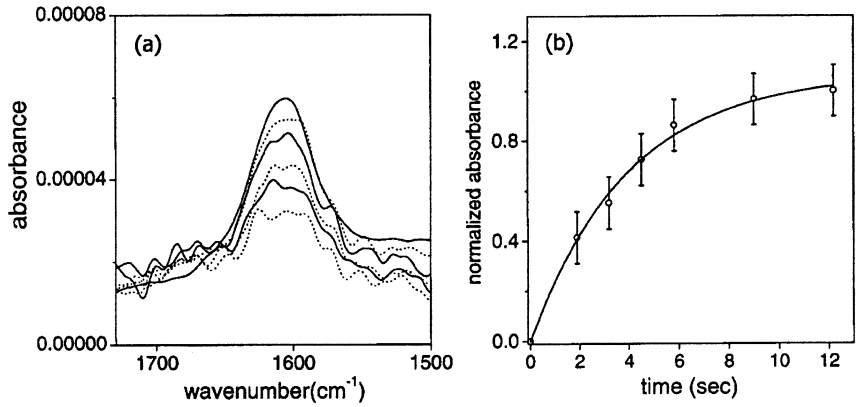

Figure 2. (a) Rapid-scan FT-IR spectra of single pulse-induced $CD_3OD + O_2$ photoreaction in a FAPO-5 sieve at 250 K recorded at 1.9, 3.2, 4.5, 5.8, 9.0, and 12.2 s after the 355 nm pulse. Alternate traces are dashed for clarity. (b) Single-exponential fit of (peak) absorbance growth gives a rise constant of $0.25 + 0.02$ s^{-1}.

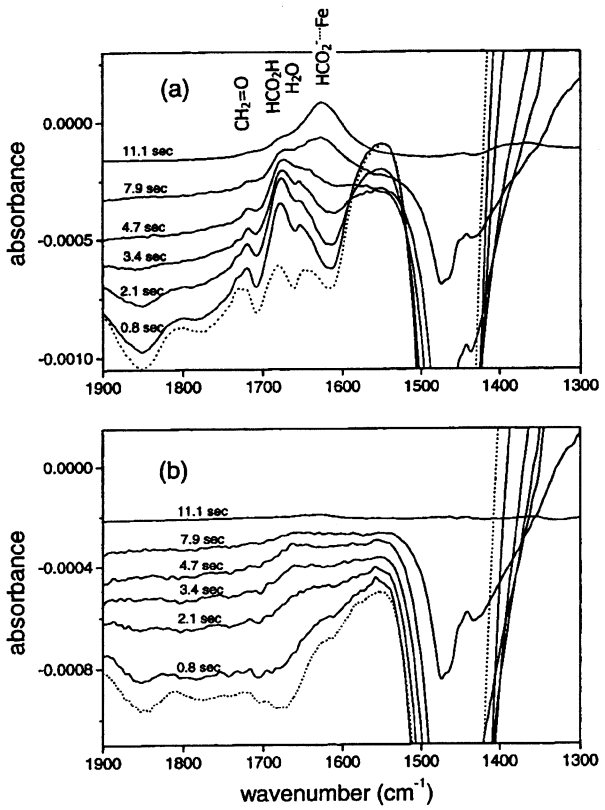

Figure 3. (a) Rapid-scan FT-IR spectra of 355 nm induced $CH_3OH + O_2$ reaction in a FAPO-5 sieve at 250 K. Spectra were recorded on the second time scale following excitation for 1.1 s by a sequence of 355 nm pulses at 10 Hz. Dotted trace is spectrum recorded during laser irradiation. (b) Result of identical experiment for the $CH_3OH + N_2$ system.

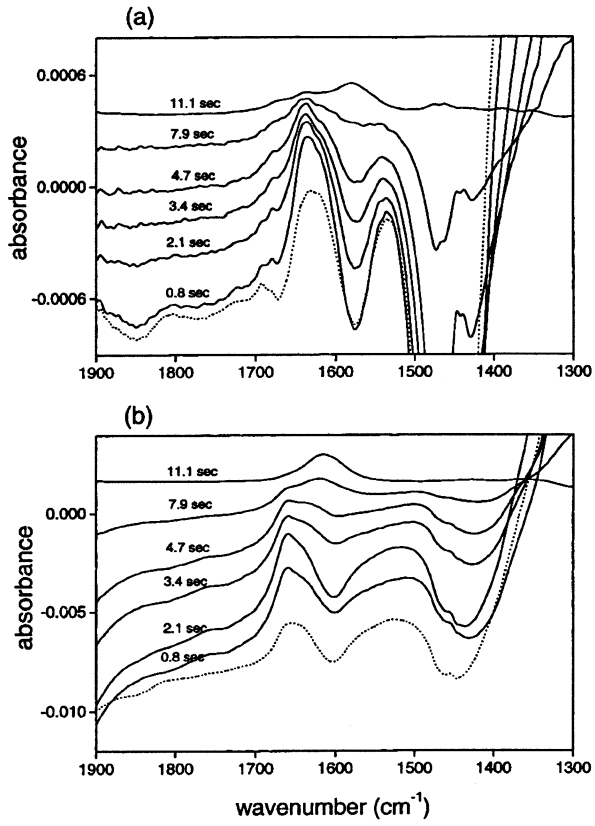

Figure 4. Rapid-scan FT-IR experiment on the second time scale as described in Figure 3 for (a) $^{13}CH_3OH + O_2$ and (b) $CD_3OD + O_2$.

desorption effects (see below). More accurate data were obtained from a $CD_3OD + O_2$ study as desorption-induced changes of methanol are outside the 2000−1300 cm^{-1} spectral range for this isotope and are presented in Figure 2a. A single-exponential fit gives a rise of DCO_2^-···Fe of $0.25 + 0.02$ s^{-1} (Figure 2b).

A 10-fold improvement of the S/N ratio was accomplished by using a train of 10 photolysis pulses instead of a single pulse. Figure 3a shows the transient absorbance spectrum of the parent $CH_3OH + O_2$ reaction. The dotted trace was recorded during 1.1 s photolysis, the subsequent curves at delays of 0.8, 2.1, 3.4, 4.7, 7.9, and 11.1 s after completion of the photolysis period.

As in the previous studies, the sieve temperature was held at 250 K. The strong bleach in the 1500−1350 cm^{-1} region is due to consumption of methanol by reaction, as well as by desorption caused by a laser-induced temperature rise of a few degrees. The spectral effects of methanol desorption due to the laser pulse can be seen when conducting experiments with N_2 instead of O_2, shown in Figure 3b. Readsorption is complete within about 10 s. The transient absorbance spectrum recorded during photolysis (dotted curve of Figure 3a) reveals the CH_2=O band centered at 1726 cm^{-1}. Figure 4a shows the corresponding $^{13}CH_2$=O absorption at 1687 cm^{-1} in similar runs with $^{13}CH_3OH + O_2$. The formaldehyde band is sufficiently separated from the nearest absorption to allow us to estimate the lifetime