



Figure S1. Time courses from transient IR spectra of the *A. vinelandii* MoFe nitrogenase hi-CO complex showing the effect of varying the size of the α -70 sidechain. Spectra are in figure 2a.

(a) Wild-type (α -70^{Val}) measured at 1880, 1904, 1936, 1960 cm^{-1} . This is the same as figure 2b.

(b) α -70^{Ala} at 1870, 1904, 1936, 1957 cm^{-1} .

(c) α -70^{Ile} at 1880, 1895, 1936, 1956 cm^{-1} . The band at 1956 cm^{-1} was obscured by the 1936 cm^{-1} band at long times.

(d) α -70^{Gly} at 1870, 1911, 1946 cm^{-1} .

Intensities in are normalized at (a-c) 150 s or (d) 120 s.