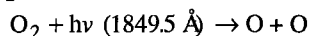
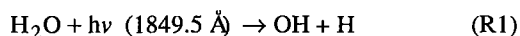


Comment on: "The measurement of tropospheric OH radicals by laser-induced fluorescence spectroscopy during the POPCORN field campaign" by Hofzumahaus *et al.* and "Intercomparison of tropospheric OH radical measurements by multiple folded long-path laser absorption and laser induced fluorescence" by Brauers *et al.*

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Calibration of laser induced fluorescence (LIF) instruments that measure OH is challenging because it is difficult to reliably introduce a known amount of this reactive radical into a measurement apparatus. In a recent paper, Hofzumahaus *et al.*, [1996] describe a novel and seemingly simple technique to accomplish this goal: they dissociate trace quantities of water vapor in air with a low pressure mercury (Hg) lamp to produce low concentrations (10^5 - 10^9 cm⁻³) of OH (R1). The lamp fluence is then calibrated by ozone actinometry (R2):



The OH concentration is inferred from the ambient water vapor and O₂ mixing ratios, the measured O₃ concentration, and the relevant cross sections:

$$[\text{OH}] = \frac{\sigma_{\text{H}_2\text{O}}[\text{H}_2\text{O}][\text{O}_3]}{2\sigma_{\text{O}_2}[\text{O}_2]}. \quad (\text{EQ1})$$

In Brauers *et al.*, [1996], an OH measurement calibrated with this technique was compared with an OH measurement by differential optical absorption spectroscopy (DOAS) [Dorn *et al.*, 1996]. Excellent agreement (within 1%) was obtained, leading the authors to conclude that the agreement "is even better than what is expected from the estimated accuracies (DOAS better than 7%, LIF 16% (1 σ))" [Brauers *et al.*, 1996]. This LIF calibration technique is also used by others and has been discussed in the literature [Aschmutat *et al.*, 1994, Reiner *et al.*, 1997, Schultz *et al.*, 1996].

Accurate absorption cross sections for O₂ and H₂O at the 1849.5 Å Hg emission wavelength are required to infer the OH density from the measured O₃ and H₂O concentration. In the studies described above the cross sections were taken from the literature: the H₂O cross section ($\sigma_{\text{H}_2\text{O}}$) from Hudson and Kieffer, [1975]; the oxygen cross section (σ_{O_2}) from Washida *et al.*, [1971]. The measurement by Washida *et al.* is difficult to interpret because the absorption coefficients are given in units of (atm⁻¹ × cm⁻¹) without discussion of base or temperature. The actual value is 2.2×10^{-20} cm²/molec (N. Washida personal communication, 1997). This is 2.3 times larger than the value used by Hofzumahaus *et al.*, [1996]. Thus, the agreement between the LIF and DOAS

measurements [Brauers *et al.*, 1996] appears to depend upon an erroneous O₂ cross section. This error translates directly into an error in the calibration of the LIF experiment (EQ1).

Because of the above discrepancy we measured the O₂ cross section using a pen ray Hg lamp with a flowing N₂ purge. We used a CsI photomultiplier tube (which is insensitive to the strong 2537 Å Hg line) equipped with an interference filter to measure the attenuation of the 1849.5 Å Hg line as a function of O₂ pressure. As we increased the optical depth, however, the calculated cross section decreased continuously. Similar behavior has been observed elsewhere [Cantrell *et al.*, 1997].

To investigate this further, we took a high resolution (0.013 Å) spectrum of the Hg lamp on the Harvard-Smithsonian 6.65 meter vacuum-ultraviolet spectrometer. Details of the experimental apparatus are given in Yoshino *et al.*, [1983]. The lamp was purged with N₂ for cooling and to prevent ozone formation. The spectrometer provides an absorption path ~1300 cm long. During the experiment we varied the amount of O₂ in the spectrometer, and the lamp operating conditions. Figure 1(a) shows an expanded portion of σ_{O_2} in the (8,0) Schumann-Runge (S-R) band [Yoshino *et al.*, 1992] superposed with the Hg lamp spectrum measured with the spectrometer evacuated. The spectrum shows that the pen ray lamp is not a line source. The transition is self-reversed, significantly broadened, and asymmetric, with a long tail to the red. The saturation effects observed are clearly understandable: σ_{O_2} is significantly higher for the portion of the lamp spectrum at shorter wavelength. This is illustrated in Figure 1(b). With the addition of $\sim 4.2 \times 10^{19}$ molec/cm² O₂ to the spectrometer (~1 torr), most of the attenuation is at the center of the S-R lines. Addition of $\sim 3.4 \times 10^{20}$ molec/cm² oxygen (about 8 torr) shows depletion of the lamp spectrum in the region of the S-R bands to essentially the dark count base line of the photomultiplier tube. However, absorption due to the unsaturated O₂ lines between 1849.5 Å and 1850.0 Å is still visible. Note that the absorption seen in the 1 torr data allows us to align the wavelength of the Hg lamp source with the oxygen absorption data of Yoshino *et al.*, [1992] to within 0.003 Å.

The effective O₂ cross section for the lamp is determined from the O₂ absorption spectrum of Yoshino *et al.*, [1992] weighted by the Hg emission spectrum observed at the spectrometer exit:

$$\sigma_{\text{O}_2}(\text{eff}) = \int I(\nu)\sigma_{\text{O}_2}(\nu)d\nu / \int I(\nu)d\nu. \quad (\text{EQ2})$$

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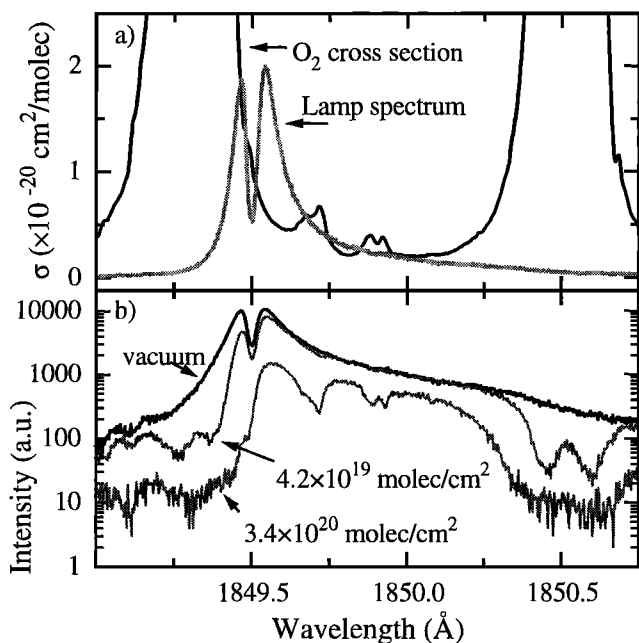


Figure 1. (a) Expanded portion of the oxygen absorption cross section [Yoshino *et al.*, 1992] superposed with the Hg spectrum measured with the spectrometer evacuated. (b) Spectrum for three different amounts of oxygen added to the spectrometer. The intensity is plotted on a log scale and the O_2 concentration shown as optical path (molec/cm^2).

$\sigma_{O_2(\text{eff})}$ depends on O_2 column and lamp operating conditions, which will change the Hg emission spectrum. In addition, any error in $\sigma_{O_2(\nu)}$ will translate directly into an error in $\sigma_{O_2(\text{eff})}$. These effects are shown in Figure 2.

The inset of Figure 2 illustrates the effect of lamp conditions on the observed spectrum. Additional cooling added to the Hg lamp (trace B) results in a reduction in spectral width by approximately 1/4 relative to the lamp with

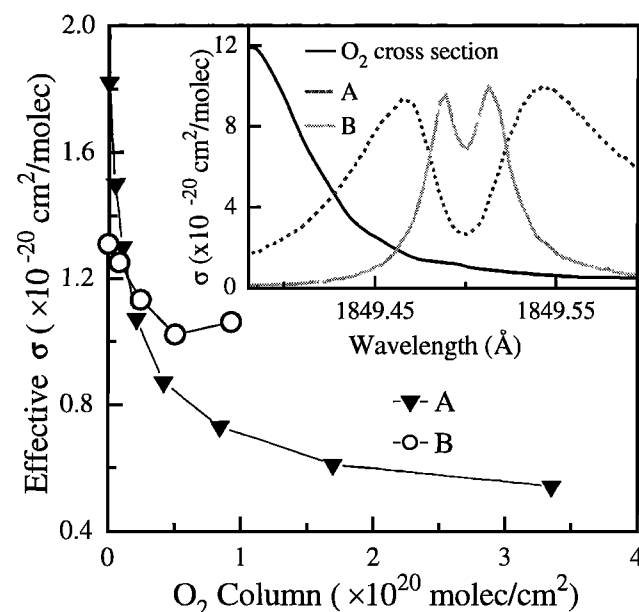


Figure 2. $\sigma_{O_2(\text{eff})}$ vs O_2 column abundance for two different Hg lamp operating characteristics (A and B). The inset shows the Hg spectra superposed on the O_2 absorption cross section [Yoshino *et al.*, 1992]. The narrower linewidth seen in (B) is from the lamp with the plasma voltage reduced by ~ 3 and the N_2 purge flow over the lamp dramatically increased relative to (A). The lamp intensity is in arbitrary units.

less cooling (A). As expected, the self reversal in B is also diminished. $\sigma_{O_2(\text{eff})}$ obtained with the lamp operating under condition A shows a variation of a factor of 3 between when the spectrometer was evacuated and when a 1.0×10^{20} molec/cm^2 O_2 optical path was present. $\sigma_{O_2(\text{eff})}$ measured with the Hg lamp operating under condition B shows a variation of 30% over the same range. In either case, it is clear that the use of a literature value for the oxygen cross section at 1849.5 Å is not appropriate for a pen ray lamp.

The effective cross section depends upon both the lamp conditions and the O_2 concentration between the lamp and the photolysis region. The lamp we used illustrates the general problem, and its characteristics may not be the same as lamps in other experiments. Thus, any attempt to determine an effective cross section using the results in Figure 2 is inappropriate; direct measurement of $\sigma_{O_2(\text{eff})}$ under field conditions is essential.

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