



Contents lists available at ScienceDirect

Journal of Quantitative Spectroscopy & Radiative Transfer

journal homepage: www.elsevier.com/locate/jqsrt



Broad-linewidth laser absorption measurements of oxygen between 211 and 235 nm at high temperatures

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ARTICLE INFO

Article history:

Received 27 May 2011

Received in revised form

25 July 2011

Accepted 4 August 2011

Available online 11 August 2011

Keywords:

UV spectrum

High-temperature

Oxygen

Herzberg continuum

Schumann–Runge transition

ABSTRACT

Absorption coefficient data are presented for molecular oxygen at temperatures between 1100 and 2000 K and discrete wavelengths between 211 and 235 nm. Measurements were made behind reflected shock waves using broad-linewidth ultraviolet laser radiation generated from a frequency-quadrupled, tunable, pulsed Ti:Sapphire laser. Test mixtures consisting of 15% O₂, 15% He and balance Ar were used to minimize the influence of vibrational relaxation on the reflected shock temperature. The experimental results are in good agreement with theoretical calculations and confirm that discrete features from the Schumann–Runge system dominate between 211 and 235 nm at temperatures higher than 1100 K.

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1. Introduction

The study of combustion chemical kinetics has been greatly facilitated by the use of laser absorption diagnostics to measure species time-histories in shock tubes [1]. Through such measurements, such as OH monitored near 307 nm and H₂O near 2.5 μm, substantial progress has been made in the understanding of combustion reactions that are important at high temperatures ($T > 1200$ K) [2]. In contrast, shock tube/laser absorption studies of combustion reactions at intermediate temperatures (850–1200 K), where hydrocarbon ignition occurs under modern engine conditions [3], are much less extensive. This deficiency can be attributed mainly to the limited optical diagnostic methods available for detecting hydrogen peroxide (H₂O₂) and hydroperoxyl radical (HO₂), which play central roles in combustion kinetics at these intermediate

temperatures. Recently, however, a new approach has been proposed, using the broad-linewidth ultraviolet (UV) laser radiation generated from a frequency-quadrupled, tunable, high-pulse-repetition-rate Ti:Sapphire laser to investigate the chemistry of these radicals in shock tube experiments [Hong et al. to be published].

Much of the past work to study H₂O₂ and HO₂ reactions in shock tubes relied on absorption of H₂O₂ and HO₂ near 220 nm [4–9] where H₂O₂ and HO₂ have absorption coefficients on the order of 1–10 [atm⁻¹ cm⁻¹] [10–12]. H₂O₂ and HO₂ absorption features at visible and infrared wavelengths are much weaker. However, it is well-known that O₂ has absorption features in the UV, which includes Schumann–Runge transitions ($B^3\Sigma_u^- \leftarrow X^3\Sigma_g^-$) and Herzberg transitions I ($A^3\Sigma_u^+ \leftarrow X^3\Sigma_g^-$), II ($c^1\Sigma_u^- \leftarrow X^3\Sigma_g^-$), and III ($A^3\Delta_u \leftarrow X^3\Sigma_g^-$) in the spectral range 180–300 nm [13]. As a major combustion reactant, O₂ is typically present at significant concentrations. Therefore, it is essential to quantify absorption due to molecular oxygen at combustion temperatures in order to accurately interpret UV laser absorption data targeted at monitoring other species, and in particular, it is necessary to quantify this absorption when broad-linewidth laser radiation is used.

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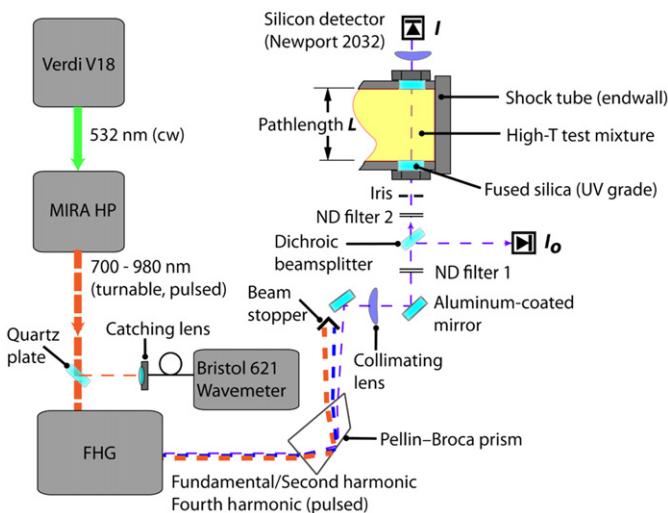


Fig. 1. Schematic of the laser setup.

Schumann–Runge and Herzberg I transitions have been the subject of numerous studies, for example, Refs. [13–36]. However, most previous studies focused on oxygen absorption coefficients at room temperatures or below, with only a few studies investigating UV oxygen absorption at high temperatures ($T > 1000$ K) [13–19]. The goal of this work is to provide high-temperature oxygen cross-section data for our broad-linewidth laser source in the 211–235 nm wavelength range.

2. Experimental setup

High-temperature test conditions were achieved in a shock tube behind reflected shock waves [37]. The stainless-steel shock tube utilized in the current studies was comprised of a 3.7 m driver section and a 10 m driven section, both of which have an inner diameter of 15.24 cm. Temperatures and pressures in the post-shock region were determined from the incident shock speed at the endwall using standard normal shock relations. The incident shock speed was measured using a series of piezoelectric pressure transducers over the last 1.5 m of the shock tube and linearly extrapolated to the endwall.

Before each experiment, the shock tube was turbo-molecular pumped to an ultimate pressure below 10^{-6} torr, with a leak and outgassing rate of $\sim 3 \times 10^{-6}$ torr/min. Mixtures were made manometrically using research-grade gases (99.999%) supplied by Praxair. Typical test mixtures used in the current study contained 15% He, 15% O₂, and balance Ar. Because of the relatively long vibrational relaxation time of O₂ in the presence of an argon carrier gas at the temperatures and pressures of the current experiments, helium was added to the test gas mixtures to shorten the vibrational relaxation time of the O₂ [38–42]. This ensured that the temperature assigned to each absorption cross-section measurement was for a thermally-equilibrated (vibrationally-relaxed) gas mixture.

Ultraviolet light was generated by quadrupling the frequency of near-infrared radiation from a pulsed

Ti:Sapphire laser as illustrated in Fig. 1. Stable mode-locking of the Ti:Sapphire laser (MIRA HP, Coherent Inc.) was achieved between 700 and 980 nm with a peak output of 1 W, a repetition rate of approximately 76 MHz, a pulse duration of approximately 2 picoseconds, and a Gaussian spectral profile with a typical FWHM of 1 nm. Ultraviolet light was stably generated by frequency conversion, using fourth harmonic generation (FHG, Coherent Inc.), to achieve output between 211 and 235 nm. The wavelength was determined from the fundamental using a Bristol 621 wavemeter, and the FWHM of the fourth harmonic light was calculated to be approximately 2 nm.

The reference beam (I_0) and the transmitted beam (I), which passed across the diameter of the shock tube at a location 2 cm from the shock tube endwall, were detected using silicon detectors (Newport 2032). Although the overall conversion rate from the fundamental wavelength to the fourth harmonic was 2–4%, the intense UV light was still destructive to the detectors. Neutral density filters were used to attenuate both the reference and signal beams to an average power of approximately 0.15 mW before they were measured by the silicon detectors with a bandwidth of 1 MHz. Owing to the high pulse repetition rate of the laser and the relatively lower bandwidth of the detector, the signal corresponds simply to average intensity or power.

The UV laser beam was guided to the shock tube test section in open air for a length of approximately 3 m. The absorption due to ambient oxygen is not a significant problem because the transmitted laser beam intensity I was always normalized by the reference beam intensity I_0 , measured just before entering the shock tube, as illustrated in Fig. 1. Any ambient oxygen absorption does not distort the spectral distribution of the laser beam, as oxygen absorption at room temperatures is a featureless continuum and only weakly depends on wavelength. Therefore, the laser beam was only weakly and uniformly attenuated by the ambient air around the laser wavelength.

3. Results and discussion

The absorption coefficient of O₂ at high temperatures was determined using the Beer–Lambert relation $-\ln(I/I^0) = \beta P_i L = \sigma N_i L = \alpha$, where α is the absorbance, β [cm⁻¹ atm⁻¹] is the absorption coefficient per atmosphere pressure, P_i [atm] and N_i [cm⁻³] are the partial pressure and number density of the absorbing species respectively, L [cm] is the pathlength, and σ is the absorption cross section per molecule [cm²].

It should be noted that calculating absorption cross section from experimentally determined laser absorbance using the Beer–Lambert relation is based on the assumption that light absorption can be linearly added over the laser linewidth. As narrow absorption lines within the Schumann–Runge band become significant at high temperatures, a nominal cross section calculated from Beer–Lambert relation underestimates the true integrated cross section, because the mixture may become optically thick at the center wavelengths of strong lines. To minimize the discrepancy between the true cross section and the nominal value inferred using the Beer–Lambert relation, all the experiments were performed in the optically thin regime with absorbances smaller than 0.3, similar to the work by Zabelinskii et al. [17] and by Bykova et al. [19]. Zabelinskii et al. [17] also reported that the cross sections measured in optically thick mixtures ($\alpha > 0.5$) were noticeably smaller than those obtained using optically thin mixtures.

A sample laser absorbance time-history at 211 nm is presented in Fig. 2. Two Schlieren spikes mark the arrival of the incident shock followed by arrival of the reflected shock at $t=0$. Before the arrival of the incident shock wave, the test gas mixture is at 295 K and 0.081 atm. Pre-shock absorption, if any, is due mainly to the weak Herzberg continuum I; here the absorption is very weak ($\sigma \approx 8 \times 10^{-24}$ [cm²] or $\beta \approx 2 \times 10^{-4}$ [atm⁻¹ cm⁻¹]) [31], and the absorbance $< 2.7 \times 10^{-5}$ is effectively zero.

Similarly, behind the incident shock wave (748 K and 0.57 atm) there is also negligible absorption.

The jump in laser absorbance at $t=0$ indicates the arrival of the reflected shock wave (1307 K and 2.2 atm). The gradual change in laser absorbance for the first 0.1 ms after the arrival of the reflected shock wave is a result of vibrational relaxation. The absorption coefficient was calculated using the mean laser absorbance after this change, between 0.1 and 2.0 ms. Using the Beer–Lambert relation, the oxygen absorption coefficient β was determined to be 0.021 [atm⁻¹ cm⁻¹] at 1307 K and 211 nm, or $\sigma = 3.8 \times 10^{-21}$ [cm²].

The variation in laser absorbance over 2 ms of test time was estimated to be $\pm 10\%$. In addition to the uncertainty in laser absorbance, another major source of uncertainty is temperature. The temperature uncertainty in test mixtures behind reflected shock waves was estimated to be ± 14 K, which includes 10 K uncertainty from shock speed determination and long-time variation over the entire test time [43], and 4 K uncertainty from vibrational relaxation. The temperature uncertainty leads to $\pm 12\%$ uncertainty in absorption cross section as it will be discussed later in the paper that it is a strong function of temperature. The overall uncertainty in absorption cross section was estimated to be $\pm 15\%$.

Similar experiments were repeated at temperatures between 1100 and 2000 K, and at discrete wavelengths between 211 and 235 nm, with an approximate step size of 4 nm. The results are summarized in Arrhenius form in Fig. 3, where the experimental data and best-fit lines are shown. The absorption experiments were all conducted at pressures near 2 atm.

The measured oxygen absorption coefficients can be compared to two recent experimental studies near these conditions: Zabelinskii et al. [17] and Bykova et al. [19], who both used D₂ lamp absorption. Fig. 4 shows a comparison of absorption cross sections from the present study at 211 nm with those of Zabelinskii et al. and

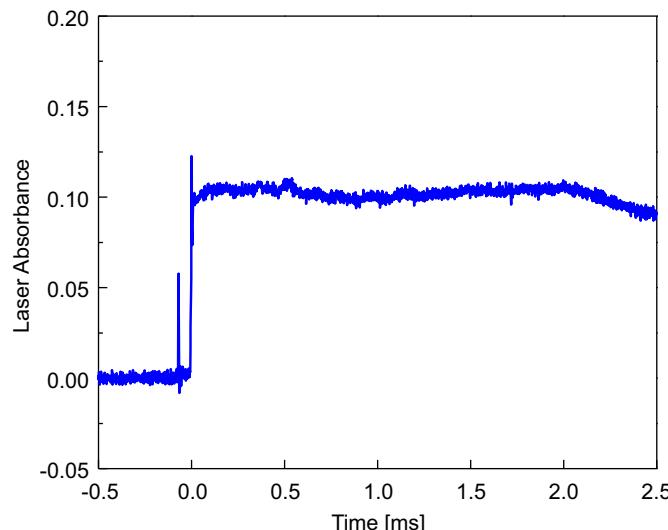


Fig. 2. Time-history of laser absorbance at 211 nm from a mixture of 15% O₂, 15% He, and balance Ar. The reflected shock conditions were 1307 K and 2.2 atm. The pathlength was 15.24 cm.

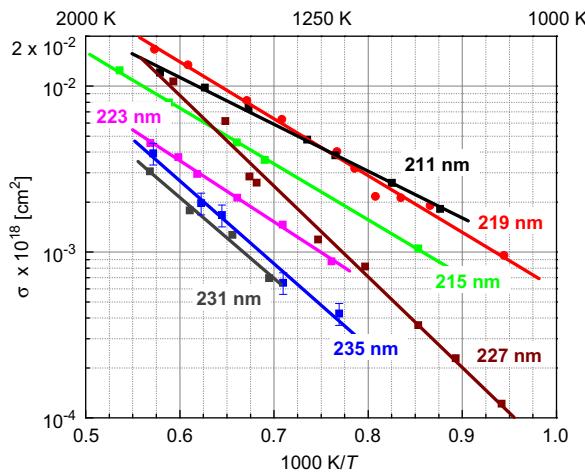


Fig. 3. Absorption coefficients of oxygen at wavelengths between 211 and 235 nm, temperatures between 1100 and 2000 K, pressures of approximately 2 atm. A test mixtures consisted of 15% O₂, 15% He, and balance Ar. Error bars are $\pm 15\%$.

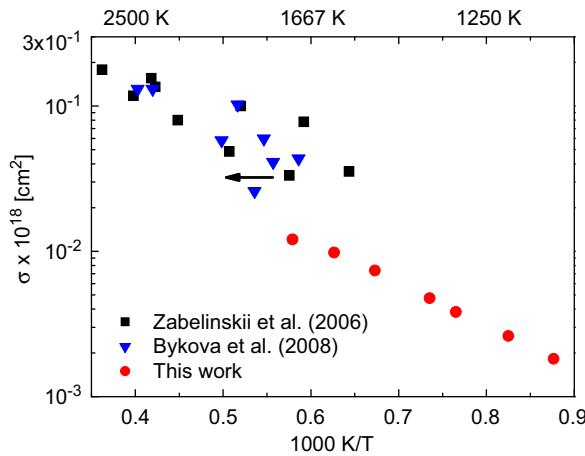


Fig. 4. A comparison of experimentally measured oxygen absorption cross-section σ at 211 nm between this work and earlier studies by Zabelinskii et al. [17] (210 nm) and by Bykova et al. [19] (210 nm).

Bykova et al. at 210 nm; significant differences with the present study are seen. In particular, larger scatter is seen with the two previous experimental data sets, and based on what is reported in the paper by Zabelinskii et al., the effects of vibrational relaxation were not accounted for in their measurements.

The temperature difference that arises from assuming thermally-equilibrated mixtures behind shock waves relative to vibrationally frozen mixtures is as high as 40 K even at Zabelinskii et al.'s lowest temperature. Given the short test time ($\sim 60 \mu\text{s}$) and test gas mixture (10% O₂ in Ar) used in their determination, the thermally frozen assumption may be a more accurate representation of the mixture conditions in their experiments. A corresponding correction would shift the data points of Zabelinskii et al. towards higher temperatures, as indicated by the arrow in Fig. 4, and in better agreement with the current data.

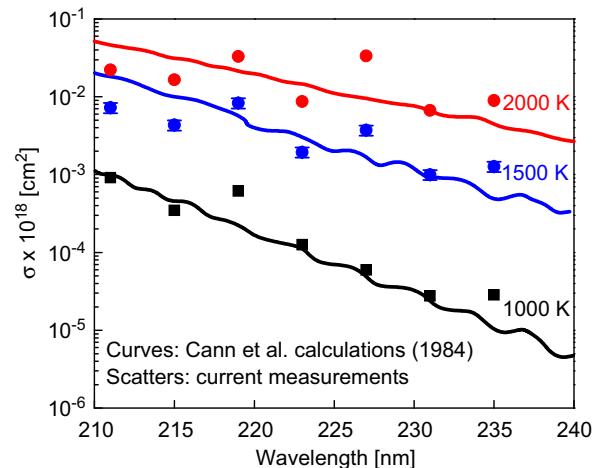


Fig. 5. A comparison between experimental results of this study (symbols) and theoretical calculations (solid lines) by Cann et al. [13]. Error bars (1500 K data) are $\pm 15\%$.

The theoretical predication by Cann et al. [13] can be compared to the experimental results of this study (Fig. 5). The experimental data at 1500 K were calculated using the best-fit lines in Fig. 3, whereas the data points at 1000 and 2000 K were estimated by extrapolating these linear best-fits. Good agreement in overall magnitude is found between the two studies. In the calculation by Cann et al. [13], a high-resolution (0.00048 nm at 1500 K), line-by-line summation was performed, which involved 21502 lines from Schumann–Runge transitions and 7518 transitions from Herzberg I transitions between 180 and 300 nm (at 1500 K). The published high-resolution spectra include degradation by a triangular instrument function of a full-width at half-maximum (FWHM) of 1 nm, similar to our laser linewidth.

In the calculated curves, ripples of small amplitudes are seen. As noted in Lee and Hanson [15], no absorption is expected from Schumann–Runge bands with $v''=0$ in the wavelength range of interest of the current study. As well, bands with $v''=1$ are at wavelengths shorter than approximately 209 nm and are hence not observable between 211 and 235 nm. Bands with $v''=2$ and higher, however, are observable at higher temperatures.

Due to the limitation of our measurement resolution, we are not able to resolve individual rotational lines. However, we were still able to observe some coarse band structures. These up-and-downs in absorption coefficient may be attributed to band structures with different v' values for the same v'' , or from bands of different v'' values. The calculations from Cann et al. [13] demonstrate similar behavior, but with smaller fluctuation amplitudes. The differences observed, at some wavelengths, are larger than our experimental error and are consistent at all temperatures for specific wavelengths, e.g. 219, 227 and 235 nm.

Pressure dependency of oxygen absorption coefficient has been repeatedly observed in measurements at temperatures near 300 K, which stems from the formation of oxygen dimer (O₂)₂. (O₂)₂ formation not only depends on

the partial pressure oxygen [27,28] but also on the partial pressures of other components in test mixtures [34,36]. However, the metastable oxygen dimer does not survive high temperatures as indicated by the study by Shadarnan [35]. At temperature above 1000 K, oxygen dimer is not expected to be present in our test mixture at any significant level, and the oxygen absorption coefficients are effectively pressure-independent at the temperatures of interest of the current study.

4. Conclusions

The absorption coefficients of molecular oxygen were measured behind reflected shock waves at wavelengths between 211 and 235 nm and temperatures between 1100 and 2000 K using a broad-linewidth UV laser. Accurate determination of the temperature of the test gas mixture was ensured using a He/Ar bath gas that minimized the influence of vibrational relaxation. The experimental results show good agreement in overall magnitude with the theoretical calculations of Cann et al. [13]. The data confirm that discrete features from Schumann–Runge system dominate between 211 and 235 nm at temperatures higher than 1100 K, whereas at room temperatures these features are too small to be observed. The availability of these data should facilitate use of broad-linewidth laser sources such as ours for absorption monitoring of H_2O_2 and HO_2 in the presence of O_2 , as may be found jointly in some combustion kinetics experiments.

Acknowledgement

This material is based upon work supported by the National Science Foundation under Grant no. 0964884.

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