The following RAIR spectra were recorded for HNCO exposures of 0.2, 0.3, 0.5 and 0.75 L. In each group of spectra, the surface was annealed to the desired temperature for 60 seconds, cooled to 90 K, then a spectrum was acquired.

- Fig. S1. RAIR spectra of the thermal evolution of 0.2 L of HNCO exposed to the Pt (111) surface at 90 K. The was surface annealed to the indicated temperature for 60 seconds, then cooled to 90 K before each spectrum was acquired.
- Fig. S2. RAIR spectra of the thermal evolution of 0.3 L of HNCO exposed to the Pt (111) surface at 90 K. The was surface annealed to the indicated temperature for 60 seconds, then cooled to 90 K before each spectrum was acquired.
- Fig. S3. RAIR spectra of the thermal evolution of 0.5 L of HNCO exposed to the Pt (111) surface at 90 K. The was surface annealed to the indicated temperature for 60 seconds, then cooled to 90 K before each spectrum was acquired.
- Fig. S4. RAIR spectra of the thermal evolution of 0.75 L of HNCO exposed to the Pt (111) surface at 90 K. The was surface annealed to the indicated temperature for 60 seconds, then cooled to 90 K before each spectrum was acquired.







