Electronic Supplementary Information (ESI):

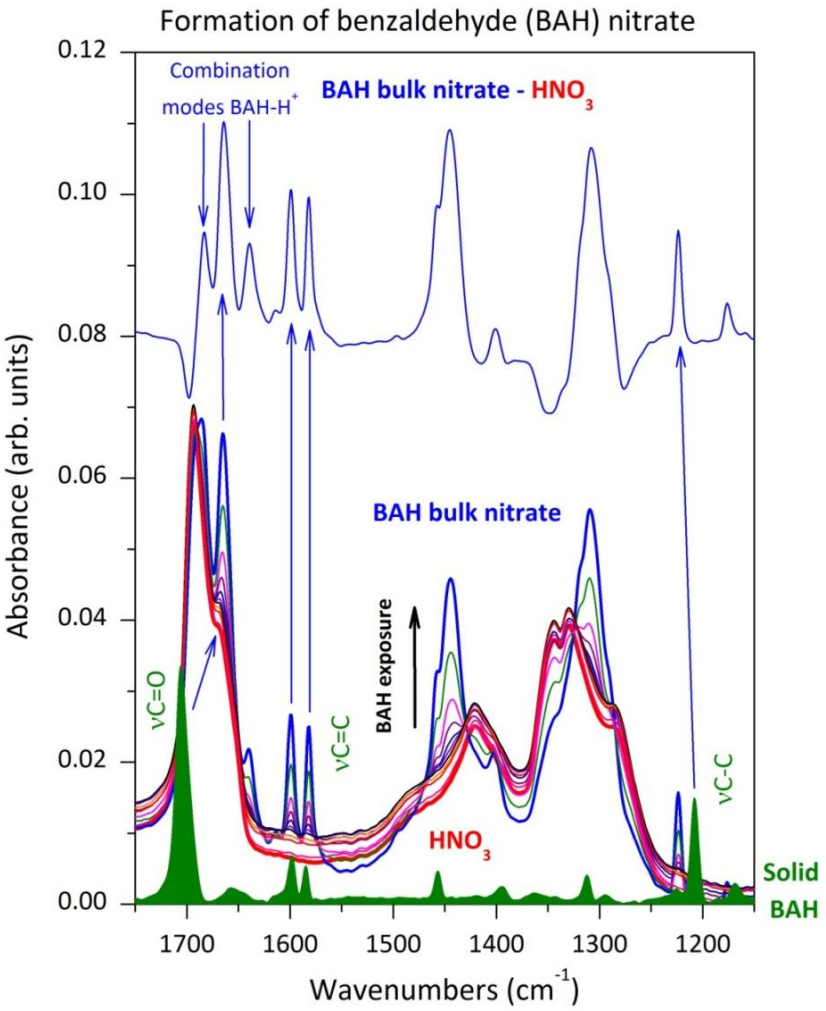

Figure S1: RAIR spectra showing the formation of the benzaldehyde (BAH) bulk nitrate. A 100 L HNO_3 film (red line) is deposited at 150 K, then annealed at 165 K and exposed to increasing amounts of BAH. The blue line shows the spectrum obtained at saturation of the BAH exposure, i.e. when no change is observed upon further addition of BAH: a bulk BAH nitrate is formed. The changes arising from the formation of the BAH bulk nitrate are better evidenced by subtraction of the spectrum of the bare HNO_3 film, as shown on the top spectrum (BAH bulk nitrate - HNO_3). The spectrum of a pure solid BAH film is presented (green line) to help the assignment of the new bands.

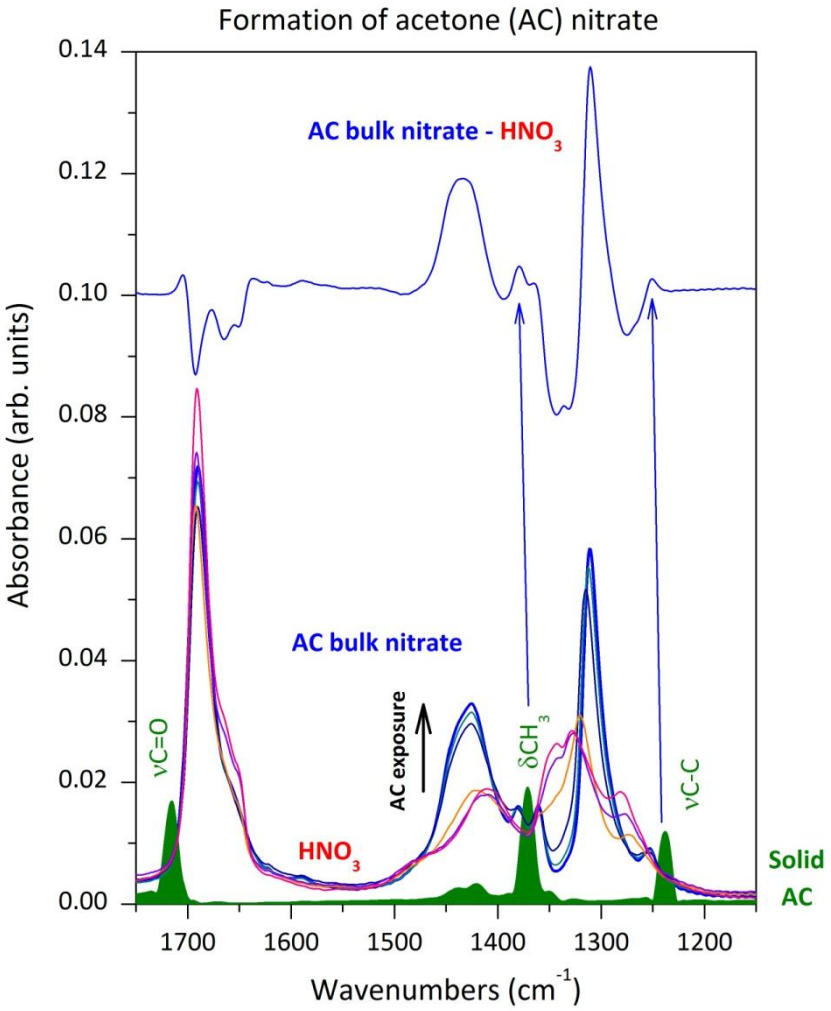

Figure S2: RAIR spectra showing the formation of the acetone (AC) bulk nitrate. The synthesis follows the same steps as previously described for benzaldehyde. Top curve: difference spectrum between the AC bulk nitrate and HNO_3.

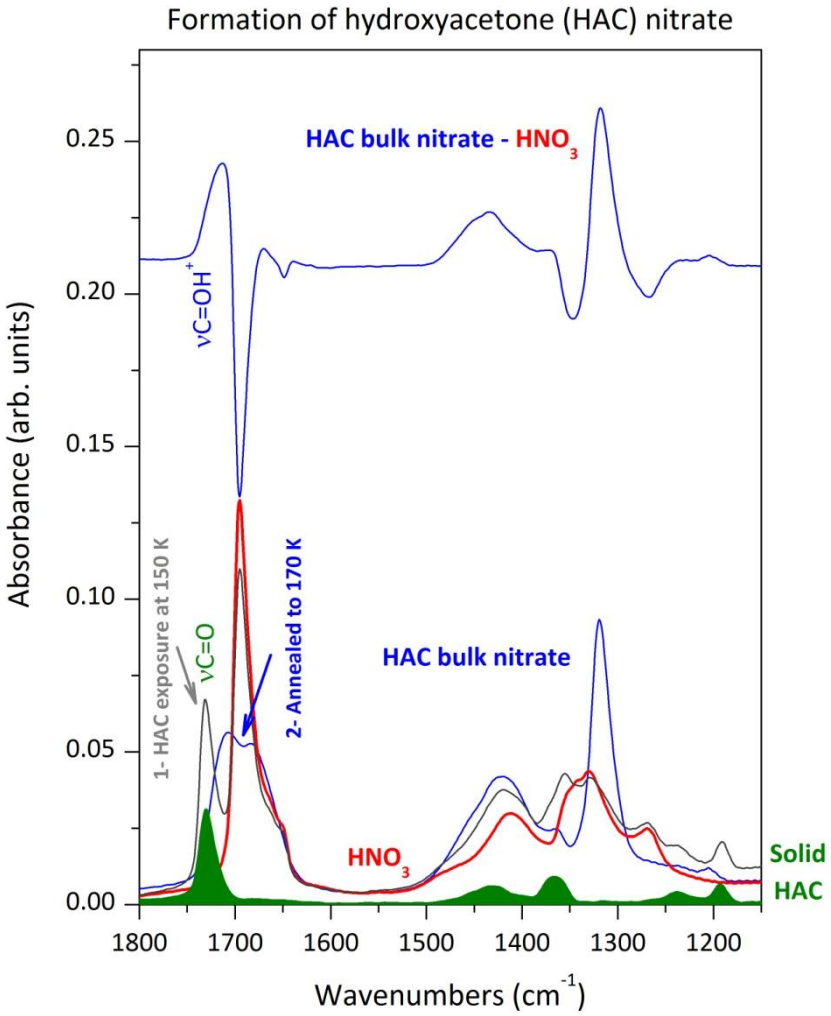

Figure S3: RAIR spectra showing the formation of the hydroxyacetone (HAC) bulk nitrate. The exposure of the HNO_3 film to HAC was realised at 150 K, and the spectra show the growth of a solid HAC layer (gray curve, labelled 1-). In a second step the film was annealed to 170 K, and the thermal agitation of the molecules triggered the mixing of the HNO_3 and HAC layers, hence the protonation reaction (blue curve, labelled 2-). Top curve: difference spectrum between the HAC bulk nitrate and HNO_3.

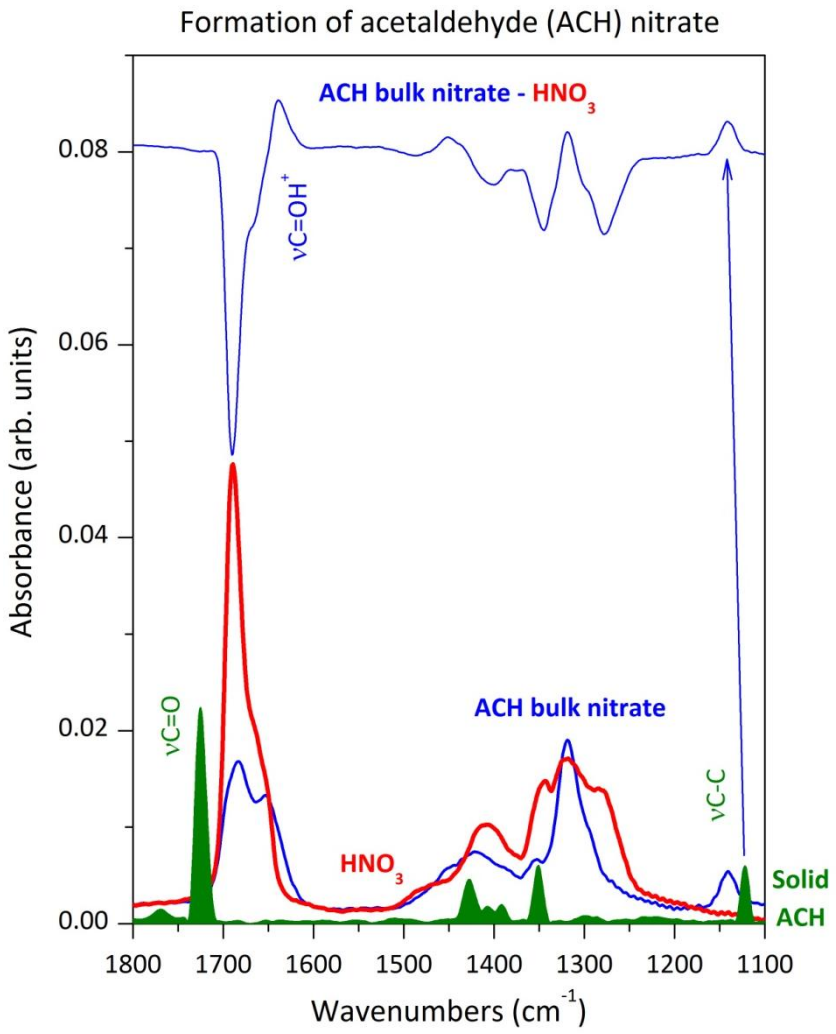

Figure S4: RAIR spectra showing the formation of the acetaldehyde (ACH) bulk nitrate. Top curve: difference spectrum between the ACH bulk nitrate and HNO_3.