Atmos. Chem. Phys. Discuss., 7, S1651–S1659, 2007
www.atmos-chem-phys-discuss.net/7/S1651/2007/

Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on “Observations of OH and HO_2 radicals in coastal Antarctica” *by* W. J. Bloss et al.

W. J. Bloss et al.

Received and published: 8 May 2007

Observations of OH and HO2 Radicals in Coastal Antarctica W.J. Bloss, J.D. Lee, D.E. Heard, R.A. Salmon, S.J.-B. Bauguitte, H.K. Roscoe and A.E. Jones

Response to Comment by T. Brauers (Atmos. Chem. Phys. Discuss. 7, S828-S830, 2007)

We would like to thank Dr Brauers for his comments on the manuscript. We accept that the analysis of the HOx vs solar irradiance relationship is less comprehensive than it might have been, but feel that adding more detail on this aspect would overly extend what is already a lengthy manuscript presenting the experimental details, measured HOx concentrations and their correlations with other chemical species - it may well be that further treatment of this behaviour in a separate paper (following the various ex-

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

amples from the Jülich group) is warranted, beyond the points which can be addressed in this response. With regard to the specific points raised :

Technical details of j(O1D) measurements, accuracy and precision: The j(O1D) measurements were performed using a 2-pi spectral radiometer, periodically inverted to obtain upward flux. The instrument was located 50m from the LIF measurement site and CASLab, within the base clean air sector $>$1 km from other buildings, at a height of ca. 2 m above the snow. The spectral radiometer used in this study was supplied by MeteorologieConsult Gmbh (Jakel et al., 2007). The device uses a 512 pixels Hamamatsu diode array, mounted in a fixed grating monolithic monochromator Zeiss Multi-Channel Spectrometer, covering a 270 - 700 nm spectral range. The optical entrance slit was coupled to a 2-pi quartz collection dome, which was heat-traced to keep it free of riming throughout its Antarctic deployment. The spectral radiometer was calibrated periodically (in Antarctica) using a spectral irradiance standard consisting of a 1000 Watt quartz-halogen tungsten coiled-coil filament lamp model FEL-A, supplied by Optronics Laboratories, Inc. The standard was used at a distance of 50 cm from the quartz collection dome, and powered at 8.00 amperes (˜110 volts) using a Xantrex stabilised DC power supply. The lamp filament current was measured across a heat sink mounted high precision resistor (200 mOhm +/- 0.1%), and a high-precision multimeter. For the calibration current and distance specified above, the high-accuracy FEL-A lamp has a stated transfer uncertainty to the NIST scale of +/-1%.

The 2-pi radiometer was periodically inverted to obtain upward flux; details of the resulting albedo function will be presented in a separate manuscript in the ACP CHABLIS special issue (Jones et al.). For the j(O1D) values, temperature-dependent ozone absorption cross sections were taken from Burrows et al. (1999) (GOME flight model) while quantum yields were taken from Talukdar et al. (1998). The uncertainty in the quantum yield data has been estimated to be +/- 10 % (IUPAC evaluation - Atkinson et al., 2004) while the recent cross section measurements are within a few (+/- 3) percent of each other. The cross section and quantum yield data was utilised in 5 K bins, resulting in an uncertainty of ca. 1.5 % in addition to their individual uncertainties. Finally the error associated with the correction for scattered light within the instrument, which followed the method described by Edwards & Monks (2003), has been estimated to be 10 % for high solar zenith angles. Adding these factors in quadrature an uncertainty in conversion of the measured flux to j(O1D) value of 26 % is obtained, to which the uncertainty of the calibration source luminosity (for which the known contributors are small - see above) must be added. Overall an accuracy of the order of 20-25 % is estimated, similar to that obtained for a similar instrument in the IPMMI intercomparison (Hofzumahaus et al., 2004). Small gaps in the j(O1D) spectral radiometer coverage (arising from technical difficulties, less than 5% of the total, spread roughly evenly through SZA-space) were filled with data from a 2-pi filter radiometer, using an entirely empirical relationship established between the two instruments, at the site, as a function of solar zenith angle.

In terms of precision, we have looked at two representative clear-sky periods (min / max SZA during the summer measurement period covered in the paper). Over 30 x 10 s individual spectra (approximately corresponding to similar time coverage to the LIF 5 x 30 s average) the mean is 2.74e-5 s-1 with a standard deviation of 3.28e-8 and 1.03e-7 +/- 1.16e-9 s-1 for the high / low light cases respectively, i.e. the scatter on the j(O1D) measurement is of order 1 %, which is negligible in terms of Figure 5 of the paper.

Precision of the HOx measurements: The contribution of instrumental factors to the precision of the HOx measurements may be estimated from the variability in the offline signal recorded by the instrument. Over the course of a day (15 Jan 2005 was used for these tests), the mean standard deviation of the offline points contributing to each OH datapoint shown was 0.53 cts s-1 relative to a mean value of 12.2 cts s-1, corresponding to about 4.3 %. This is the same (fractional) precision as one obtains on average for the online points, for either OH or HO2, suggesting that the dominant sources of this uncertainty relate to the collection and counting of the signal, be that fluorescence, scattered laser light or scattered solar radiation (although little diurnal variation is apparent, as would be expected if transmitted 308 nm solar radiation were responsible). Irrespective of the cause, the statistical error of the measurement is around 5 % - thus the majority of the ordinate scatter apparent in Figure 5 is due to variations in OH levels, from day to day, at the same j(O1D) level. As discussed above, the scatter from the j(O1D) measurement is negligible.

Power-Law Relationship: The power-law relationship obtained for OH has been compared with other studies from this LIF instrument in Table 2 within the manuscript. With regard to the measurements mentioned in the comment, the following table expands that given, to include the relationship for our calculated OH levels (as shown in Figure 7 in the manuscript - note this is not strictly a “model” result in that no integrations are reported in this paper; rather it is a simple calculation) and other measured OH levels from the literature, including those mentioned in the comment.

X = a x { j(O1D) / 1e-5 s-1}ˆb + c

where X = OH / 1e5 molecule cm-3 or X = HO2 / 1e7 molecule cm-3.

This Work

1 Observed - Linear: a = 2.22; b = 1 (fixed); c = 0 (fixed)

2 Observed - Power: a = 3.89; b = 0.51; c = 0 (fixed)

3 Observed - Power/Intercept: a = 2.52; b = 0.74; c = 1.06

Calculated OH : a = 4.66; b = 0.63; c = 0

Literature Values

Brauers et al. (2001) ALBATROSS, Tropical Atlantic, a = 13.7; b = 1 (fixed); c = 0 (fixed)

Holland et al. (2003) BERLIOZ - Rural Germany, a = 20; b = 1 (fixed); c = 0 (fixed)

Smith et al. (2006) NAMBLEX, Mace Head, Ireland, a = 14.7; b = 0.84; c = 4.4

Rohrer & Berresheim (2006) Hohenpeissenberg Observatory, a = 24; b = 1; c = 1.3

Berresheim et al. (2003) MINOS (Coastal Crete), a = 72, b = 0.68, c = 1

Notes: Values from literature adapted to be in terms of OH/1e5 rather than OH/1e6 for consistency; BERLIOZ values estimated from figure in manuscript (values not given).

Several points are apparent from this table: Firstly, the parameter a, which can be thought of as roughly relating absolute solar intensity to OH levels, is much smaller for CHABLIS than for the other datasets. This is likely to reflect the much lower ozone levels ($<$10 ppb for Halley c.f. $>$30-50 ppb typical for the other sites) and lower absolute humidity (a factor of 3 - 5 lower than during NAMBLEX at Mace Head, for example), hence reduced OH production for a given ozone photolysis rate. The much larger value for the MINOS campaign in Crete likely reflects in part higher ozone levels (50 - 70 ppb) but mostly recycling of HO2 to OH, driven by NO levels of a few hundred ppt. Support for this comes from the reduction in the b-parameter - as Rohrer & Berresheim (2006) have discussed, the parameter a may be considered to reflect the dependence of OH upon precursor and co-reactant concentrations, such as O3, H2O and hydrocarbons, while the exponent b represents all the photolytic processes influencing OH, including j(NO2) and j(HCHO) amongst others, which reflect HO2 to OH conversion, and the intercept c allows for nighttime sources of OH. A value of b below unity broadly indicates greater secondary sources of OH, predominantly cycling via HO2. In the case of MINOS, the reduced value for b reflects HCHO photolysis and HO2 + NO; in the case of Mace Head (Smith et al., 2006) it reflects in part NO-driven and in part XO (IO or BrO)-driven HO2 to OH conversion, while in the present work (CHABLIS) it reflects largely XO-driven conversion with a smaller contribution from NO.

We might also expect b to be influenced by the overall HOx level - as the alternative fate for HO2 is peroxy-radical recombination, which displays a second order dependence upon HO2 + RO2, at lower overall HOx levels, the influence of a given level of XO or NO (i.e. its ability to convert HO2 to OH) is increased, which will be reflected in a lower value for b. In the case of the OH values shown in Figure 7 of the manuscript, i.e. those calculated using the steady-state expression (Scenario 3), the fit to measured j(O1D) returns a slightly higher value for a and a lower value for b than the measured data (power/intercept formula, 3), reflecting the fact that the calculation clearly overestimates the OH maxima. Interestingly the intercept c is found to be zero (within uncertainty) in this case, suggesting that the steady-state calculation fails to encompass the actual atmospheric processes responsible for the non-zero intercept in the real data - possibly this could be photolysis of HONO (present at levels significantly below those indicated by the soluble nitrite measurements) or hydrogen peroxide. Following from all of the above it is striking that the Hohenpeissenberg dataset is so well represented with a value of unity for b.

With regard to the use of (chi-squared) to compare the “goodness of fit” for the three versions of equation E3, in terms of increasing complexity (use of the parameters a, b and c), the values of (chi-squared) / DoF (ca. 3500 datapoints; 1-3 fitted parameters) are 8.34, 7.16 and 7.07 for options 1, 2 and 3 respectively, indicating a substantial improvement going from the linear (1) to the power (2) form of equation E3, and a small improvement in fit quality with inclusion of the intercept c (3).

Intercept in OH - j(O1D) plot: The non-zero intercept in the OH - j(O1D) relationship arises from photolytic OH production routes which have contributions from longer-wavelength photolysis than does jO(1D), for example, HCHO (followed by HO2 + NO and/or HO2 + XO), H2O2, potentially HONO (see however comments in the discussion) and HOI / HOBr. During the HOx measurement period at Halley, the conditions were never dark, to our human perception - thus while j(O1D) fell to 2.6 % of its maximum value at “night”, j(NO2) was always greater than 10% of its corresponding maximum, and j(HOBr) / j(HOI) would display still weaker SZA dependencies. As the O(1D)+H2O route only accounts for ca. 1/3 - 1/2 of overall HOx production during austral summer at Halley (Bloss et al., 2006), an intercept in a plot of OH vs. j(O1D) is to be expected in this environment. We also note that the occurrence of multiple OH / HOx production mechanisms, rather than the single O3 + hv; route, may contribute to the scatter in Figure 5 referred to above, i.e. broaden the range of OH levels which are observed for a given j(O1D).

As an aside, a non-zero intercept for OH - j(O1D) relationships should in principle be observed at all locations, as a consequence of “dark” mechanisms for HOx radical production, for example alkene ozonolysis and reactions of the nitrate radical, however these two mechanisms are not expected to be significant in this case - at observed ozone and alkene levels (ca. 10 ppb for O3, 30 ppt for ethane, 10 ppt for propene) OH production rates of 30 and 180 cm-3s-1 are calculated, far lower than the 1e5 - 1e6 cm-3s-1 resulting from photolytic routes. For NO3, our modeled NO3 ranges from 1e4 - 1e5 cm-3 (consistent with the failure to observe NO3 by DOAS, with a detection limit of ca. 20 - 30 ppt, (5 - 7) x 1e9 cm-3 - A. Saiz-Lopez, personal communication). To obtain OH production rates comparable with the lowest OH concentrations, ca. 10ˆ5 cm-3s-1, even assuming a fast rate coefficient of 1e-12 cm3 molecule-1 s-1 (NO3 + isoprene), unsaturated compound mixing ratios of 8 ppb or more are required - orders of magnitude higher than those observed (Read et al., 2007). Note that the intercept reported for this “clean” environment is more than an order of magnitude smaller than that observed in more polluted areas (e.g. 1.5e6 molecules cm-3 reported by Holland et al. (2003) during BERLIOZ).

The comment alludes to the performance of the LIF instrument at low OH, presumably a reference to the possibility of an interference signal within the system, arising from photolysis of ambient ozone and the subsequent reaction of O1D with H2O, and excitation of the resulting OH, within a single laser pulse. We observed no such artifact signal, above the detection limit (1.5 x 1e5 molecule cm 3), during tests in Antarctica, in which C3F6 was added to the sampled air to remove any OH. Calculations by Zeng et al. (1998) have shown that for 308 nm on-resonance LIF, the interference signal is estimated to be equivalent to 0.4 % of an assumed ambient level of 10ˆ6 molecule cm-3, for laser parameters broadly similar to those employed during CHABLIS, and ambient conditions of 50 ppb O3 and 40% RH. As the actual ozone levels were much lower (mean 9 ppb, max 16 ppb during the summer LIF measurement period), and the air much drier than at lower latitudes, the artifact signal is expected to be smaller during CHABLIS - we believe the non-zero OH intercept with j(O1D) to be a real feature of the atmosphere rather than an instrumental artifact.

References

Atkinson, R., Baulch, D.L., Cox, R.A., Crowley, J.N., Hampson, R.F., Hynes, R.G., Jenkin, M.E., Rossi, M.J. and Troe, J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume I - gas phase reactions of Ox, HOx, NOx and SOx species, Atmos. Chem. Phys., 4, 1461-1738, 2004.

Berresheim, H., Plass-Dülmer, C., Elste, T., Mihalopoulos, N. and Rohrer, F.: OH in the coastal boundary layer of Crete during MINOS: Measurements and relationship with ozone photolysis, Atmos. Chem. Phys., 3, 639-649, 2003.

Bloss, W.J., Lee, J.D., Heard, D.E., Salmon, R.A., Bauguitte, S.J.-B. and Jones, A.: Box model studies of radical levels during the CHABLIS campaign at Halley Base, Antarctica, Geophys. Res. Abstr., 8, 03328, 2006.

Brauers, T., Hausmann, M., Bister, A., Kraus, A. and Dorn, H.P.: OH radicals in the boundary layer of the Atlantic Ocean 1. Measurements by long-path laser absorption spectroscopy, J. Geophys. Res., 106, 7399-7414, 2001.

Burrows, J.P., Richter, A., Dehn, A., Deters, B., Himmelmann, S., Voigt, S. and Orphal, J.: Atmospheric remote sensing reference data from GOME: Part 2 temperature dependent absorption cross-sections of O3 in the 231-794 nm range, J. Quant. Spect. Rad. Trans. 61, 509-517, 1999.

Edwards, G.D. and Monks, P.S.: Performance of a single-monochromator diode array spectroradiometer for the determination of actinic flux and atmospheric photolysis frequencies, J. Geophys. Res. 108, doi:10.1029/2002JD002844, 2003.

Hofzumahaus, A. et al., Photolysis frequency of Oň3 to O(1D): Measurements and modeling during the International Photolysis Frequency Measurement and Modeling Intercomparison (IPMMI), J. Geophys. Res., 109, doi:10.1029/2003JD004333, 2004.

Holland, F., Hofzumahaus, A., Schäfer, R., Kraus, A. and Pätz, H.W.: Measurements of OH and HO2 radical concentrations and photolysis frequencies during BERLIOZ, J. Goephys. Res., 108 (D4), doi:10.1029/2001JD001393, 2003.

Jakel, E., Wendisch, M., Blumthaler, M., Schmitt, R., and Webb, A. R.: A CCD Spectroradiometer for Ultraviolet Actinic Radiation Measurements, J. Atmos. Oceanic. Tech. 24, 449-462, 2007.

Read, K. A., Lewis, A. C., Salmon, R. A., Jones, A. E. and Bauguitte, S.: OH and halogen atom influence on the variability of non-methane hydrocarbons in the Antarctic Boundary Layer, Tellus B, 59, 22-38, 2006.

Rohrer, F. and Berresheim, H.: Strong correlation between levels of tropospheric hydroxyl radicals and solar ultraviolet radiation, Nature, 442, 184-187, 2006.

Smith, S. C., Lee, J. D., Bloss, W. J., Johnson, G. P., Ingham, T., and Heard, D. E.: Concentrations of OH and HO2 radicals during NAMBLEX: Measurements and steady state analysis, Atmos. Chem. Phys., 6, 1435-1453, 2006.

Talukdar, R.K., Longfellow, C.A., Gilles, M.K. and Ravishankara, A.R.: Quantum yields of O(1D) in the photolysis of ozone between 289 and 329 nm as a function of temperature, Geophys. Res. Lett., 25, 143-146, 1998.

Zeng, G., Heard, D.E., Pilling, M.J. and Robertson, S.H.: A master equation study of laser-generated interference in the detection of hydroxyl radicals using laser-induced fluorescence, Geophys. Res. Lett., 25, 4497-4500, 1998.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 2893, 2007.