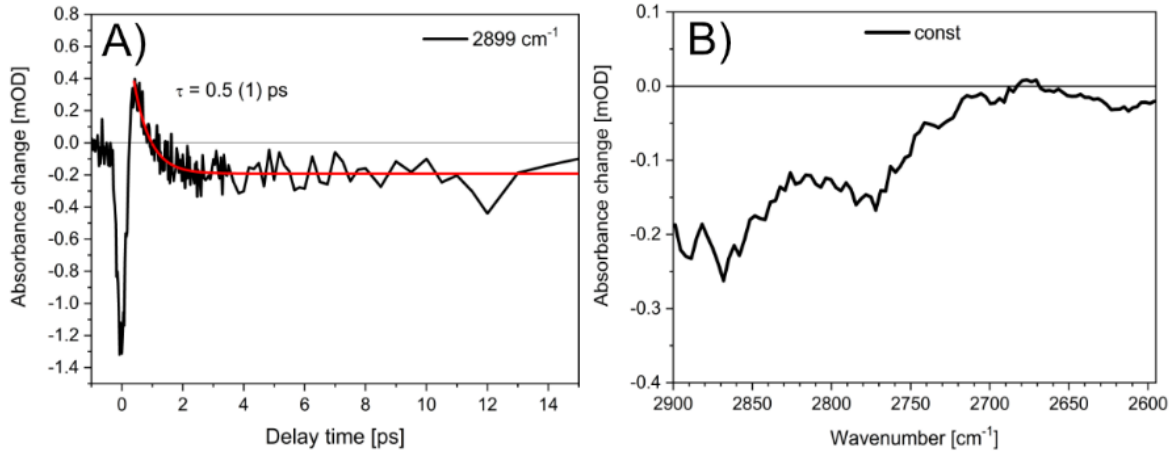
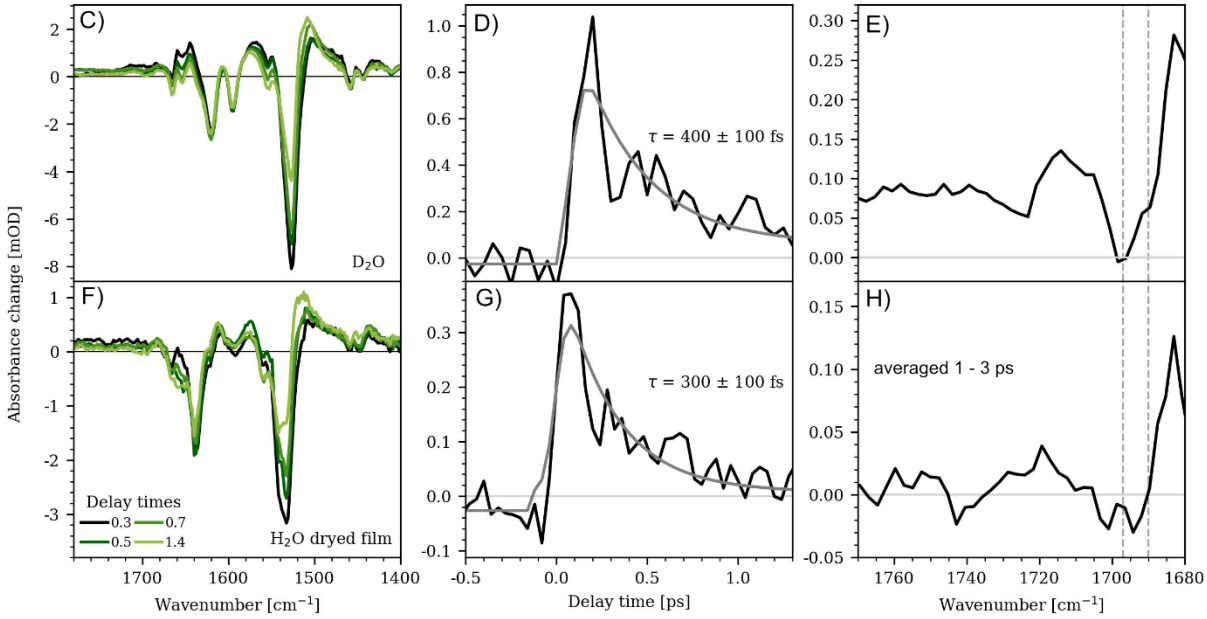
Extended Data Figure 6: Continuum band measurements

The broad continuum band (CB) in *Hs*BR is also observed in H_2O-gel upon photoexcitation at 570 nm. The dynamics show a non-linear signal around zero followed by an instantaneous positive signal that decays with 0.5±0.1 ps either to zero or to a small negative signal. The transient at 2899 cm^{-1} presented in A) decays to a constant negative signal on a time-scale of K formation. A global analysis of dynamics in this range shows a decay of an instantaneous positive signal with 0.5 (1) ps to a negative signal in the range from 2900 to 2700 cm^{-1} as depicted in B). The remaining negative signal agrees with the reported CB observed in cryo-trapped K intermediate at 77 K.[44] These signatures of a CB in K intermediate are located on the high energy side between OH stretching and OH bending vibration. In D_2O we see no or negligible contributions of a negative CB in K intermediate.



The CB is observed in D_2O (C, D, and E) and in H_2O films dried at a relative humidity of 52% (F, G, and H).[1] Absorbance difference spectra for isotropic polarization at selected delay times are presented in C and F. The CB averaged from 1700 to 1780 cm^{-1} in D_2O and from 1700 to 1800 cm^{-1} in H_2O film show similar decay constants of 0.4 (1) ps (in D), and 0.3 (1) ps (in G), respectively. At delay times averaged from 1 to 3 ps the isotropic absorbance difference spectra show negative and positive peak pairs in the carbonyl region around 1720 cm^{-1}. Spectral shifts between E and H are due to D/H exchange.



[1] O'Brien, F.E.M. The Control of Humidity by Saturated Salt Solutions. *J. Sci. Instrum.* **25**, 73 (1948)