High-frequency wavelength modulation spectroscopy (WMS) has been applied to the detection of the hydroperoxyl radical (HO₂) in a laser photolysis and long-path absorption pump-probe kinetics reactor with a near-infrared distributed feedback diode laser. The HO₂ is formed by the 355-nm photolysis of Cl₂ in the presence of CH₃OH and O₂ and monitored by a phase-sensitive detection of the second-harmonic (2f) signal in the 2ν₁ 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 HO₂ 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 HO₂ self-reaction rate constant at 295 K. © 1997 Optical Society of America

1. Introduction

The hydroperoxyl radical (HO₂) is an important intermediate in hydrocarbon combustion with its critical role in the initiation of autoignition¹,² and in atmospheric chemistry.³ In combustion kinetics, studies of HO₂ reactions, where many important reactions are much slower than the self-reaction, a low HO₂ concentration is required. This requirement, in turn, calls for a sensitive means of detecting HO₂ with sufficient time resolution to yield kinetic parameters. Conventional optical detection methods have limited usefulness because the UV absorption spectrum of HO₂ 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 species⁷ 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 (~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 ~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 (I₀) 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.
and not by the WMS detection. We also note that HO₂ 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 HO₂ absorption lines are available. High-frequency WMS¹¹,¹² and FM¹³,¹⁴ 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 feedback diode laser operating at 1.5 μm using modulation of the injection current, and the laser is used to probe the HO₂ radical in the v₁ 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 HO₂ 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:

\[ \text{Cl}_2 \rightarrow 2\text{Cl}, \]
\[ \text{Cl} + \text{CH}_3\text{OH} \rightarrow \text{CH}_2\text{OH} + \text{HCl}, \quad (1) \]
\[ \text{CH}_2\text{OH} + \text{O}_2 \rightarrow \text{HO}_2 + \text{CH}_2\text{O}. \quad (2) \]

Rate constants for reactions (1) and (2) are 5.7 × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹ and 9.1 × 10⁻¹² cm³ molecule⁻¹ s⁻¹, respectively.¹⁵ Species concentrations are chosen so that production of HO₂ would be essentially complete before any reactions of HO₂ took place; specifically the contribution of Cl + HO₂ and CH₂OH + HO₂ reactions are minimized. However, measurements made at higher initial Cl concentrations, even where secondary reactions of intermediates with HO₂ are evident, give results for the HO₂ 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 CaF₂ windows. Flows of 1% Cl₂ in He, 10% O₂ in Ar, neat CH₃OH, and Ar buffer are controlled by mass flow controllers. Pressures are measured with a capacitance 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 Cl₂ 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 HO₂ are taken with a dc-coupled photodiode detector while the diode laser current is ramped slowly. We measured the transmitted power without HO₂ (I₀) 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 HO₂ 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 HO₂ 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 HO₂ 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
contributes approximately 60% to the observed line-width.

Photolysis of the Cl2/CH3OH/O2 mixtures gives large 2f WMS signals at the 2n1 transition. Peak absorption of ~0.1% at the 6625.8-cm⁻¹ line is attainable under typical conditions (approximately 175 mTorr each of Cl2 and O2 and 250 mTorr CH3OH 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 HO2 at 6625.8 cm⁻¹,16,17 we calculate a minimum detectable concentration ~ of approximately 3 × 10¹³ HO2 molecules cm⁻³ at 295 K. This performance corresponds to a minimum detectable absorbance of 5 × 10⁻⁹ 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-

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 HO2 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 HO2 concentration with the measured HO2 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 [Cl2] are shown in
The measured rate constant with Cl2 concentration or radical concentration. No systematic variations in tolysis and probe beams. Fluctuations in photolysis ture and current. Other sources of error could tions, which is due to drifts in diode laser tempera-
literature values. The recommended bimolec-
Atkinson 

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 acquisi-
tions, which is due to drifts in diode laser tempera-
ture 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 photo-
ysis and probe beams. Fluctuations in photolysis laser power or changes in reactant concentration should have a small effect on the rate constant determin-
tion, since we use a direct measurement of the radical concentration. No systematic variations in the measured rate constant with Cl2 concentration or photoysis power were observed. It is known that nonuniform reactant concentrations cause an overesti-
mate of second-order rate coefficients by absorption measurements, but this effect should be much smaller than the present statistical uncertainty. The accuracy of the line strength of the HO2 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 (–I0 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.

To improve time-resolved 2f WMS for second-order kinetics, diode laser frequency stabilization such as a line-locking technique 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 reason-
able accuracy without external stabilization of the probe laser.

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