Time-resolved wavelength modulation spectroscopy measurements of HO₂ kinetics

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High-frequency wavelength modulation spectroscopy (WMS) has been applied to the detection of the hydroperoxyl radical (HO$_2$) in a laser photolysis and long-path absorption pump-probe kinetics reactor with a near-infrared distributed feedback diode laser. The HO$_2$ is formed by the 355-nm photolysis of Cl$_2$ in the presence of CH$_3$OH and O$_2$ and monitored by a phase-sensitive detection of the second-harmonic ($2f$) signal in the $2\nu_1$ band with a 1.5-μm diode laser directly modulated at 5 MHz. The measured $2f$ WMS signal is calibrated by direct absorption and converted to an absolute number density with the known absorption line strength of the HO$_2$ line at 6625.80 cm^{-1}. The utility of time-resolved WMS as a second-order kinetics probe is demonstrated through the measurement of the HO$_2$ self-reaction rate constant at 295 K. © 1997 Optical Society of America

1. Introduction

The hydroperoxyl radical (HO$_2$) is an important intermediate in hydrocarbon combustion with its critical role in the initiation of autoignition[1,2] and in atmospheric chemistry.[3] In combustion kinetics, studies of HO$_2$ reactions, where many important reactions are much slower than the self-reaction, a low HO$_2$ concentration is required. This requirement, in turn, calls for a sensitive means of detecting HO$_2$ with sufficient time resolution to yield kinetic parameters. Conventional optical detection methods have limited usefulness because the UV absorption spectrum of HO$_2$ is broad and structureless due to predissociation and is overlapped by many other species, including alkyl peroxy radicals.

Diode-laser-based detection methods can provide the needed sensitivity and selectivity. High-frequency wavelength modulation spectroscopy (WMS) gives excellent detection limits even when relatively weak near-infrared transitions are used. Reports of detection sensitivities close to the detector shot-noise limit have appeared under favorable conditions.[4,5] Time resolution that is useful for gas kinetics studies has been demonstrated with FM spectroscopy,[6] and transient FM spectroscopy has now found applications in the spectroscopy of reactive species[7] and in the study of chemical kinetics in the pseudo-first-order limit.[8] However, the application of high-frequency WMS to time-resolved gas phase kinetics study or application of modulation techniques to second-order kinetics has not, to our knowledge, been clearly demonstrated. We distinguish FM from WMS because of the frequency of the modulation used. Although the difference may seem only semantic, WMS can be much easier to implement because the lower-frequency ($\sim$10 MHz) electronic components are simpler to use than are the microwave components needed for FM spectroscopy at near-IR wavelengths.

In addition to the high detection sensitivity, species selectivity, and the time resolution required, the diode-laser-based WMS measurement should be proportional to the time-dependent concentration of the monitored species, and the calibration step should be convenient and reliable. The optical signal resulting from WMS measurement is linearly proportional to the absolute absorbance in optically thin limit (absorbance of $\sim$1% or less), and the proportionality constant is established easily by comparison with direct absorption measurement. Though not utilized in this experiment, the near-IR WMS signal can be detected with an InGaAs photodiode detector capable of simultaneously monitoring ac (WMS) and dc (I_0) components for real-time normalization of the WMS signal. The reliability of calibration is often limited by the signal level of the direct absorption measurement

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and not by the WMS detection. We also note that HO_2 kinetics can be probed in the mid-IR with lead-salt diode lasers when vibrational fundamental bands are accessed. All three band strengths have been determined experimentally,[9,10] and much stronger HO_2 absorption lines are available. High-frequency WMS[11,12] and FM[13,14] spectroscopy utilizing lead-salt diode lasers are well established.

Some of the considerations of using laser photolysis to prepare the reactant and to monitor either the reactant or the product concentration with a time-resolved absorption technique include (1) the nanosecond-to-microsecond time scale for the collisional thermalization of the nascent reactant or product should be fast compared with the reaction rates to be studied; and (2) the periodic probe beam steering, termed thermal lensing, that is caused by the radial acoustic waves formed inside the cylindrical photolysis cell by the photolysis pulse should be minimized. As discussed below, the $2f$ WMS signal is related linearly to the change in absorbance.

In the present research we describe the utility of time-resolved WMS as a kinetics probe, including application to second-order reaction kinetics where absolute concentrations of reactants need to be measured. We directly modulated a distributed feed-back diode laser operating at 1.5 μm using modulation of the injection current, and the laser is used to probe the HO_2 radical in the ν_1 first overtone band. The midterm (~45 min) stability of the $2f$ WMS signal calibration in our setup was found to be ±14%, as measured by the deviation in measured HO_2 self-reaction rate constants.

2. Experiment

The hydroperoxyl radical is produced by photolysis of chlorine in the presence of methanol and oxygen with the following reaction sequence:

$$Cl_2 \xrightarrow{h\nu} 2Cl,$$

$$Cl + CH_3OH \rightarrow CH_2OH + HCl, \tag{1}$$

$$CH_2OH + O_2 \rightarrow HO_2 + CH_2O. \tag{2}$$
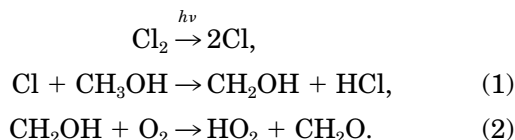
Rate constants for reactions (1) and (2) are 5.7×10^{-11} cm^3 molecule^{-1} s^{-1} and 9.1×10^{-12} cm^3 molecule^{-1} s^{-1}, respectively.[15] Species concentrations are chosen so that production of HO_2 would be essentially complete before any reactions of HO_2 took place; specifically the contribution of Cl + HO_2 and $CH_2OH + HO_2$ reactions are minimized. However, measurements made at higher initial Cl concentrations, even where secondary reactions of intermediate products with HO_2 are evident, give results for the HO_2 self-reaction rate constant in agreement with the other determinations.

The experimental apparatus is shown schematically in Fig. 1. The reaction cell is a 150-cm-long stainless-steel cell equipped with 3° wedged CaF_2 windows. Flows of 1% Cl_2 in He, 10% O_2 in Ar, neat CH_3OH, and Ar buffer are controlled by mass flow controllers. Pressures are measured with a capaci-
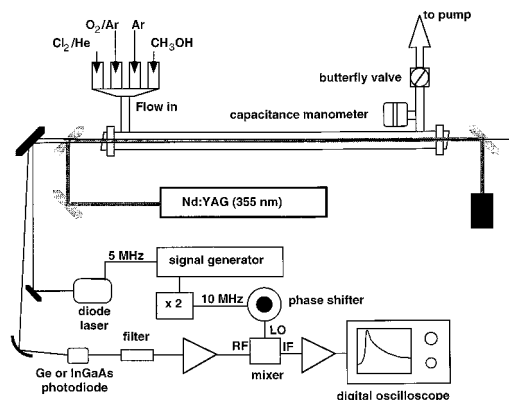

Fig. 1. Schematic of the experimental apparatus. The demodulated signal is amplified by a variable-gain amplifier with a variable high-pass and low-pass filter. Typically the signal was low-pass filtered at 100 kHz, which determines the detection bandwidth. RF, relative frequency; IF, intermediate frequency; LO, local oscillator.

tance manometer attached to the outlet of the cell, and the total pressure (50 Torr in the present experiments) is controlled actively with a butterfly valve in the outlet. The Cl_2 is photolyzed with between 35 and 70 mJ/pulse of 355-nm light from a Nd:YAG laser. We combined the photolysis beam with the diode laser probe beam using a dichroic mirror. A second dichroic mirror removes the pump beam while allowing the near-IR beam probe beam to make a second pass through the cell. The probe beam is an output from a distributed feedback InGaAsP diode laser that is frequency modulated at 5 MHz when the injection current is modulated directly. The transmitted diode beam is imaged onto either an InGaAs or a Ge photodiode. The output of the photodiode is then filtered and demodulated at twice the frequency of modulation ($2f$), and the resulting demodulated signal is amplified and digitized with a digital oscilloscope. Spectra are taken with a gated integrator/boxcar averager combination.

To calibrate the $2f$ WMS absorption signal, direct absorption spectra of HO_2 are taken with a dc-coupled photodiode detector while the diode laser current is ramped slowly. We measured the transmitted power without HO_2 (I_0) by chopping the diode beam. The signal is amplified 100 to 1000 times, and the resultant direct absorption line shapes are fitted to a Voigt profile. We took transient HO_2 traces using both direct absorption and $2f$ WMS under the same photolysis conditions, with the diode laser frequency fixed at the center of the absorption. The peak transient absorption, taken at the highest point in the HO_2 time evolution, is then used in conjunction with the measured line profiles to calibrate the $2f$ WMS signal strength. Figure 2 shows a FM and a direct absorption scan over the pair of HO_2 lines at 6625.80 and 6625.68 cm^{-1} as (a) and (b), respectively. The dashed curve in Fig. 2(b) is a fit to a Voigt profile that was used to estimate the peak absorbance. Under the conditions of the experiment (50-Torr total pressure), collisional broadening
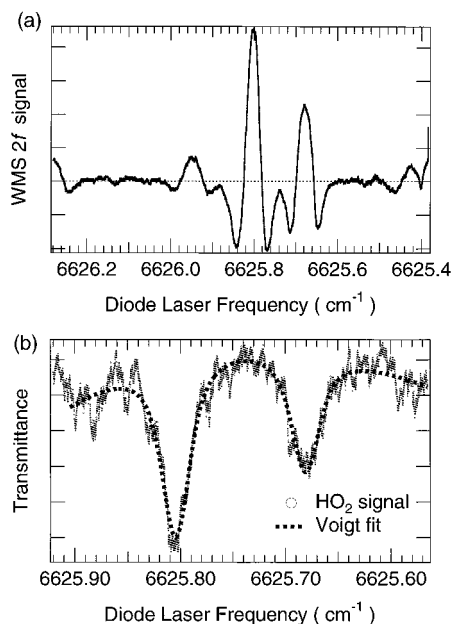
Fig. 2. Spectra of HO_2 formed by photolysis of $Cl_2/CH_3OH/O_2$ mixtures with (a) $2f$ WMS detection and (b) direct absorption. The acquisition conditions are identical. We used the Voigt fit (dashed curve) to the direct absorption lines to calibrate the $2f$ WMS signal for absolute HO_2 concentration measurements, using the line strengths of Ref. 17.

Fig. 3. Experimental time-resolved $2f$ WMS traces of HO_2, taken under the optimum detection phase setting for maximum $2f$ signal intensity. The insert shows a time-resolved direct absorption measurement with the probe laser tuned off the HO_2 absorption feature and indicates the extent of probe beam steering by the thermal lensing. The contribution of thermal-lensing noise at the modulation frequency is much smaller than for direct absorption and results almost exclusively from residual amplitude modulation.

contributes approximately 60% to the observed linewidth.

Photolysis of the $Cl_2/CH_3OH/O_2$ mixtures gives large $2f$ WMS signals at the $2\nu_1$ transition. Peak absorption of $\sim0.1\%$ at the 6625.8-cm^{-1} line is attainable under typical conditions (approximately 175 mTorr each of Cl_2 and O_2 and 250 mTorr CH_3OH at 50-Torr total pressure) with 75 mJ/pulse of 355-nm light. The detected $2f$ WMS signals show a signal-to-noise ratio of ~10 for single-shot detection. From the previously measured absorption line strengths of HO_2 at 6625.8 cm^{-1},[16,17] we calculate a minimum detectable concentration (single-shot signal-to-noise ratio of 1) of approximately 3×10^{13} HO_2 molecules cm^{-3} at 295 K. This performance corresponds to a minimum detectable absorbance of 5×10^{-4} in a 1-MHz detection bandwidth, or 5×10^{-7} in a 1-Hz detection bandwidth assuming a square-root improvement of the signal-to-noise ratio with increased signal-averaging time. This noise estimate does not include the contribution of the thermal-lensing noise transmitted through amplitude modulation of the probe laser intensity, which is shown for a direct absorption measurement in the insert of Fig. 3. Thermal lensing, which is an important noise source in many laser pump-probe experiments, is considerably reduced in WMS detection and contributes principally by way of residual amplitude modulation. The minimum detectable absorbance observed in the present time-resolved experiments is comparable to our previously reported mid-IR diode laser modula-
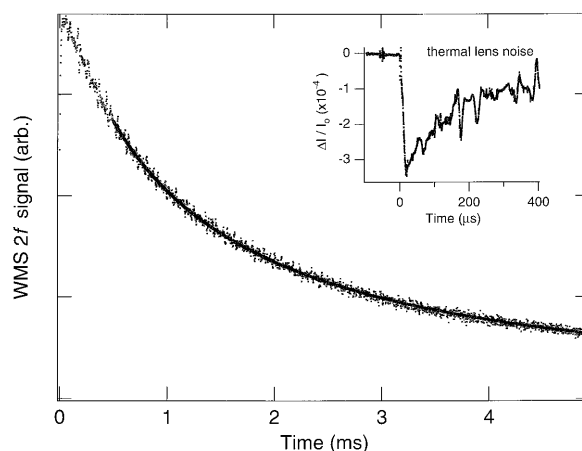
tion experiments[11,12] and is ~30 times the detector shot-noise limit.

3. Results and Discussion

This study demonstrates the utility of time-resolved $2f$ detection signal of WMS as a tool to study reaction kinetics, including second-order reactions. Although pseudo-first-order kinetic studies require measurement of only relative concentration, a second-order reaction kinetic study such as the HO_2 self-reaction requires absolute concentration measurements. Figure 3 shows a time-resolved $2f$ WMS signal detected at the optimum detection phase (i.e., the strongest $2f$ WMS signal). Use of such a time-resolved $2f$ WMS signal for kinetics studies also requires that the observed signal be related easily to the time-dependent concentration of the absorbing species. Once the $2f$ WMS signal is calibrated against a direct absorption spectrum at a given detection electronics setting (i.e., detection phase, modulation frequency, etc.), any drifts in the calibration factor will stem from (1) drifts in the diode laser output frequency or power that are due to temperature and injection current drift; and (2) drifts in experimental conditions such as total cell pressure, precursor gas flows and compositions, and the pump-probe beam overlap.

A direct absorption spectrum acquired immediately after a $2f$ WMS measurement under identical experimental conditions is used to calibrate the $2f$ signal level to the absorbance. The absorbance is then converted into absolute HO_2 concentration with the measured HO_2 line strength of Ref. 17 to calculate the peak cross section and the optical path length. The calibrated $2f$ WMS trace and several successive traces taken at varying $[Cl_2]$ are shown in
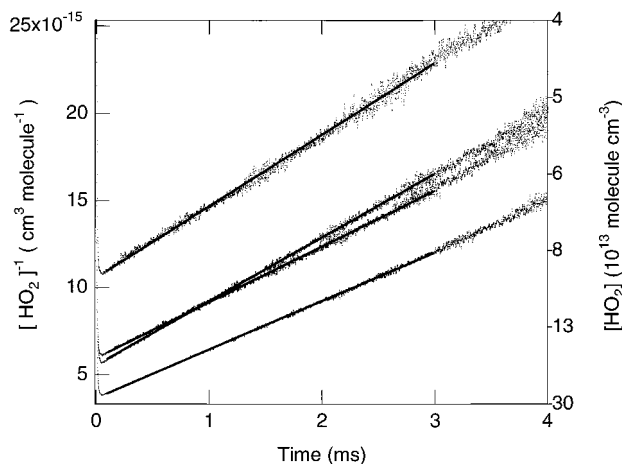
Fig. 4. Typical kinetic decay traces for HO_2 self-reaction, $[HO_2]^{-1}$ versus time, taken with calibrated $2f$ WMS detection with Cl_2 concentrations varied over a factor of 3. The initial HO_2 concentrations used in the rate constant determinations vary from 9×10^{13} to 7×10^{14} molecules cm^{-3} (not all traces are displayed in this figure). The average of the linear fits to $[HO_2]^{-1}$ versus time gives a second-order rate constant of $2.1 \pm 0.3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 293 K.

Fig. 4 in the form of a $1/[HO_2]$ versus time plot. The second-order rate constant obtained from the average of all these measurements is $2.1 \pm 0.3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} and is in reasonable agreement with literature values.[15,18,19] The recommended bimolecular and termolecular rate coefficients of the review of Atkinson *et al.* yields 1.8×10^{-12} cm^3 molecule^{-1} s^{-1} at 50 Torr and 295 K.[18] The current measurements are slightly higher than the recommended value. The fits to a second-order decay are quite good, and the stated error bars in the measured rate constant are indicative of the overall statistical experimental uncertainty. The major contribution to the statistical error in the rate coefficient determination is believed to be drifting of the center frequency of the diode laser output during ~45 min of data acquisitions, which is due to drifts in diode laser temperature and current. Other sources of error could include drift in the diode laser power and changes in the beam profiles or in the overlap between the photolysis and probe beams. Fluctuations in photolysis laser power or changes in reactant concentration should have a small effect on the rate constant determination, since we use a direct measurement of the radical concentration. No systematic variations in the measured rate constant with Cl_2 concentration or photolysis power were observed. It is known that nonuniform reactant concentrations cause an overestimate of second-order rate coefficients by absorption measurements,[20] but this effect should be much smaller than the present statistical uncertainty. The accuracy of the line strength of the HO_2 transition is estimated at approximately 20%, which could be an additional source of systematic error.

Unlike direct absorption detection following laser photolysis, where the probe beam attenuation that is due to time-dependent buildup of deposits on windows can be interpreted as a reduction in absorbance, WMS is sensitive only to spectrally structured absorption features. In addition, $2f$ WMS detection offers an inherent advantage of dual detection of both ac ($2f$) and dc ($\sim I_0$ in the optically thin limit) signals with the same detector for direct normalization of the $2f$ WMS signal. The effects of collisional broadening are important in the calibration of the $2f$ WMS signal under our conditions, and line broadening of course reduces the sensitivity of any transient absorption technique. Separate measurements of line shapes may be required for kinetic determinations at different pressures; analysis of complete line shapes also allows better reproducibility in concentration determination.[17] To improve time-resolved $2f$ WMS for second-order kinetics, diode laser frequency stabilization such as a line-locking technique[21] should be implemented to minimize the output frequency drifts. For now, our results indicate that a single calibration to a direct absorption signal suffices to give line-center concentration measurements of reasonable accuracy without external stabilization of the probe laser.

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