Direct In Situ Quantification of HO_2 from a Flow Reactor

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Supplementary Material

Review of Spectral Data

A number of experimental Faraday rotation spectra of the HO_2 Q-branch spectral feature at 1396.90 cm^{-1} were acquired at different temperatures of the atmospheric flow reactor. In these experimental spectra a vertical offset voltage was observed due to the electromagnetic interference (EMI) from the Helmholtz coils. This EMI, if not completely eliminated by EMI shielding, induces parasitic pickup in electrical circuits of the system at the modulation frequency of the magnetic field. The EMI pickup in the pre-amplifier electronics of the photodetection system manifests itself as an offset in the signal demodulated by the lock-in amplifier. This effect is relatively easy to account for in signal post processing by simple offset correction. A similar effect can be observed for the EMI pickup in the laser driving electronics, which results in residual amplitude modulation (RAM) of the EC-QCL. The effect of EMI-induced laser RAM is more complex because this parasitic signal is also affected by the optical transmission of the system. To some degree this reintroduces problems with optical interference fringing and sample absorption in the experimental spectra that normally are suppressed in FRS with pure sample modulation. Figure 1 shows a spectrum acquired at the flow reactor exit without dimethyl ether (no HO_2 generation). The scan clearly shows optical fringing and a slowly varying baseline. Such baseline scans can be used to remove these unwanted background signals from the experimental spectra in the post-processing. While the overall ability to remove the slowly varying offset using this method was quite successful, removal of the optical fringes was not reliable. This is due to a gradual drift in the optical system alignment that slowly varies the fringe pattern during the measurement. Given the time required to collect one spectrum in this prototype system, the suppression of optical fringes originating from EMI-induced laser RAM effects was not possible. However, for the purpose of non-linear fitting of the data to the spectral model, the free spectral range of the fringe was small enough that it didn't lead to a significant interference with the fit to the experimental signal. The fringe can clearly be observed in the fit residuals. Figures 2-9 show the experimental spectra after subtraction of the background scan shown in Figure 1. The result of the fitting of the spectral model to the experimental data is shown along with the resulting fit residuals in each figure. The figures contain spectra acquired at different reactor temperatures between 623K and 823K, corresponding to exit (sample) temperatures from 398 K to 698 K. The exit temperatures reflect the average radial temperature gradient 2 mm from the exit of the flow reactor, and were used to determine HO_2 concentration data shown in Figure 4 in the main paper.

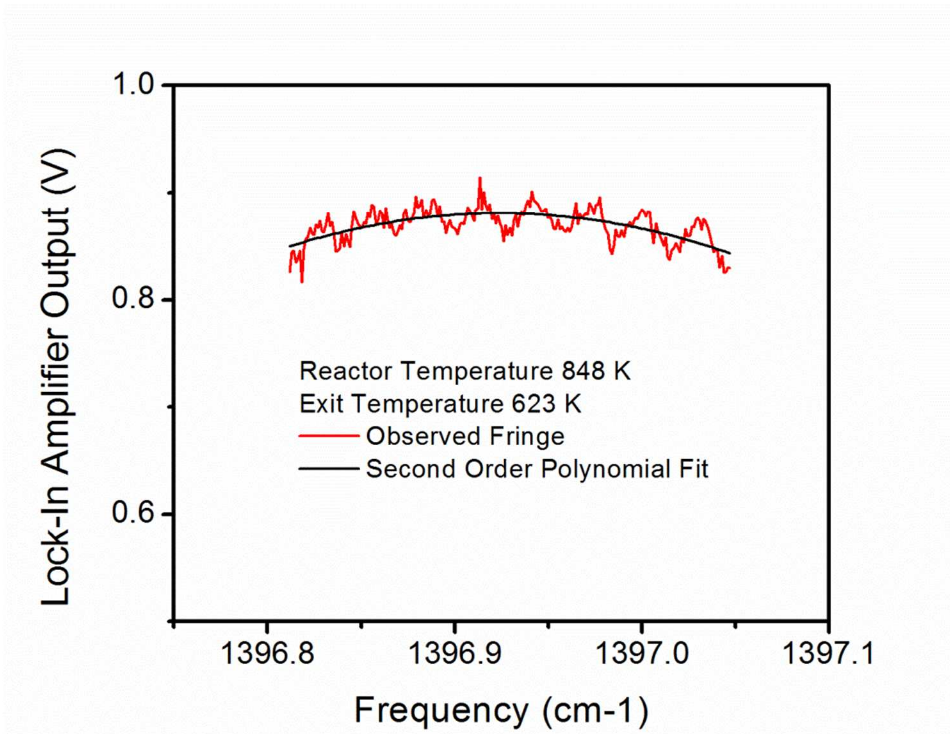

Figure 1: Background spectrum of the reactor exit without dimethyl ether present.

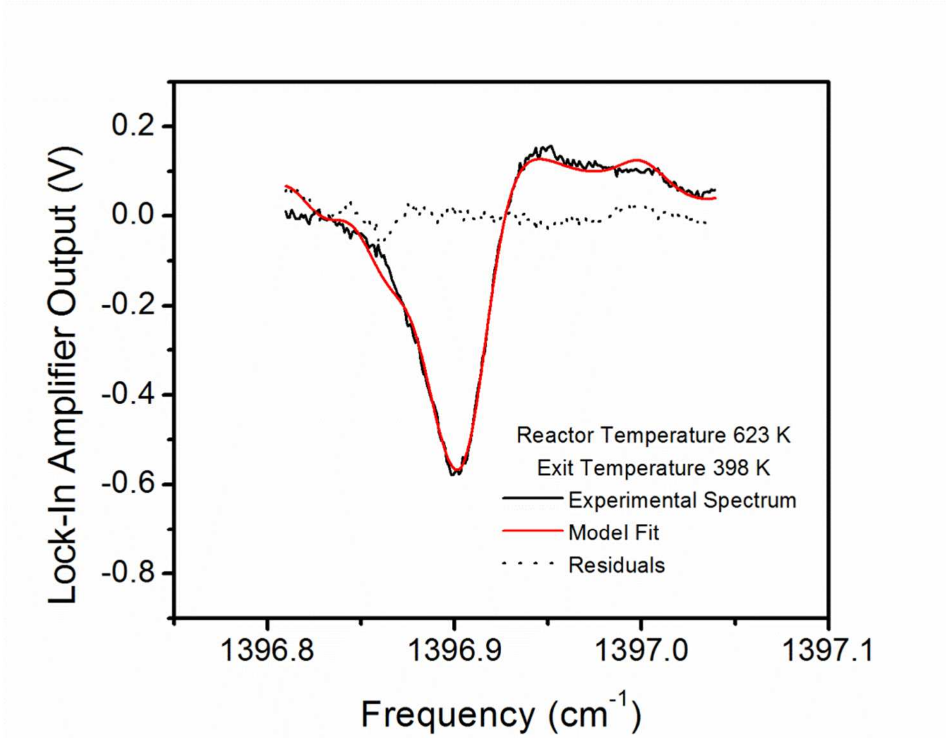

Figure 2: HO_2 spectrum at a reactor temperature of 623 K and an average exit temperature of 398 K.

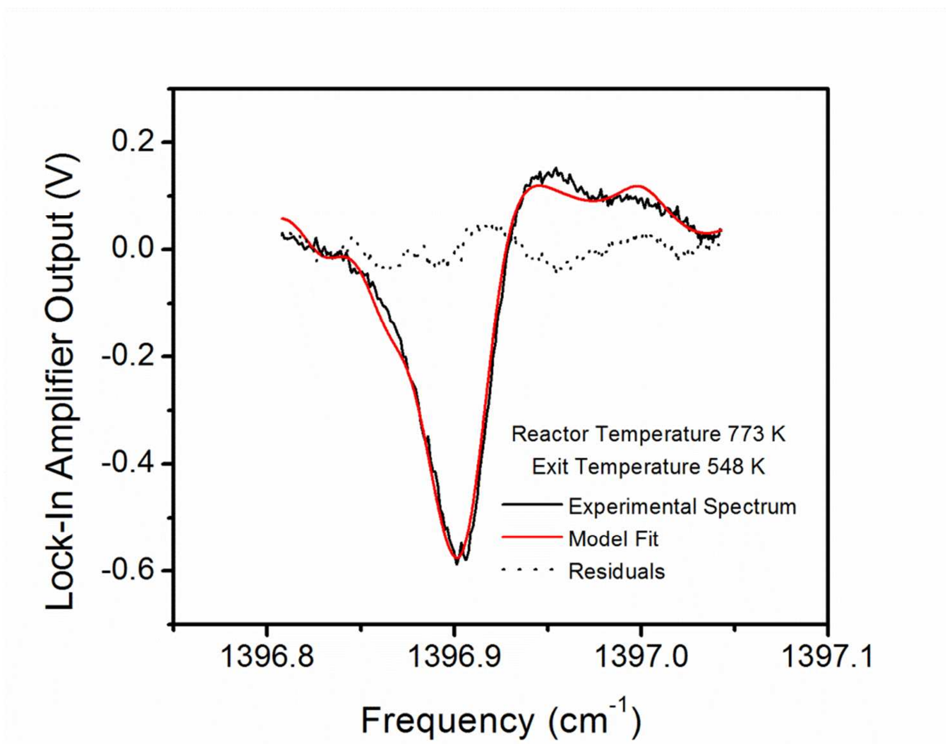

Figure 3: HO_2 spectrum at a reactor temperature of 773 K and an average exit temperature of 548 K.

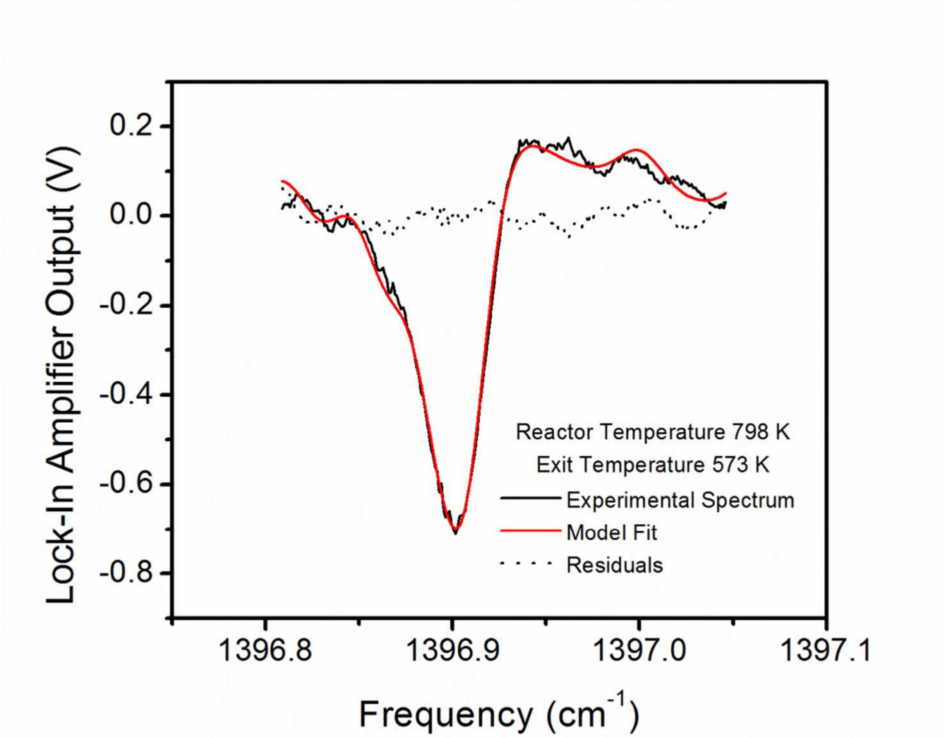

Figure 4: HO_2 spectrum at a reactor temperature of 798 K and an average exit temperature of 573 K.

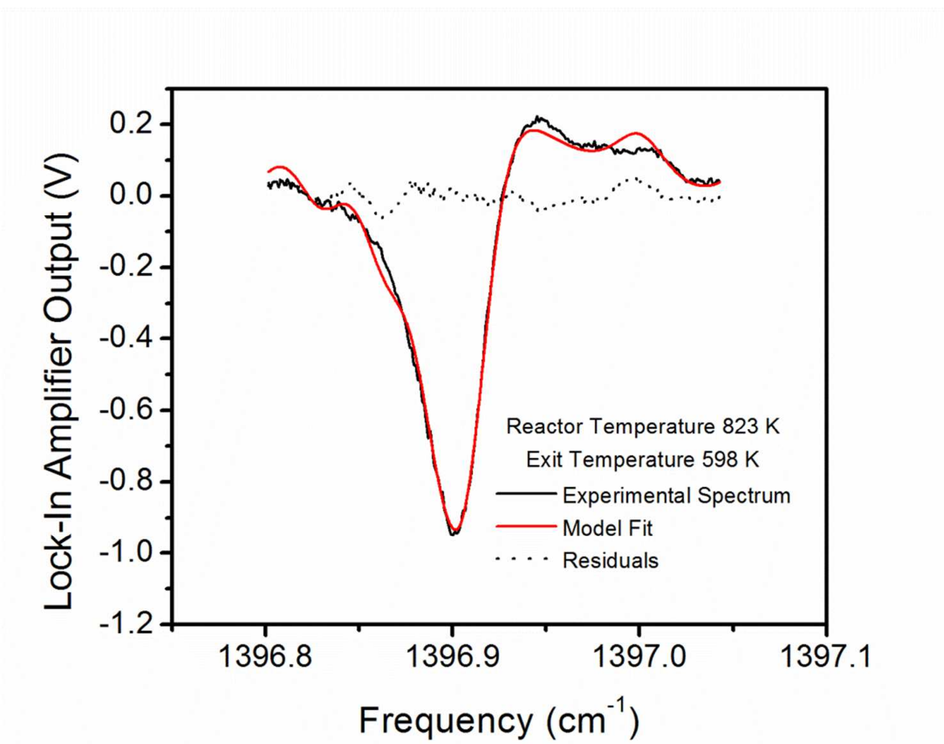

Figure 5: HO_2 spectrum at a reactor temperature of 823 K and an average exit temperature of 598 K.

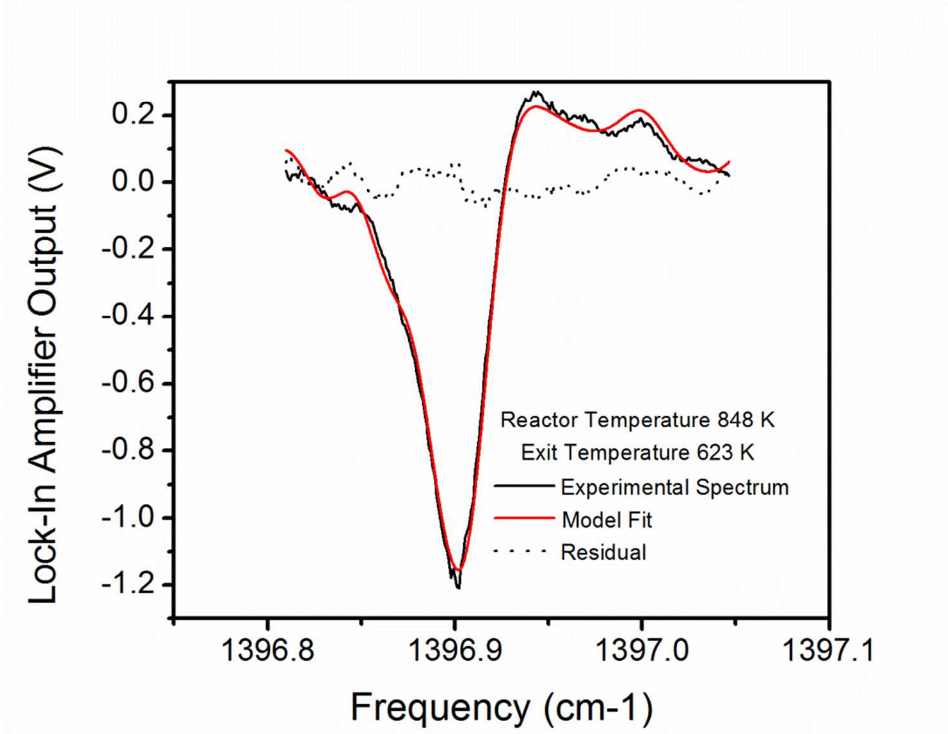

Figure 6: HO_2 spectrum at a reactor temperature of 848 K and an average exit temperature of 623 K.

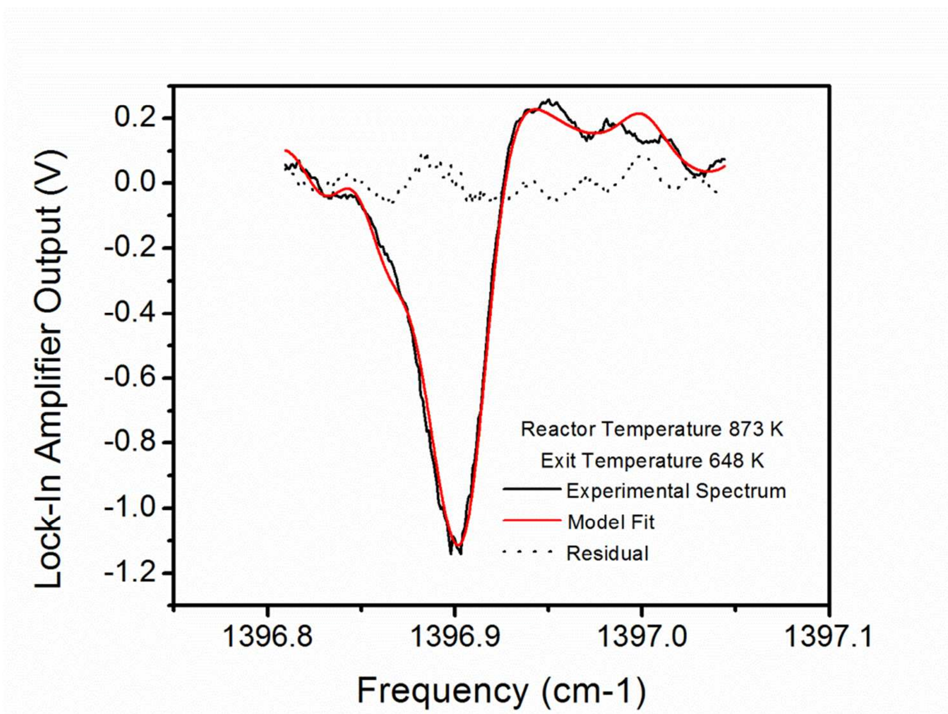

Figure 7: HO_2 spectrum at a reactor temperature of 873 K and an average exit temperature of 648 K.

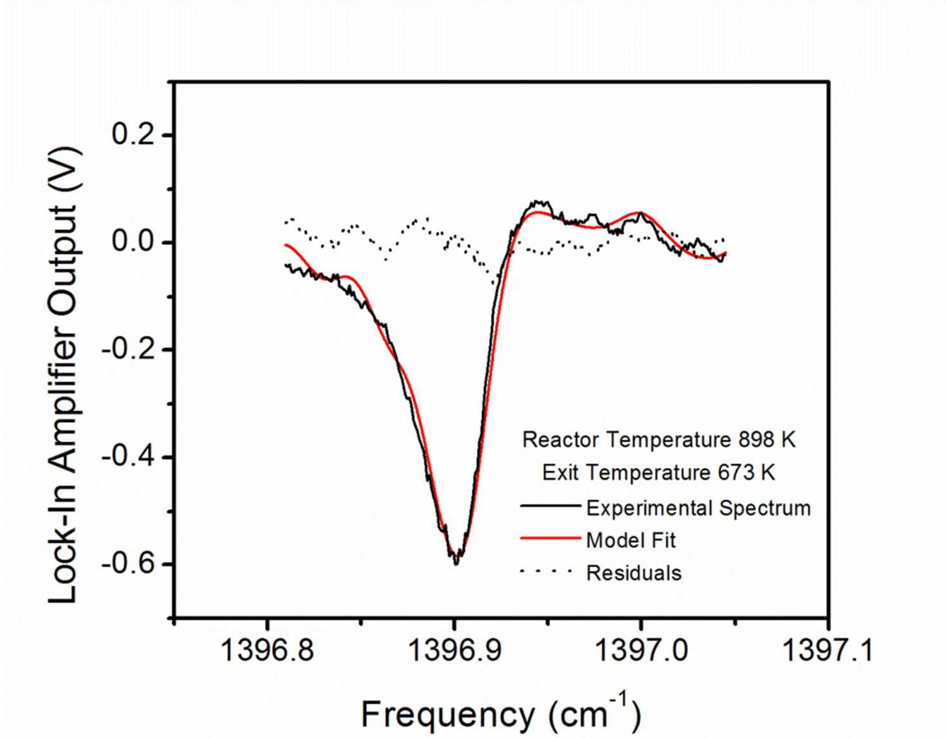

Figure 8: HO_2 spectrum at a reactor temperature of 898 K and an average exit temperature of 673 K.

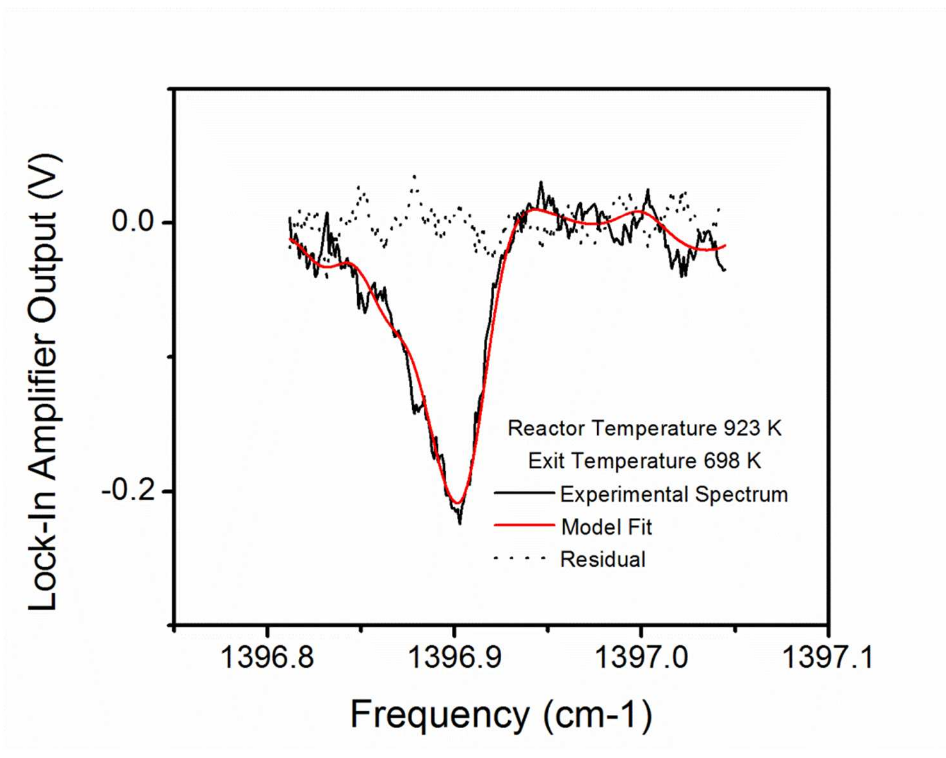

Figure 9: HO_2 spectrum at a reactor temperature of 923 K and an average exit temperature of 698 K.