

consisted of recording an interferogram of 109 ms duration (double-sided/forward-backward) at a fixed delay of 12 ms after the 355 nm laser pulse. The mirror velocity was 160 kHz, and the spectral resolution was 4 cm^{-1} . Start of the interferogram acquisition following a laser pulse was triggered by an optical pulse diverted from the photolysis laser beam (Si photodiode EG&G model SGD-444). To ensure that the time delay between the laser pulse and the start of interferogram acquisition was the same after each pulse ($12.0 \pm 0.2\text{ ms}$), the Nd:YAG laser was triggered by a TTL pulse from the FT-IR instrument coincident with the forward turn of the moving mirror. The TTL pulse was sent through a home-built rate divider before entering the laser in order to suppress all pulses during a 2.56 s period needed for the transient species to decay (section III). A second interferogram was recorded and stored during the last forward-backward motion of the mirror just before the next photolysis pulse. A total of 200 such sets of interferogram pairs (hence, single beam spectra) resulting from 200 laser pulses were stored and constitute an "experiment". Final 100 ms spectra were obtained by ratioing the single beam spectrum just after the n th pulse against the single beam spectrum just before that pulse. The 200 ratioed spectra from the 200 pulses were then averaged, furnishing the 100 ms absorbance spectrum of that experiment. A total of 40 such experiments were conducted and averaged in order to improve the S/N ratio. Calculations were carried out with a MACRO program executed within the Bruker OPUS software. A second method of measuring millisecond spectra consisted of recording a (single-sided/forward only) interferogram of 25 ms duration at a fixed delay of 11 ms after the 355 nm pulse. Separation of laser pulses was 73 ms. A total of 200 such interferograms resulting from 200 laser pulses were stored separately. Final 25 ms spectrum of the experiment was obtained by ratioing the single beam spectrum of the n th pulse against the single beam spectrum of pulse $n - 1$, and averaging all 200 absorbance spectra. Typically, 10 such experiments were conducted and averaged to improve the sensitivity.

Slow runs on the time scale of seconds were conducted in two ways. The first method consisted of the recording of 99 interferograms following a single Nd:YAG laser pulse (double-sided/forward-backward at 160 kHz and 4 cm^{-1} resolution). Again, the laser was triggered by the forward motion of the interferometer mirror, using a rate divider to suppress TTL pulses from the FT-IR instrument for a period of 12.8 s between laser pulses. A total of 10 consecutive interferograms were automatically averaged, furnishing interferogram time slices (stored in "buffers") at 1.28 s resolution. To simplify the data analysis, buffers Nos. 6–9 were averaged to yield a single time slice of 5.1 s duration. Hence, the data stored after each photolysis pulse consisted of seven averaged interferograms (resulting in seven single beam spectra) taken at 0.6, 1.9, 3.2, 4.5, 5.8, 9.0, and 12.2 s after the laser pulse (midpoints). A total of 50 such sets of seven single beam spectra generated by 50 laser pulses were stored as the result of one experiment. Final time-resolved spectra for a given time delay were obtained by ratioing each of the 50 corresponding stored single beam spectra (one of the seven averages after each pulse) against the single beam spectrum taken just before the pulse. These 50 ratioed spectra were then average to yield the absorbance time slice for a given delay. The results of 5–10 such experiments were further averaged for S/N improvement.

In our second approach for obtaining rapid scan spectra on the time scale of seconds, we employed substantially longer photolysis light exposure while using the same method of interferogram recording just described. The sample was again

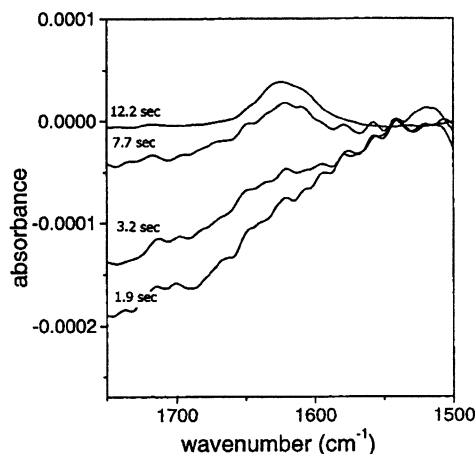


Figure 1. Rapid-scan FT-IR spectra on the second time scale of $\text{CH}_3\text{OH} + \text{O}_2$ photoreaction induced by single 355 nm pulses in a FAPO-5 sieve at 250 K.

excited 50 times at intervals of 12.8 s, but each exposure consisted of 10 laser pulses over a period of 1.1 s. This was accomplished by passing the 355 nm Nd:YAG beam (train of 10 Hz pulses) through a mechanical shutter (UniBlitz driver model D122 with a head (Vincent Assoc.) featuring a 13 mm diameter aperture) of 1.1 s duration. Opening of the shutter was initiated by a TTL pulse of the FT-IR instrument synchronous with a forward turn of the moving mirror. Data were evaluated as described for the first method. The first buffer contained the average of the spectra recorded *during* 1.1 s irradiation, and subsequent spectra correspond to delays of 0.8, 2.1, 3.4, 4.7, 7.9, and 11.1 s after completion of photolysis light exposure.

Experiments in the step-scan mode at $5\text{ }\mu\text{s}$ resolution were conducted with the same spectrometer, using methods described in detail in previous reports.^{5–7} The same HgCdTe infrared detector was used as in the rapid-scan runs. Measurements focused on the spectral region $1550\text{--}1350\text{ cm}^{-1}$ using folding limits 1606 and 1339 cm^{-1} and a band-pass filter (University of Reading Infrared Multilayer Laboratory model 21K), installed in front of the infrared detector. Spectral resolution was 4 cm^{-1} , resulting in step-scan runs involving 135 mirror positions. At each mirror position, five laser-induced decays were recorded and averaged. Photolysis pulses were separated by 100 ms.

Methanol (EM Science, 99.8%), methanol- D_4 (Aldrich, 99%D), and methanol- ^{13}C (Aldrich, 99% ^{13}C) were degassed by freeze-pump-thaw cycles before use. Oxygen and nitrogen gas (Air Products, 99.997%) were used as received. Hydroxymethyl-hydroperoxide was synthesized inside FAPO-5 by reaction of H_2O_2 loaded into the sieve with adsorbed $\text{CH}_2=\text{O}$ gas according to the method described in the preceding paper².

III. Results

To find out about the reaction steps immediately preceding formation of the final products, rapid scan runs were conducted on a time scale of seconds. Experiments using single 355 nm photolysis pulses followed by recording of interferograms over a period of 12.8 s revealed the growth of $\text{HCO}_2^-\cdots\text{Fe}$ at 1625 cm^{-1} , which is complete within 10 s at 250 K. The band, which is assigned to (symmetric) formate based on the characteristic 10 cm^{-1} isotope shift of $\text{HC}^{18}\text{O}^{16}\text{O}^-$, overlaps with H_2O coproduct.¹ Figure 1 shows rapid-scan spectra recorded 1.9, 3.2, 7.7, and 12.2 s after the pulse. The result of five 50-shot experiments of the $\text{CH}_3\text{OH} + \text{N}_2$ system was subtracted from the spectra of $\text{CH}_3\text{OH} + \text{O}_2$ runs to cancel out methanol