SUPPORTING INFORMATION:
Dynamics of collisions and uptake of alcohol molecules with hydrated nitric acid clusters

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1 Experiment

1.1 The absolute and relative pickup cross sections: errors and uncertainties

The measurements to determine the pickup cross sections σ_p reported in Table 1 in the main article were repeated several times and thus the statistical errors could be obtained. However, larger error bars can be introduced by uncertainty in the pickup pressure P_p, as discussed already in our previous publication.[1] The pickup pressure of the order of 10^{-5}–10^{-4} mbar can be measured preciously by an ion gauge and finely controlled by a needle valve (the background pressure in the chamber is better than 10^{-6} mbar). However, the ion gauge shows the pressure value calibrated for air (N_2) and to obtain the corresponding absolute pressure for each measured alcohol vapor, correction factors have to be introduced. These values (summarized in Tab. S1) are derived from the absolute electron impact ionization cross-sections of the molecules,[2] and for some molecules, they can also be found in the ionization gauge manual.[3] Note that different values can be found in the literature. The uncertainties in the correction factors contribute to the errors in σ_p determination according to the Eq. (1) in the main article. In addition, we have varied the pickup pressures to see how a moderate change in P_p is reflected in the evaluated σ_p value. These factors are also considered in the error bars in Tab. 1 in the main article.

Tab. S1 The used gas correction factors CF_{ig}.

Molecule	CF_{ig}
Methanol	1.8
Ethanol	3.0
1-Propanol	4.1
Isopropanol	4.1
1-Butanol	5.1
2-Butanol	5.2
Isobutanol	5.3
tert-Butanol	5.4
1-Pentanol	6.4

We relate the relative pickup cross section to methanol, since it has the largest pickup cross section, it is the smallest alcohol investigated here, and it is our benchmark system used in the previous uptake studies.[1,4] The absolute pickup cross section reported for methanol under the same expansion conditions was $\sim20\,\text{Å}^2$,[4] almost four times smaller than the present value. Comparison of the pure $(HNO_3)_M(H_2O)_N$ cluster mass spectra in the present and previous work (Fig. S1 and Fig. 2a in Ref. 4, respectively) suggests that larger clusters are generated in the present experiment despite nominally the same expansion parameters. The cluster size distribution is a sensitive function of the expansion conditions. A slightly larger nozzle diameter can increase the mean cluster size significantly. Strictly speaking, the Hagena's scaling law[5–7] cannot be applied here to obtain the mean cluster size, yet the qualitative dependence on the nozzle diameter d probably still follows $\bar{N} \propto d^\gamma$, where $\gamma \approx 2$. Due to the long-term use with nitric acid the actual nozzle diameter might be somewhat larger now than in the previous experiments. We can see some wear of the nozzle under a microscope. Critical parameter is also the reservoir temperature measured by a thermocouple attached to the reservoir. The measured value is sensitive to the thermocouple contact and the actual element has been replaced several times. Since we are heating the reservoir close to the nitric acid boiling point (356 K), a small change in the temperature can lead to significantly different concentration of the nitric acid vapor in the expanding gas and subsequently to a different cluster size distribution. In the present case, somewhat higher temperature could yield the larger clusters. In summary, the absolute pickup cross sections are sensitive to the cluster size and thus to the expansion conditions, nevertheless, the relative trends between the pickup of individual alcohol molecules are general and robust.

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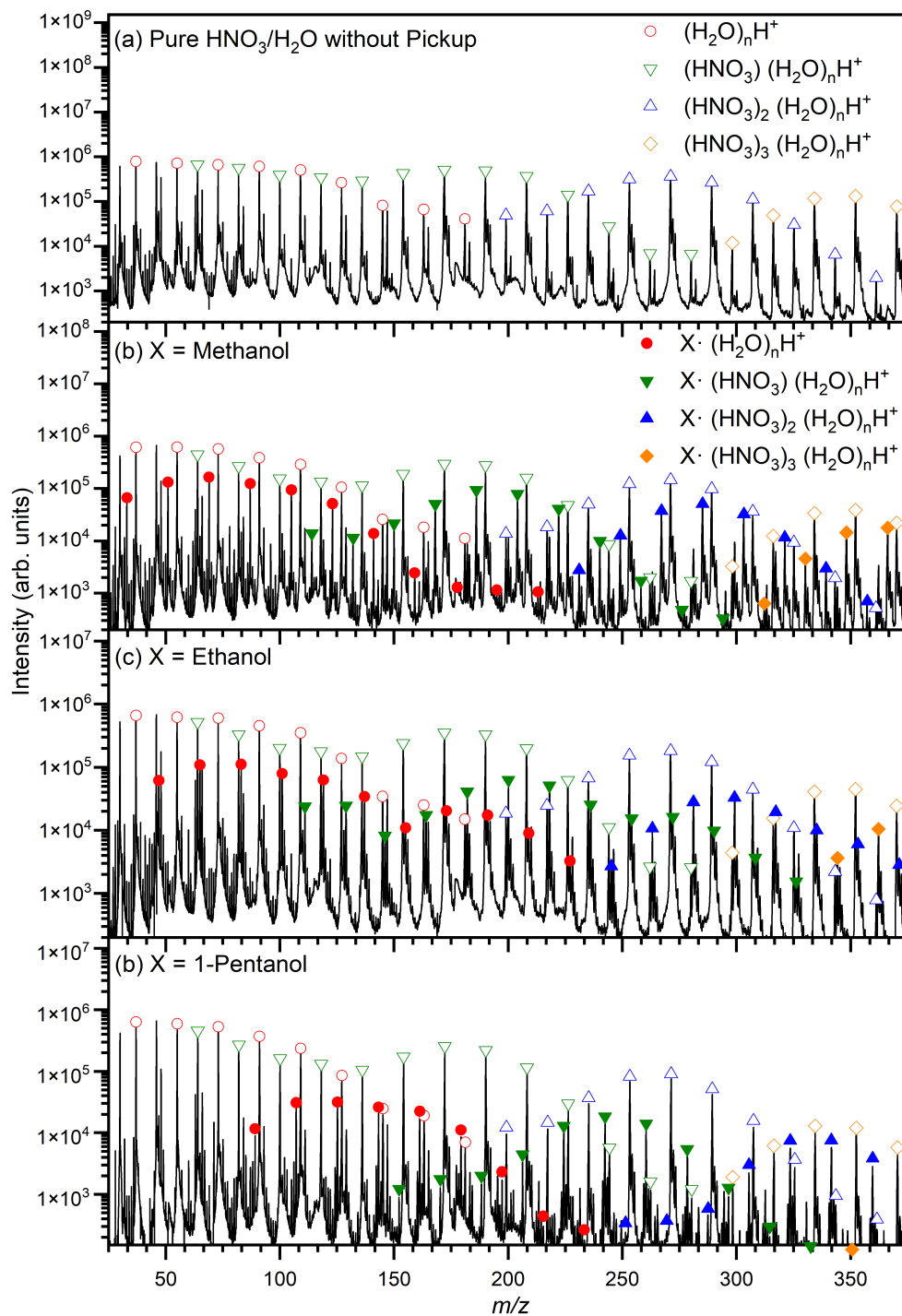
1.2 Mass spectra

Fig. S1 Mass spectra of pure $(HNO_3)_M(H_2O)_N$ clusters (a), and the mass spectra after the pickup of methanol (b), ethanol (c), and 1-pentanol (d). The full symbols indicate the different $(HNO_3)_m(H_2O)_nH^+$ series and the empty symbols label the corresponding $X \cdot (HNO_3)_m(H_2O)_nH^+$ series (detailed below). The two prominent unlabeled peaks are attributed to NO^+ ($m/z = 30$) and NO_2^+ ($m/z = 46$).
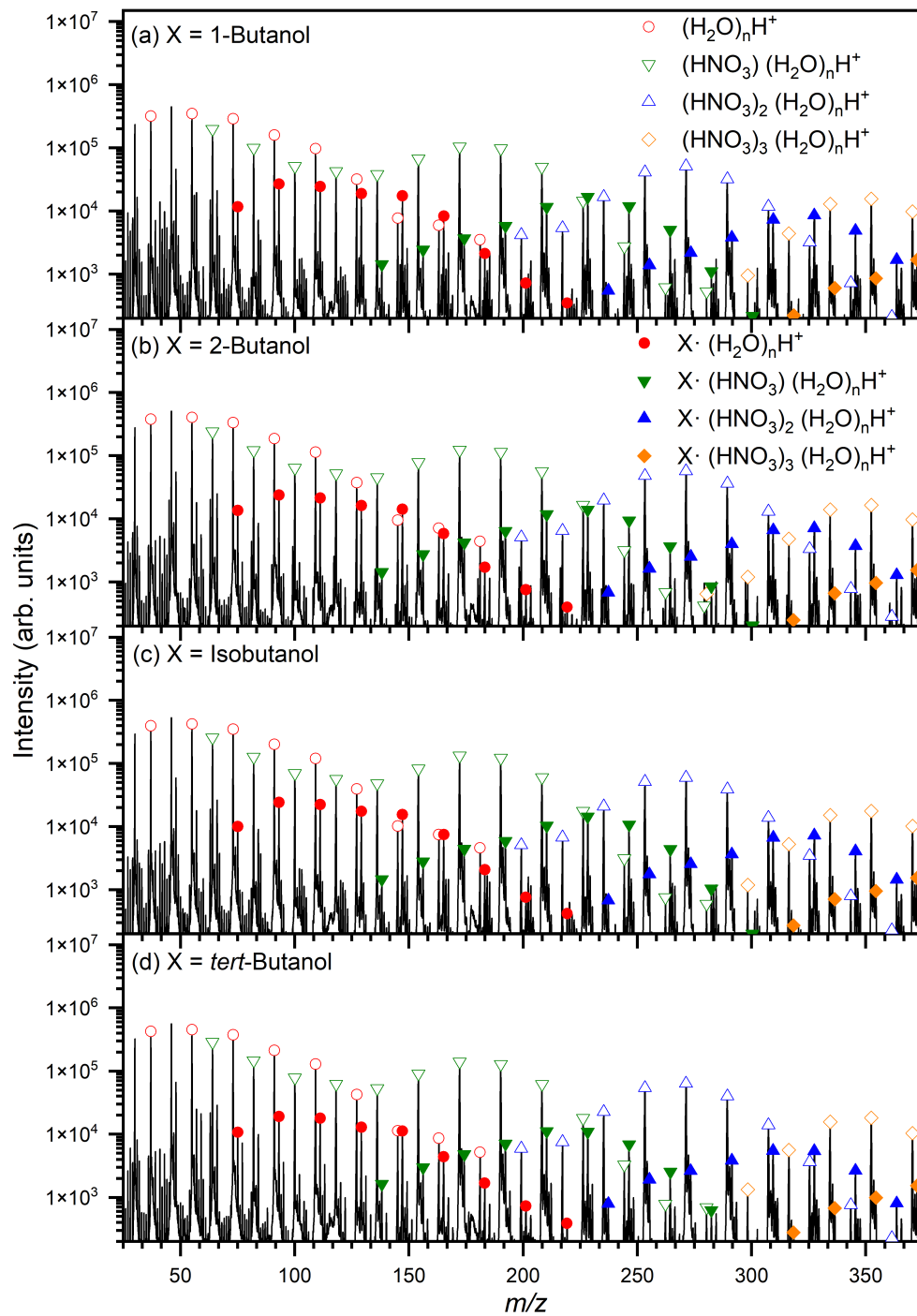
Fig. S2 Mass spectra of the $(HNO_3)_M(H_2O)_N$ clusters after the pickup of 1-butanol (a), 2-butanol (b), isobutanol (c), and *tert*-butanol (d). The full symbols indicate the different $(HNO_3)_m(H_2O)_nH^+$ series and the empty symbols label the corresponding $X \cdot (HNO_3)_m(H_2O)_nH^+$ series (detailed below).
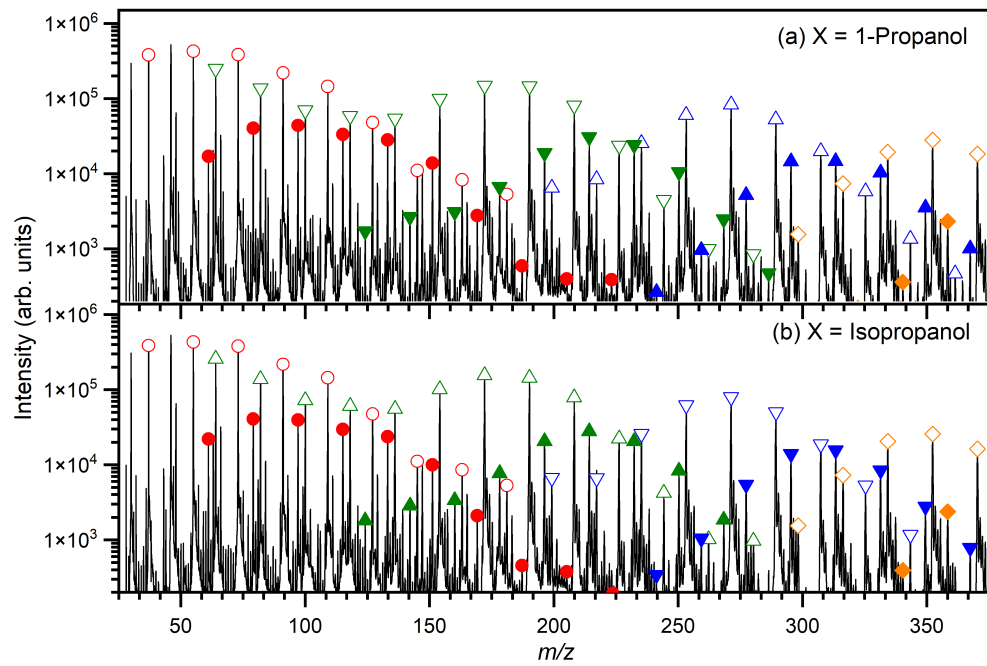
Fig. S3 Mass spectra of the $(HNO_3)_M(H_2O)_N$ clusters doped with 1-propanol (a) and isopropanol (b). The full symbols indicate the different $(HNO_3)_m(H_2O)_nH^+$ series and the empty symbols label the corresponding $X\cdot(HNO_3)_m(H_2O)_nH^+$ series (detailed below).
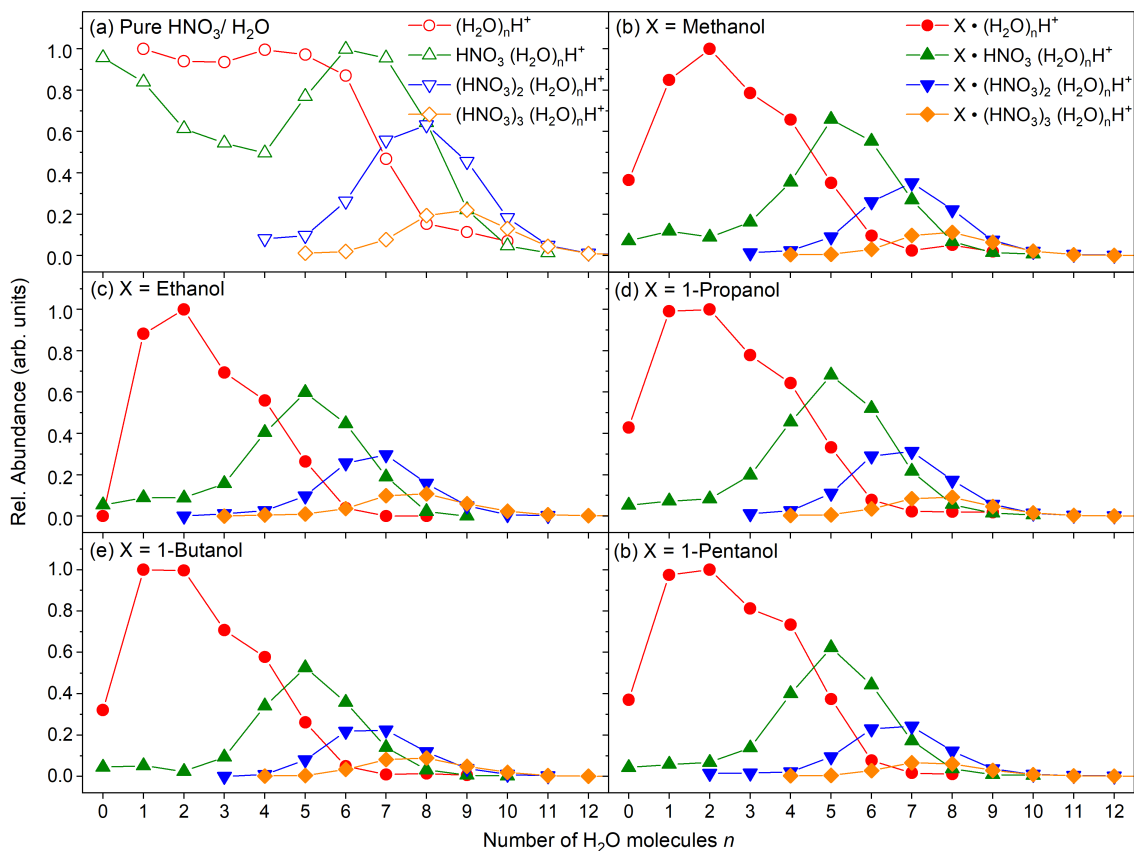
1.3 Ion series

Fig. S4 Relative abundances of pure $(HNO_3)_m(H_2O)_nH^+$ and doped $X \cdot (HNO_3)_m(H_2O)_nH^+$ cluster ions from the mass spectra in Figs. S1-S3 as a function of the number of water molecules n.
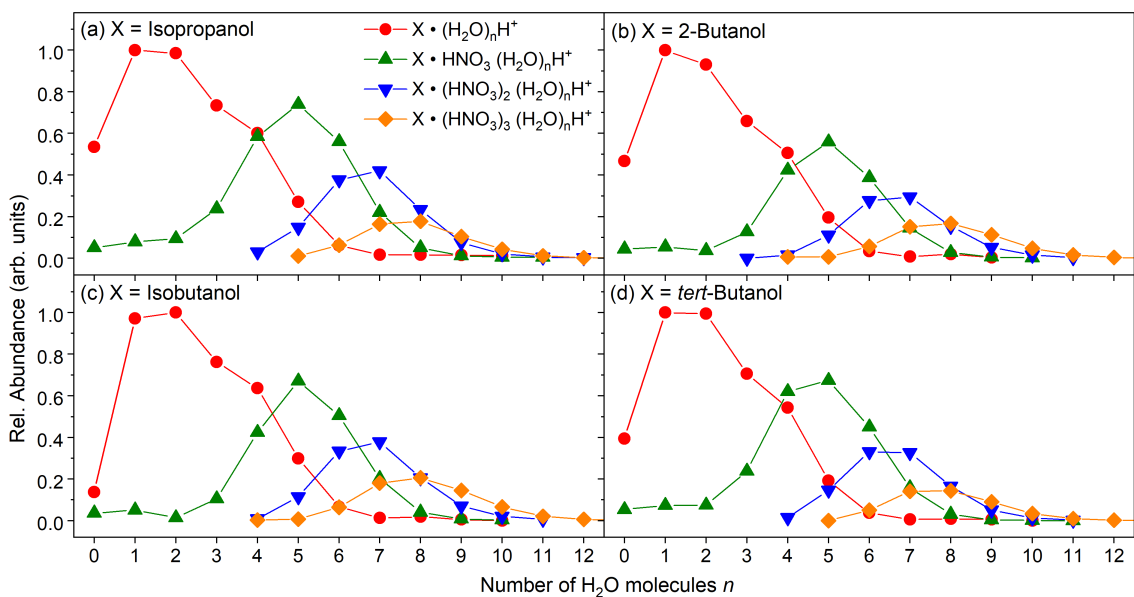

Fig. S5 Relative abundances of the doped $X \cdot (HNO_3)_m(H_2O)_nH^+$ cluster ions from the mass spectra for isopropanol (Figure S3) and isomers of butanol (Figure S2) as a function of the number of water molecules n.
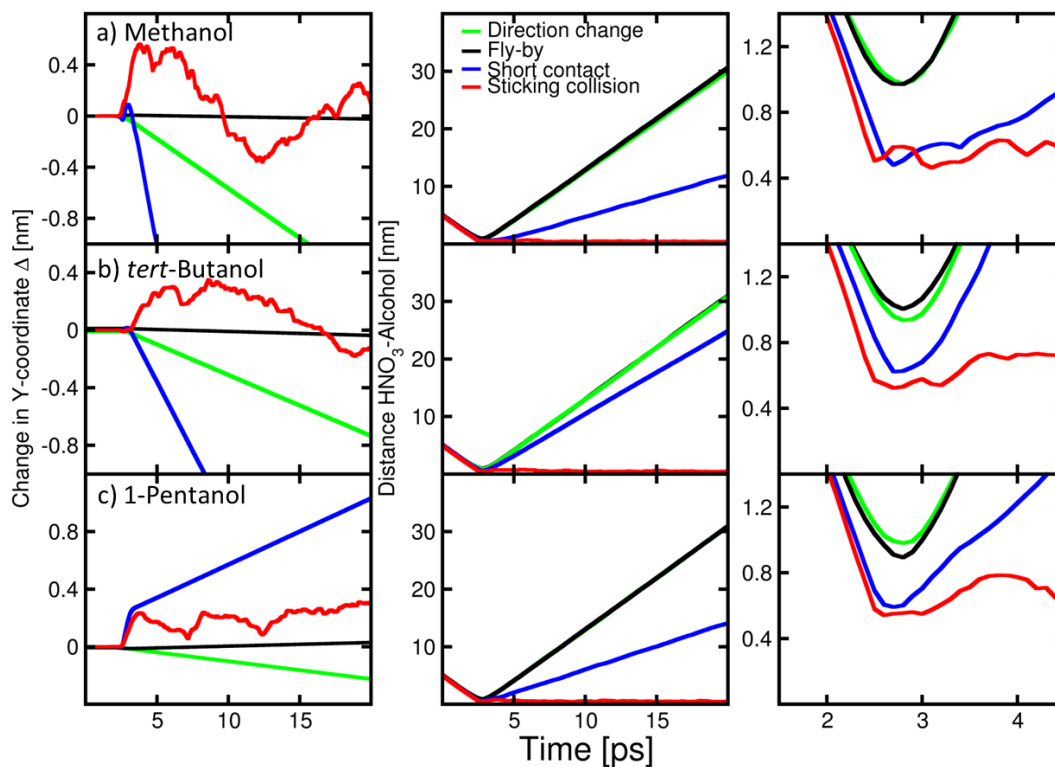
2 Theoretical data

Fig. S6 Examples of the time evolution of the change in the Y-coordinate of the COM of the alcohol with respect to its original value (the first column) and the distance between the COM of the alcohol and the $(H_3O^+ \cdot NO_3^-)$ ion (labeled as HNO_3) (the second and the third column which zooms in the second column). The first row shows results for methanol, the second row for *tert*-butanol and the last row for 1-pentanol. Different colours represent different processes: direction-change (green), fly-by (black), short contact (blue) and sticking collision (red).
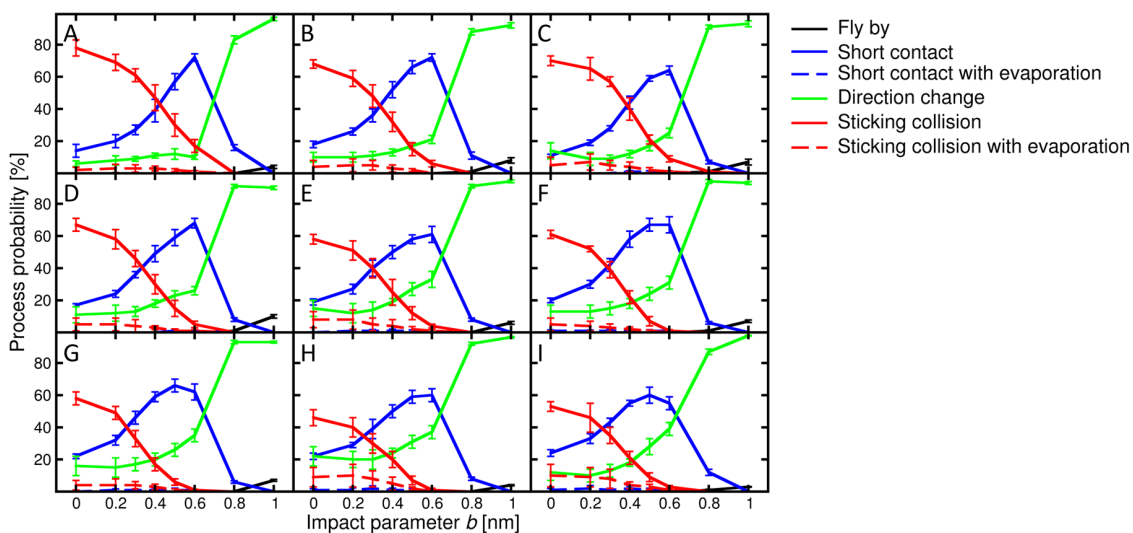

Fig. S7 Probability of the individual processes taking place after the alcohol–aqueous nitric acid cluster encounter as a function of the impact parameter b: fly by (black), sticking (red), direction change (green), and short contact (blue). Solid/dashed lines depict processes with/without water evaporation. Section A: methanol; section B: ethanol; section C: 1-propanol; section D: isopropanol; section E: 1-butanol; section F: 2-butanol; section G: isobutanol; section H: *tert*-butanol; section I: 1-pentanol.
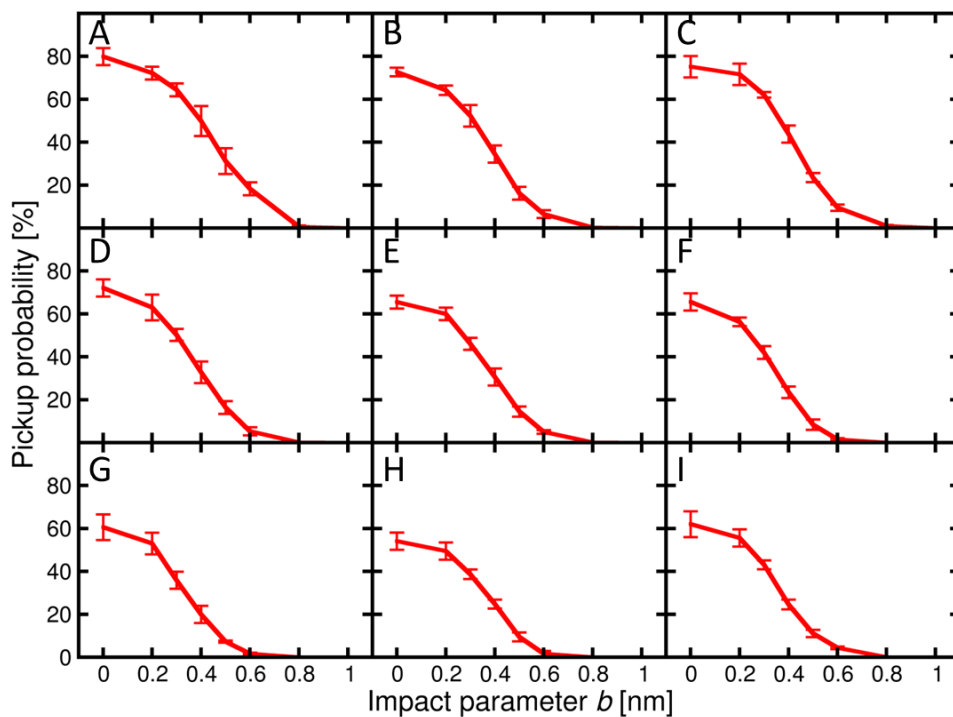
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Fig. S8 Sticking probability (with and without water evaporation added) as a function of the impact parameter $b = 0$ for all measured alcohols. Section A: methanol; section B: ethanol; section C: 1-propanol; section D: isopropanol; section E: 1-butanol; section F: 2-butanol; section G: isobutanol; section H: *tert*-butanol; section I: 1-pentanol.

Fig. S9 Momentum p transferred to the cluster for various processes as a function of the impact parameter b exemplified for all measured alcohols. The dashed line is the average momentum transferred to the cluster. Section A: methanol; section B: ethanol; section C: 1-propanol; section D: isopropanol; section E: 1-butanol; section F: 2-butanol; section G: isobutanol; section H: *tert*-butanol; section I: 1-pentanol.
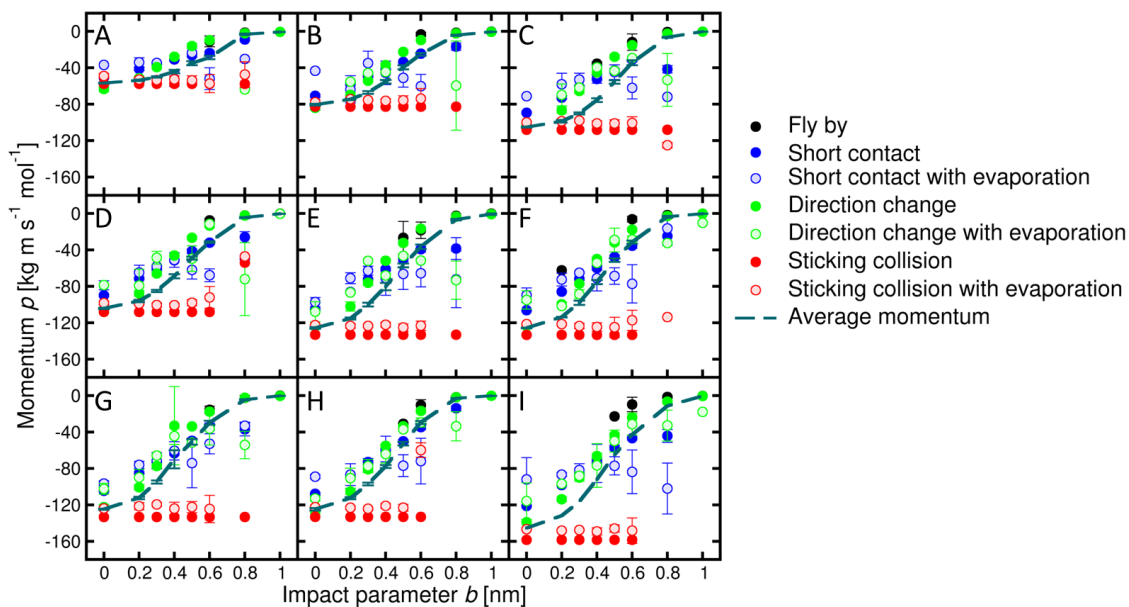
Notes and references

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