zero point energy difference upon adsorption and the temperature dependence, at 200 to 250 K the adsorption energy is reduced to about 0.32 to 0.30 eV at the PBE level.

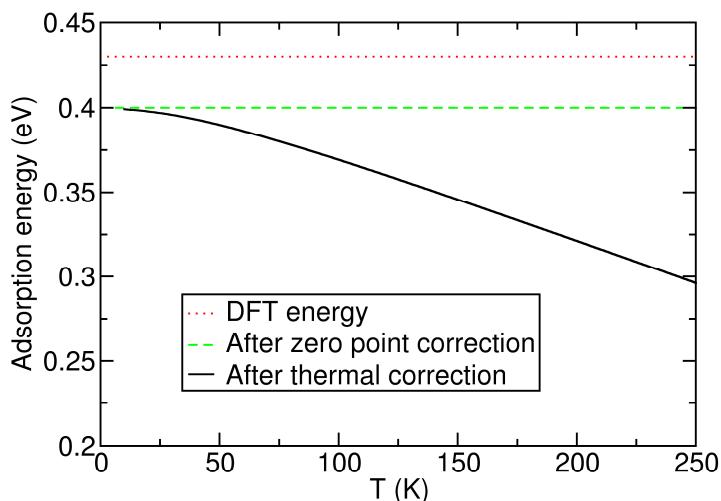


Fig. S2: The adsorption energy with thermal correction. The dotted red line shows the adsorption energy of 0.43 eV for a Class IV structure calculated in the main text. The dashed green line refers to the adsorption energy with zero point energy correction, 0.03 eV. The solid black line is for the adsorption energy with temperature dependence.

Energy difference between methyl and carbonyl peaks determined by different exchange-correlation (xc) functionals

The experimentally observed splitting between the carbonyl and the methyl related peaks in acetone vapor is 1.6 eV. In the calculations reported in the main manuscript we report that this value is overestimated in the GGA-PBE calculations by 0.8 eV. A similar value was also reported in Refs. ⁱⁱⁱ and ^{iv}, although the origin of this discrepancy was not discussed. In order to understand if this overestimate is related to the choice of exchange-correlation (xc) functional we calculated the XAS spectrum for acetone vapor with several different xc functionals. In Fig. S3 we report the results obtained with PBE (the functional used in this study), LDA, and PBE0^v, a “hybrid” xc functional. It can be seen from the Fig. S4 that the energy difference between methyl and carbonyl group is indeed sensitive to the choice of xc functional. Specifically, the energy difference for PBE (and also BLYP, not shown) is about 2.4 eV, while for LDA it is 2.3 eV, and the hybrid PBE0 results in the best agreement with experiment at 2.1 eV.

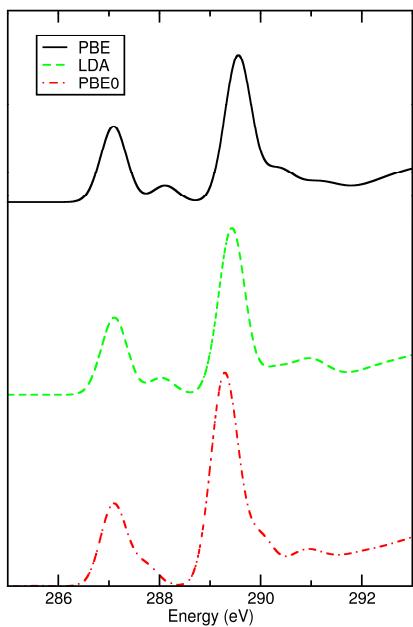


Fig. S3: Carbon K-edge NEXAFS for acetone vapor (isolated molecule) obtained with three different xc functionals. As we have done in the main manuscript, the first peak has been fixed at 287.1 eV in all three spectra.

In order to answer the question why the methyl-related C K edge XAS peak shifts and broadens, but not the carbonyl peak, an orbital analysis is done by the means of projected density of states (PDOS) on these two C atoms located at the carbonyl and methyl groups by the GAPW all-electron calculation. For the results see Fig. S4, for a discussion the main article.

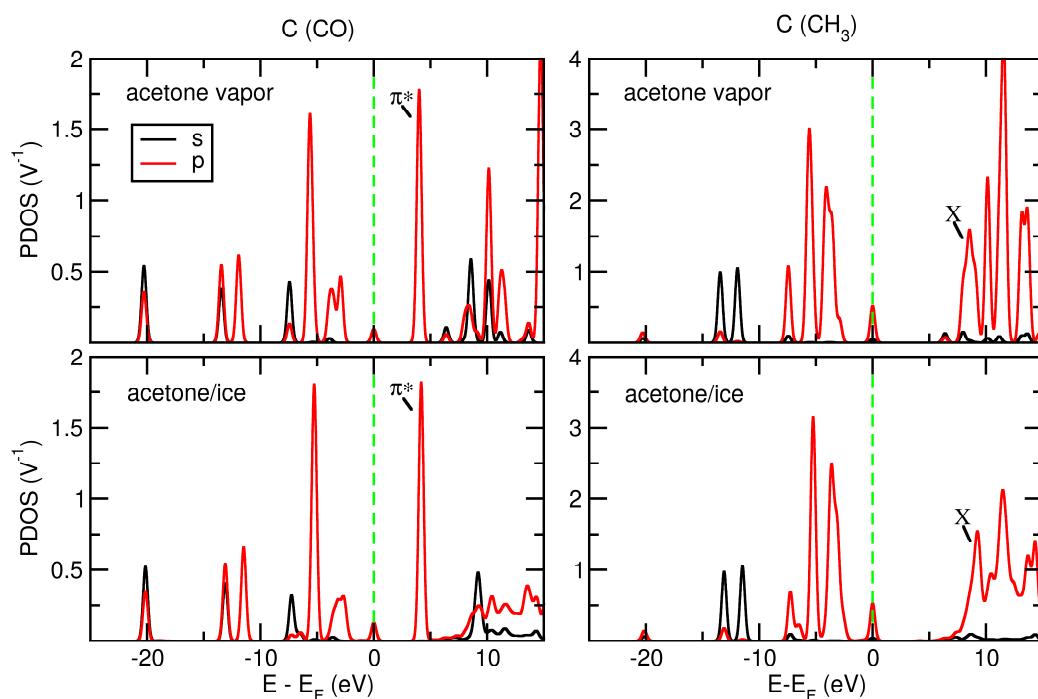


Fig. S4: Partial density of states (PDOS) on C atoms at the carbonyl (left) and methyl (right) groups of acetone in the gas phase and on the ice surface. The two upper panels are for the acetone gas (isolated molecule), and the lower panels correspond to the acetone adsorbed on ice in the Class IV adsorption structure. The black and red solid lines are the PDOS on the s and p orbitals of the C atoms. The energy zero is the Fermi level, labeled by the dashed green line.

Coverage-dependent C K-edge NEXAFS spectra

To investigate possible interaction between acetone molecules at surface we have taken C K-edge NEXAFS spectra as a function of coverage at 227 K (see Fig. S4). Even though the signal-to-noise ratio for the low-coverage data is not optimal, it is apparent that the up-shift and broadening of the methyl peak does not depend on coverage, *i.e.* likely not due to acetone-acetone interactions. The change in relative intensity of the carbonyl and methyl peak in Figure S4 cannot be explained at this time. It could be due to either a change in the orientation of the acetone molecule as the film grows, or caused by artifacts in the normalization for the incident photon flux intensity, which has a stronger effect for spectra with low signal level (*i.e.* at low coverages).

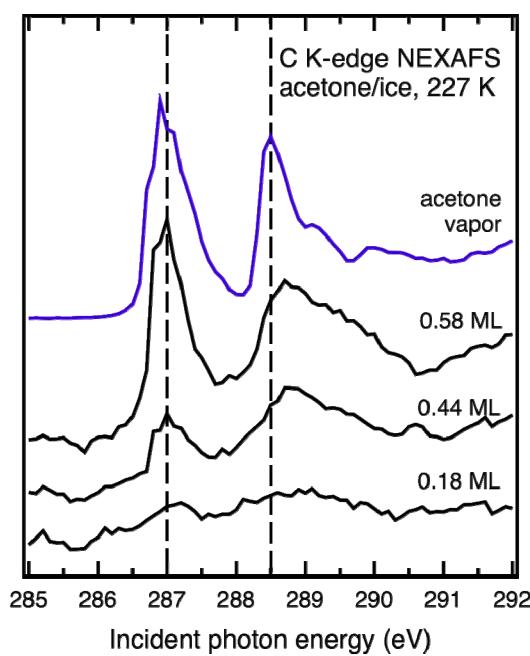


Fig. S4: Carbon K-edge NEXAFS spectra of acetone adsorbed on ice at 227 K as a function of acetone coverage. A spectrum of acetone vapor is also shown for comparison. The acetone coverage is calculated from C 1s and O 1s XPS spectra.

References

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