

# Off-axis cavity ringdown measurements of trace iodine

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## Abstract

Off-axis cavity ringdown spectroscopy has been employed to measure trace levels of molecular iodine using continuum absorptions near 404 nm and 469 nm. Iodine concentrations ranging from 0 to  $2 \times 10^{12}$  molecules/cm<sup>3</sup> were accurately measured to within  $\pm 4\%$  and a measurement precision of  $7.8 \times 10^{11}$  molecules/(cm<sup>3</sup> Hz<sup>1/2</sup>) in a 1 cm pathlength was empirically determined. The system, which does not require calibration and works in a variety of background gases, should find utility in quantifying residual iodine in oxygen–iodine chemical lasers and flow tube experiments. © 2007 Elsevier B.V. All rights reserved.

**Keywords:** Molecular iodine; Off-axis cavity ringdown spectroscopy; COIL; EOIL; Oxygen–iodine laser

## 1. Introduction

Both the chemical oxygen–iodine laser (COIL) and the electric oxygen–iodine laser (EOIL) rely on dissociating molecular iodine (I<sub>2</sub>) to form I<sup>\*</sup>(<sup>2</sup>P<sub>1/2</sub>) atoms which then laser near 1315 nm. In the COIL, the mechanism of this dissociation involves energy transfer from O<sub>2</sub>(a<sup>1</sup>Δ<sub>g</sub>) and O<sub>2</sub>(b<sup>1</sup>Σ<sub>g</sub><sup>-</sup>) and is still not well-understood [1]. In the EOIL, this is further complicated by the presence of oxygen atoms [2] which rapidly react with I<sub>2</sub> to produce IO that subsequently dissociates into iodine atoms and O<sub>2</sub>. In order to improve laser performance and better understand the reaction mechanisms, a rapid and quantitative measurement of molecular iodine is required for oxygen–iodine laser and flow tube applications. Moreover, since I<sub>2</sub> is almost completely dissociated in the laser gas flow, the sensor must be capable of quantifying I<sub>2</sub> at very low trace levels.

Rawlins et al. [3] have developed a sensor that exploits optical absorption near 485 nm from I<sub>2</sub>(X) into a predissociative continuum. The instrument uses light from a filtered, broadband LED that is collimated through the sample and collected onto detector that is digitized with very high precision (20-bit). The amount of light absorbed is then directly proportional to the I<sub>2</sub> density via the Beer-Lambert Law, and the use of continuum absorption essentially eliminates dependencies on temperature and the I<sub>2</sub> internal state distribution. The analyzer was shown to have

a detection limit of  $6 \times 10^{11}$  molecules/(cm<sup>3</sup> Hz<sup>1/2</sup>) in a 5 cm long microwave discharge flow reactor, resulting in a reduced detection limit of  $3 \times 10^{12}$  molecules cm/(cm<sup>3</sup> Hz<sup>1/2</sup>) in a 1 cm optical pathlength.

A similar system was recently described by Mainuddin et al. [4] and demonstrated in an operating COIL flow. Filtered light ( $490 \pm 5$  nm) from tungsten halogen lamp was passed through the gas sample and focused onto a detector and the I<sub>2</sub> concentration was determined from the amount of light absorbed by the sample as described above. The system, whose primary purpose was to monitor the iodine feed line and not to detect trace I<sub>2</sub> levels, was extensively calibrated and shown to operate in a working COIL system.

The system presented here differs substantially from those described above. Foremost, the sample is enclosed in a high-finesse optical cavity and off-axis cavity ringdown spectroscopy is used to quantify the I<sub>2</sub> concentration. This greatly enhances the minimum detectable concentration and allows for accurate quantification of very low levels of I<sub>2</sub>. Moreover, unlike the devices described above, the analyzer utilizes two multiplexed wavelengths (e.g. 404 nm and 469 nm) to distinguish between I<sub>2</sub> continuum absorption and other optical losses (e.g. aerosol scattering).

## 2. Technical approach

The concentration of I<sub>2</sub> can be determined using absorption spectroscopy. The fractional amount of light absorbed after

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passing through the sample,  $A$ , is given by:

$$A = 1 - \exp(-\alpha L) \quad (1)$$

where  $L$  is the length (cm) of the sample and  $\alpha$  is the absorbance. The absorbance can be expressed as

$$\alpha = \sigma_{\text{ABS}} N_{\text{ABS}} + \sigma_{\text{AS}} N_{\text{AS}} + \sigma_{\text{RS}} N_{\text{RS}} \quad (2)$$

where  $N_{\text{ABS}}$  is the number density of absorbing  $\text{I}_2$  molecules (molecules/cm<sup>3</sup>) and  $\sigma_{\text{ABS}}$  is the frequency-dependent absorption cross-section (cm<sup>2</sup>/molecule), an intrinsic property of the molecule. Other factors can also contribute to the optical attenuation of the beam, including aerosol scattering (AS) and Rayleigh scattering (RS), and appropriate cross-sections and number densities for these scattering particles have been included in the equation. Note that, if absorption at a single frequency is monitored, it is impossible to distinguish between  $\text{I}_2$  absorption and other factors that occlude the light beam (e.g. aerosol or Rayleigh scattering).

The  $\text{I}_2$  absorption cross-section has been measured by various groups [5–8] and is shown in Fig. 1 for wavelengths <500 nm. At these wavelengths, the  $\text{I}_2$  absorptions represent transitions between the bound, ground state and predissociated continuum states. These transitions are especially attractive for  $\text{I}_2$  quantification because the fractional absorption does not depend on internal state distribution of the molecule, a quantity that is highly variable in the supersonic, reactive laser gas flow. Here, we use two lasers to measure absorptions at both 469 nm and 404 nm. The latter wavelength has minimal  $\text{I}_2$  absorption and is used to compensate for other optical losses (e.g. scattering).

For trace levels of  $\text{I}_2$ , the amount of light absorbed is very minimal and conventional absorption spectroscopy is inadequate. An attractive alternative involves using a high-finesse optical resonator to provide extraordinarily long effective optical path-lengths and using cavity ringdown spectroscopy [9] to quantify the absorption loss at a given wavelength. In cavity ringdown spectroscopy, the sample is bound by two highly reflective mirrors (e.g.  $R \sim 99.99\%$  typical) and laser light is coupled into the

optical cavity. In order to avoid complications due to cavity resonances, the light is non-resonantly coupled into the cavity in an off-axis fashion (off-axis cavity ringdown spectroscopy) [10].

Once the light intensity has attained steady-state, the laser is rapidly shut off and the light decays exponentially out of the cavity with a given time constant,  $\tau$ , that depends on the mirror reflectivity,  $R$ , the speed of light,  $c$ , and other losses in the sample:

$$\tau = \frac{L}{c(1 - R e^{-\alpha L})} \quad (3)$$

Note that, for a given  $R$ ,  $\tau$  is an absolute measure of optical loss in the sample and can therefore provide an accurate determination of  $\alpha$  without any external calibration. The optical extinction,  $\varepsilon$  in m<sup>-1</sup>, is directly related to the cavity ringdown time:

$$\varepsilon = \frac{1}{\tau c} \quad (4)$$

For small absorbances, the optical extinction can be expressed as

$$\varepsilon = \varepsilon_0 + \alpha \quad (5)$$

where  $\varepsilon_0 = 1/(\tau_0 c)$ , the empty cavity extinction in the absence of optical loss ( $\alpha = 0$ ), is inversely proportional to  $\tau_0$ , the cavity ringdown time in the absence of optical loss ( $\alpha = 0$ ). For many aerosol particles the scattering is relatively wavelength independent (e.g. Mie scattering), hence the dual-wavelength cavity ringdown system can be utilized to determine the  $\text{I}_2$  density by combining the equations above and canceling the effects due to aerosol scattering:

$$N_{\text{ABS}} = \frac{(\varepsilon^{469} - \varepsilon^{405}) - [(\varepsilon_0^{469} - \varepsilon_0^{405}) + (\sigma_{\text{RS}}^{469} - \sigma_{\text{RS}}^{405}) N_{\text{RS}}]}{\sigma_{\text{ABS}}^{469} - \sigma_{\text{ABS}}^{405}} \quad (6)$$

where the superscripts are the measurement wavelength (nm). For many oxygen–iodine gas flows, in which a relatively low pressure of helium is the dominant stream component, the Rayleigh scattering becomes negligible (e.g.  $\sigma_{\text{RS}} \sim 0$ ) and the equation is further simplified.

### 3. Experimental set-up

The experimental set-up is shown in Fig. 2. A gas cylinder of high-purity (Matheson Tri Gas) He,  $\text{N}_2$ , or  $\text{CO}_2$  is connected to two mass flow controllers (Omega Engineering, 0–1000 cm<sup>3</sup>/min, 0–10 cm<sup>3</sup>/min) that were independently calibrated to within  $\pm 1\%$ . The slower flow passes through a 375 ml Teflon vessel (Saville Corporation) containing 25 g of  $\text{I}_2$  that is held at 0 °C using an ice water bath. This saturated  $\text{I}_2$  stream, which contains  $(1.08 \pm 0.02) \times 10^{15}$  molecules/cm<sup>3</sup> of  $\text{I}_2$  [11–13], is then recombined with the faster flow to create a gas stream that can be varied in  $\text{I}_2$  concentration between 0 and  $3 \times 10^{13}$  molecules/cm<sup>3</sup>. The combined stream is flowed through a Teflon membrane filter to remove any residual particulates and assure good mixing between the gas streams.

A portion of this mixed gas stream ( $\sim 400$  cm<sup>3</sup>/min) is drawn into a 83 cm long high-finesse optical cavity bounded by two highly reflective mirrors (Los Gatos Research Incorporated) of

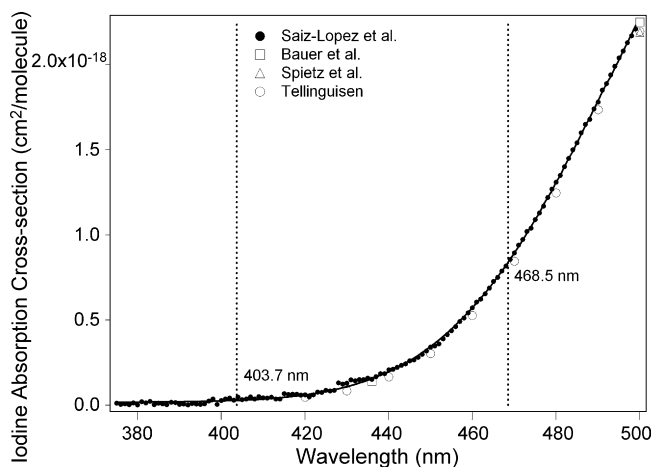


Fig. 1. Iodine ( $\text{I}_2$ ) absorption cross-section from 400 nm to 500 nm as measured by several groups. The recent data of Saiz-Lopez et al. was fit (solid black line) to a smooth function to determine the cross-sections at the probed wavelengths indicated by dashed lines.

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