Short comment on Washenfelder et al. in AMTD

Ryan Thalman, Snow College, Richfield, UT, USA

Overall, some nice work on the part of the authors to combine a new light source development with untested wavelength/reflectivity ranges of highly reflective mirrors in an effort to sample formaldehyde, a key product of atmospheric oxidation processes.

General Comments:

Some discussion or comparison of the output of the laser-driven arc lamp with respect to LEDs or a conventional Xe-arc lamp would have been useful to illustrate how much this offers as an improvement over previously available light sources. Real numbers, even just in terms of absolute power (after filtration), wavelength coverage and light source stability without coupling to the cavity, would have been highly valuable to the community.

It is recommended that the most recent NO_2 cross-sections be used (Vandaele et al., 2002) rather than the old 1998 one.

It seems that every time anything is published using a broadband cavity enhanced instrument there is discussion about what to name the instrument and the technique. I appreciate that the authors have gone with a more generalized name (BBCES – BroadBand Cavity Enhanced Spectroscopy) as previous versions of the name were too specific to absorption (IBBCEAS or BBCEAS) when cavity enhanced instruments, due to the extremely long path lengths are measuring extinction (absorption + scattering). Techniques that exclusively use a differential fitting algorithm (DOAS), and not the classic cavity equations that depend on absolute intensity (Fiedler et al. 2003) can probably justify the DOAS tag, but by design the instruments are really extinction instruments and not pure absorption instruments (a good example of this is the various aerosol ring-down instruments which cannot measure the aerosol absorption (Pettersson et al., 2004). I suggest that the authors either keep the name as given, or add an extra E (BBCEES) for extinction if there is really a desire to specify what property is being measured using spectroscopy.

P. 9935 ln 25 – If mirror purges were not used for this design, what would the effect of adding mirror purges be on an actual field instrument (the stated goal of this work)? Also, there is no discussion of what the expected sampling losses might be and how to deal with them.

p. 9937 ln 15 – Here and in previous works the authors have stated empirical fit values for the Rayleigh scattering cross-sections of N_2. The work by Bodhaine et al. (1999) contains no data for N_2, only values for the scattering of air and the equations for calculating the King correction factor for N_2. The only way to get the relationships presented in this work as the calibration standard for N_2 is to fit the scattering cross-section calculated from theory (see equations in Bodhaine, Bates 1980 and Sneeps and Ubachs, 2005) using the refractive index of air and the King correction factor for N_2 (given in Bodhaine). The minimum error between the stated equation for the Rayleigh scattering given in the text and that calculated by theory (refractive index for N_2 and the King correction factor) is 4.5% in the range of interest. The values for O_2 have a minimum error of 10% over the range of interest. This has been discussed previously in the literature (Thalman et al. 2014) and the values for the calculated scattering cross-sections have been verified by measurement with cavity ring-down (N_2) and BBCES relative to N_2 (Air and O_2). Fits to the data of Shardanand and Rao (1977) also have issues because of the high uncertainty (~10%) of those measurements.

The effect of the bias of these cross-sections is as follows:

Using the values given in the paper, it is possible to calculate what the ratio of the spectra intensities for Air and He were in the calibration (at 25C and 630 Torr). The mirror reflectivity can then be recalculated using that ratio and the theory values for air. This yields a mirror reflectivity of 0.99922 instead of 0.99926 (at 330 nm).

If we then apply this further to the calculation of the concentrations of NO_2 at 330 nm, I calculate that the values reported in the paper are ~5% lower than they should be due to the use of the incorrect Rayleigh scattering cross-sections (for both the mirror calibration and for the calculation of the extinction (equation 1). This corrects the scale factor mentioned in the comparison to the cavity ring-down instrument (Section 4.2) to a slope of ~1.02 by removing the bias introduced by the choice of Rayleigh scattering cross-sections (assuming the retrieval only at a single wavelength for the sake of calculation, the actual bias will depend on the wavelength window selected for the fit and the change in the mirror reflectivity combined with the Rayleigh scattering over that range).

In previous publications by this group of co-authors on aerosol extinction (Washenfelder et al. 2013) this bias is likely accounted for in the calibration of the sample length with NO_2 when using mirror purges.

NOTE:

Below is the set of equations for common gases used in cavity instrument calibration (fixing typos in the table in Thalman et al. 2014)

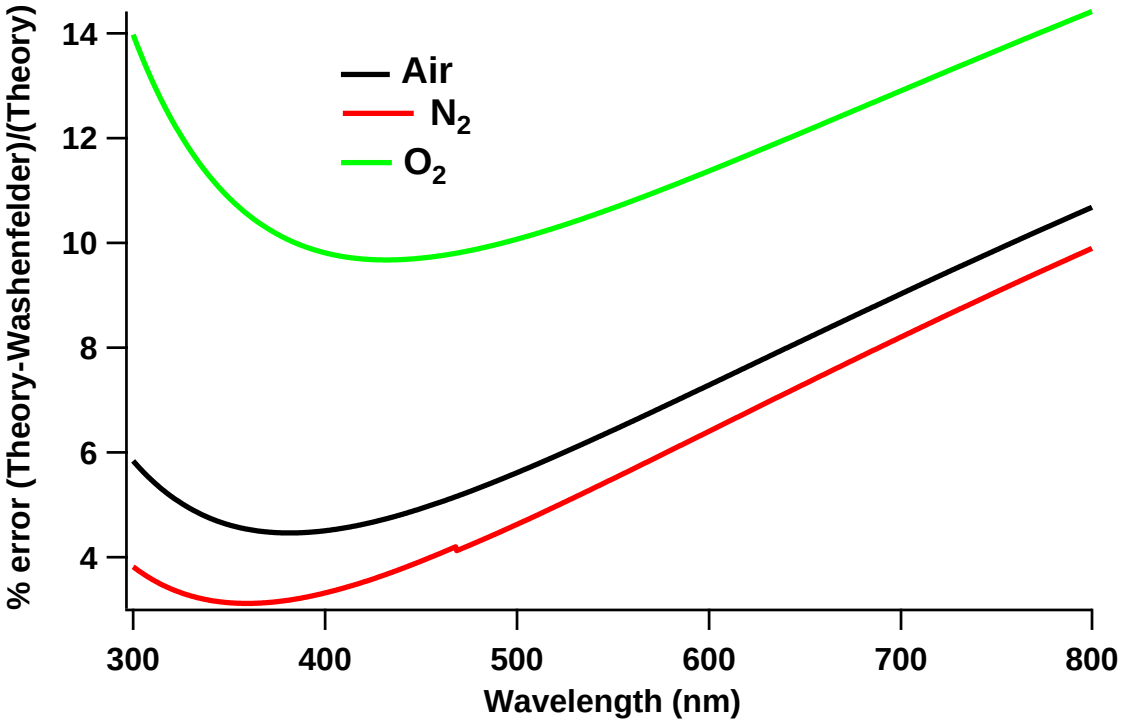
$$\sigma(\nu) = \frac{24\pi^3\nu^4}{N^2}\left(\frac{n_\nu^2-1}{n_\nu^2+2}\right)^2 F_k(\nu), \quad (1)$$

$$(n-1)\times 10^8 = A + \frac{B}{C-\nu^2} \quad (2)$$

Table 1: Terms for use in Equation 2 for the refractive index and for the King Correction Factor.

Gas	A	B	C	King Correction Factor	Ref.
He[a,b]	2283	1.8102×10^{13}	1.5342×10^{10}	$F_k(\nu) = 1$	11-13
N_2[a,c]	5677.465	318.81874×10^{12}	14.4×10^9	$F_k(\nu) = 1.034 + 3.17\times10^{-12}\,\nu^2$	5,9
N_2[a,d]	6498.2	307.4335×10^{12}	14.4×10^9	$F_k(\nu) = 1.034 + 3.17\times10^{-12}\,\nu^2$	5,9
Ar[a,e]	6432.135	286.06021×10^{12}	14.4×10^9	$F_k(\nu) = 1$	5,8
O_2[f,g]	20564.8	2.480899×10^{13}	4.09×10^9	$F_k(\nu) = 1.09 + 1.385\times10^{-11}\nu^2 + 1.448\times10^{-20}\nu^4$	5

[a] Use $N = 2.546899 \times 10^{19}$ molecules cm^{-3} in Eq. 1; [b] $14285 < \nu < 33333$ cm^{-1}; [c] $21360 < \nu < 39370$ cm^{-1}; [d] $4860 < \nu < 21360$ cm^{-1}; [e] $5000 < \nu < 33000$ cm^{-1}; [f] Use $N = 2.68678 \times 10^{19}$ molecules cm^{-3} in Eq. 1; [g] $18315 < \nu < 34722$ cm^{-1}.


% error (Theory-Washenfelder)/(Theory)
14
12
10
8
6
4
Air
N2
O2
300
400
500
600
700
800
Wavelength (nm)

References

Bates, D. R., Rayleigh-Scattering by Air, *Planetary and Space Science*, 1984, **32**(6), 785-790.

Bodhaine, B. A.; Wood, N. B.; Dutton, E. G.; Slusser, J. R., On Rayleigh Optical Depth Calculations, *J.Atmos.Oceanic Technol.*, 1999, **16**(11), 1854-1861.

Fiedler, S. E., Hese, A., and Ruth, A. A.: Incoherent broad-band cavity-enhanced absorption spectroscopy, Chem.Phys.Lett., 371, 284-294, 2003.

Pettersson, A.; Lovejoy, E. R.; Brock, C. A.; Brown, S. S.; Ravishankara, A. R., Measurement of aerosol optical extinction at 532 nm with pulsed cavity ring down spectroscopy, *J.Aerosol Sci.*, 2004, **35**(8), 995-1011.

Shardanand and Rao, A. D. P. "Absolute Rayleigh Scattering Cross Sections of Gases and Freons of Stratospheric Interest in the Visible and Ultraviolet Regions," NASA Technical Note D-8442, 1977.

Sneep, M.; Ubachs, W., Direct measurement of the Rayleigh scattering cross section in various gases, *J.Quant.Spectrosc.Radiat.Transfer*, 2005, **92**(3), 293-310.

Thalman, R., Zarzana, K. J., Tolbert, M. A., and Volkamer, R.: Rayleigh scattering cross-section measurements of nitrogen, argon, oxygen and air, J. Quant. Spectrosc. Radiat. Transfer, 147, 171-177, 2014.

Vandaele, A. C., Hermans, C., Fally, S., Carleer, M., Colin, R., Merienne, M. F., Jenouvrier, A., and Coquart, B.: High-resolution Fourier transform measurement of the NO2 visible and near-infared absorption cross sections: Temperature and pressure effects, J. Geophys. Res., 107, 4348, doi:10.1029/2001JD000971, 2002.

Washenfelder, R.A., Flores, J.M., Brock, C.A., Brown, S.S., Rudich, Y. Broad-band measurements of aerosol extinction in the ultraviolet spectral region. Atmos. Meas. Tech., 2013; 6(4):861–77.