GEOPHYSICAL RESEARCH LETTERS, VOL. 24, NO. 23, PAGES 3039-3040, DECEMBER 1, 1997

Reply

A. Hofzumahaus, T. Brauers, U. Aschmutat, U. Brandenburger, H.-P. Dorn, M. Hausmann, M. Heßling, F. Holland, C. Plass-Dülmer, M. Sedlacek, M. Weber, and D. H. Ehhalt

Institut für Atmosphärische Chemie, Forschungszentrum Jülich, Jülich, Germany

In a recent paper by *Brauers et al.* [1996], we reported an OH intercomparison performed as part of the field campaign "POPCORN" in 1994. Two different OH instruments participated in the comparison, a laser spectrometer based on differential optical absorption spectroscopy (DOAS) [*Dorn et al.*, 1996], and a laser-induced fluorescence (LIF) instrument [*Hofzumahaus et al.*, 1996] which was calibrated by a photochemical OH source [*Aschmutat et al.*, 1994]. The OH concentration supplied by the calibration source is calculated; its value depends on the ratio σ_{H2O}/σ_{O2} of the absorption cross-sections of H_2O and O_2 at the 185 nm Hg-line. In their Comment, *Lanzendorf et al.* argue that our LIF calibration was based on a value for σ_{O2} which is too low by a factor 2.5 in apparent conflict with the good agreement found between the OH measurements by LIF and DOAS. Moreover, *Lanzendorf et al.* report new measurements showing that the effective σ_{O2} derived from Penray lamp emissions is not a constant, but can vary with experimental conditions. Their Comment raises several questions which we address in this paper.

1. How did we derive an apparently wrong O_2 absorption cross-section from the work of Washida et al. [1971] ?

For O_2 we used the effective absorption coefficient published by *Washida et al.* [1971]. They reported $\varepsilon = 0.236$ $cm^{-1}atm^{-1}$ at 184.9 nm for a mercury lamp and $\varepsilon = 0.0186$ $cm^{-1}atm^{-1}$ at 193.1 nm for a carbon lamp. As *Lanzendorf et al.* point out correctly, and this did not escape our notice, *Washida et al.* did not specify either base or temperature for their absorption coefficients. However in a comparison with literature, *Washida et al.* [1971] noted close agreement at 193.1 nm with the value (0.023 cm^{-1} at NTP) by *Watanabe et al.* [1953] who explicitly stated base e and 273 K. For this reason we naturally assumed that *Washida et al.* used the same convention, which is now in obvious disagreement with the private communication (base 10, 298K) by *Washida* [1997] quoted in *Lanzendorf et al.* Thus, we used an incorrect σ_{O2} (0.88×10^{-20} cm^2) a factor 2.5 smaller than the value (2.2×10^{-20} cm^2) *Washida et al.* [1971] had measured.

2. What is the correct σ_{O2} value for our LIF calibration?

In their Comment, *Lanzendorf et al.* present newly measured data of the effective O_2 absorption cross-section for Hg Penray lamp emission. They find that the effective σ_{O2} depends on the O_2 column and on lamp conditions, a behavior that was also observed in another study [*Cantrell et al.*, 1997].

Following these studies, we have measured specifically the effective σ_{O2} for our experimental conditions. In our LIF calibration device, synthetic air (at 1 atm) flows through a tube with an internal radius of 0.95 cm and is exposed to the radiation of a Hg Penray lamp. The light path between the lamp and the tube is constantly purged by a slow flow of N_2. After irradiation a small part of the central gas flow in the tube is sampled for calibration. Hence, we need to know the local effective σ_{O2} value in the photolysis region in the tube's centre, i.e. for lamp radiation that has passed an O_2 column of 4.9×10^{18} cm^{-2} (the amount between the inner wall and the centre of the flow tube). We have determined the local effective σ_{O2} value from measurements of apparent absorption cross-sections σ^*_{O2} of different O_2 columns (x) according to equations (1) and (3).

$$\sigma^*_{O2}(x) = (1 / x) \ln [I_0 / I(x)] \quad (1)$$

$$\sigma_{O2}(x) = - d [\ln I(x)] / dx \quad (2)$$

$$= \sigma^*_{O2}(x) + x [d\sigma^*_{O2}(x) / dx] \quad (3)$$

Here, I and I_0 denote the intensities of the lamp radiation after passing a 10 cm cell (with Suprasil windows) with and without absorbing gas, respectively. The radiation was detected by a combination of a CsI phototube and a 185nm interference filter (FWHM= 27.5 nm). σ^*_{O2} was measured as a function of O_2 pressure for seven Hg lamps in use in our laboratory all operated under the same experimental conditions as during LIF calibration. In all cases, σ^*_{O2} and the effective σ_{O2} were found to decrease linearly with increasing O_2 column in the range (1-9) $\times 10^{18}$ cm^{-2}. The effective σ_{O2} values for a given O_2 column are different for each lamp (Figure 1) and range between 1.1×10^{-20} cm^2 and 1.4×10^{-20} cm^2 for our calibration conditions (O_2 column = 4.9×10^{18} cm^{-2}). Our cross-sections and their O_2 column dependence are very similar to the results by Lanzendorf et al. at small O_2 columns ($< 1 \times 10^{19}$ cm^{-2}) (see Figure 1) and confirm that the effective σ_{O2} at the 184.95 nm Hg-line must be measured specifically for each experiment that uses ozone actinometry. Our measurements are considerably smaller than the value of 2.2×10^{-20} cm^2 by *Washida et al.* [1971] and closer to the old value we had used before. Note that the 194.23 nm Hg^+-line has a negligible influence on our results since measurements with a vacuum spectrometer (1 nm bandwidth) in our laboratory have shown that its intensity and effective O_2 absorption cross-section are smaller by two orders of magnitude, each.

3. Implications for our OH intercomparison 1994

The new values for σ_{O2} seem to call in question the good agreement of the OH concentrations measured by DOAS and LIF in 1994. We note, however, that the LIF calibration depends on the ratio σ_{H2O}/σ_{O2} of the absorption cross-sections of H_2O and O_2, and that there are also new measurements of σ_{H2O} with higher values than the one we used. The old H_2O absorption cross-section (5.5×10^{-20} cm^2 at 185 nm) in our

Paper number 97GL02947.
0094-8534/97/97GL-02947$05.00

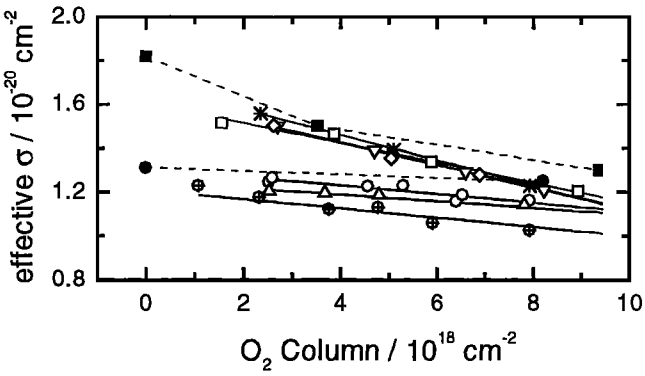

Figure 1. Local effective absorption cross-section σ_{O2} in the photolysis region vs. O_2 column between lamp and photolysis region. Open symbols represent the results for our seven Hg-Penray lamps, all operated under same conditions (15mA lamp current, in a slow flow of dry nitrogen). Filled squares and filled circles represent data from Figure 2 (case A and B, respectively) by Lanzendorf et al. for two different Hg lamp operating characteristics.

calibration is the one recommended by NASA/JPL [*De More et al.*, 1994]. Recently, *Yoshino et al.* [1996] published a new value of 1.0×10^{-19} cm^2 at 185 nm, while *Cantrell et al.* [1997] reported 7.14×10^{-20} cm^2 for the 184.95 nm Hg-line.

Since the three H_2O cross-sections differ considerably, we have also measured an H_2O cross-section with the experimental set-up described above and find a value of 7.0×10^{-20} cm^2 confirming the results by *Cantrell et al.* [1997]. This value is further supported by another recent study at MPI-Mainz (J. Crowley, private communication) yielding $\sigma_{H2O} = 7.3 \times 10^{-20}$ cm^2 for the Hg-line.

In the light of the new data, it appears that we used absorption cross-sections for H_2O and O_2 which were both considerably too low. In order to reevaluate the LIF calibration we need to calculate the ratio σ_{H2O}/σ_{O2} for the new cross-section data. Unfortunately, we have no knowledge which one of our Hg-lamps was used for calibration during POPCORN. Thus, any of the curves in Figure 1 could equally apply. Using the full range of the effective σ_{O2} in Figure 1 at an O_2 column of 4.9×10^{18} cm^{-2} and using $\sigma_{H2O} = 7.1 \times 10^{-20}$ cm^2 we calculate a new ratio σ_{H2O}/σ_{O2} between 5.1 and 6.5. The old value was 6.25. Depending on which Hg lamp we used for calibration, we now calculate the possible systematic deviation of LIF relative to DOAS to be between -18 % and +4 %.

The Comment by *Lanzendorf et al.* states that we claimed an "excellent agreement (within 1 %)". It is true that we found a linear correlation between DOAS and LIF with a regression line which had a slope of (1.01 ± 0.04) indicating very good agreement [see *Brauers et al.*, 1996]. However, it also should be noted that we specified two errors for the slope. The first, the 1σ statistical error of 0.04 is the result of the regression analysis and is caused by the random measurement errors of both OH instruments. The other is systematic and is due to the uncertainty (less than 7%) of the OH absorption cross-section [*Dorn et al.* 1995; *Hausmann et al.*, 1997] and the LIF calibration for which we estimated a total uncertainty of 16%, noting that this "does not contain the (unknown) contribution for σ_{O2}" [*Hofzumahaus et al.*, 1996].

4. How stable is the LIF calibration under field conditions?

The final aspect is the stability of the O_3 actinometer in the LIF calibration under field conditions. *Lanzendorf et al.* show that the effective σ_{O2} value depends not only on the O_2 column, but also on the lamp voltage, a behaviour that we have reproduced in our absorption experiments. During POPCORN the O_2 column and lamp current were kept constant in our calibration system. Under these conditions we observed a day-to-day variability of the measured O_3 in the calibration gas of 7% (1σ) which is partly due to the 4% measurement error of O_3. The small residual variability represents a conservative upper limit for changes of σ_{O2} in our experiment. This and the fact that we obtained good relative agreement between DOAS and LIF over the whole campaign demonstrates that the LIF calibration system has reliably traced instrumental changes in LIF detection sensitivity which were as large as a factor two [*Hofzumahaus et al.*, 1996].

References

Aschmutat, U., M. Heßling, F. Holland, and A. Hofzumahaus, A tunable source of hydroxyl (OH) and hydroperoxy (HO_2) radicals: In the range between 10^6 and 10^9 cm^{-3}, in *Physico-Chemical Behaviour of Atmospheric Pollutants*, edited by G. Angeletti and G. Restelli, 811-816, European Commission, Brussels, 1994.

Brauers et al., Intercomparison of tropospheric OH radical measurements by multiple folded long-path absorption and laser-induced fluorescence. *Geophys. Res. Lett. 23*, 2545-2548, 1996.

Cantrell, C. A., A. Zimmer, and G. S. Tyndall, Absorption cross sections for water vapor from 183 to 193nm, *Geophys. Res. Lett. 24*, 2195-2198, 1997.

De More et al., Chemical kinetics and photochemical data for use in stratospheric modeling, *NASA - JPL Publication 94-26*, 1994.

Dorn, H.-P., R. Neuroth, and A. Hofzumahaus, Investigation of OH absorption cross-sections of rotational transitions in the $A^2\Sigma^+$, v'=0 - $X^2\Pi$, v"=0 band under atmospheric conditions: Implications for tropospheric long-path absorption measurements, *J. Geophys. Res. D 100*, 7397-7409, 1995.

Dorn, H.-P., U. Brandenburger, T. Brauers, M. Hausmann, and D. H. Ehhalt, In-situ detection of tropospheric OH radicals by folded long-path laser absorption. Results from the POPCORN field campaign in August 1994, *Geophys. Res. Lett. 23*, 2537-2540, 1996.

Hausmann, M., U. Brandenburger, T. Brauers, and H.-P. Dorn, Detection of tropospheric OH radicals by long-path differential optical absorption spectroscopy: Experimental setup, accuracy and precision, *J. Geophys. Res. 102*, 16011-16022, 1997.

Hofzumahaus, A., U. Aschmutat, M. Heßling, F. Holland, and D. H. Ehhalt, The measurement of tropospheric OH radicals by laser-induced fluorescence spectroscopy during the POPCORN field campaign, *Geophys. Res. Lett. 23*, 2541-2544, 1996.

Lanzendorf et al., Comment on "The measurement of tropospheric OH radicals..." by Hofzumahaus et al. and "Intercomparison of tropospheric OH radical measurements..." by Brauers et al., *Geophys. Res. Lett.*, this issue, 1997.

Washida, N, Y. Mori, and I. Tanaka, Quantum yield of ozone formation from the photolysis of the oxygen molecule at 1849 and 1931 A, *J. Chem. Phys. 54*, 1119-1122, 1971.

Watanabe, K., E. C. Y. Inn, and M. Zelikoff, Absorption coefficients of oxygen in the vacuum ultraviolet, *J. Chem. Phys. 21*, 1026-1031, 1953.

Yoshino, K., J. R. Esmond, W. H. Parkinson, K. Ito, and T. Matsui, Absorption cross-section measurements of water vapor in the wavelength region 120 to 188 nm, *Chem. Phys. 211, 387-391*, 1996.

A. Hofzumahaus, T. Brauers, H.-P. Dorn, M. Hausmann, F. Holland, M. Sedlacek, M. Weber, and D. H. Ehhalt, Institut für Atmosphärische Chemie, Forschungszentrum Jülich, D-52425 Jülich, Germany. (e-mail: a.hofzumahaus@fz-juelich.de)

(Received May 5, 1997; revised October 1, 1997;
accepted October 8, 1997)