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Cavity-enhanced absorption using an atomic line source: application to deep-UV measurements

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Optical cavities are commonly used to increase the sensitivity of absorption measurements, but have not been extensively used below 300 nm, mainly owing to the limited light sources at these wavelengths. While some progress has been made using cavity ring-down spectroscopy, these systems rely on complex and expensive lasers. Here we investigate an approach combining Cavity-Enhanced Absorption Spectroscopy (CEAS) with an inexpensive low vapour pressure mercury lamp for sensitive absorption measurements at 253.7 nm. We demonstrate that the CEAS absorption in our system is 50 times greater than the absorption found in a single-pass configuration; using this approach, we obtained limits of detection of 8.1 pptv (66 ng m^{-3}) for gaseous elemental mercury and 8.4 ppbv for ozone. We evaluate the performance of the system and discuss potential improvements and applications of this approach.

Absorption spectroscopy has long been a fundamental analytical tool and much effort has gone into increasing its sensitivity. The Beer-Lambert law governing absorption indicates two strategies for doing so. One approach is to improve the signal-to-noise ratio to discriminate smaller changes in intensity. The other method, and the focus of this report, is to lengthen the path of photons through the sample. Optical cavities, in which photons are reflected through the sample multiple times, are a particularly promising approach of effectively extending the pathlength and have found much recent application in the detection of trace gases.[1–3] Compared to earlier Herriott or White multipass cells, optical cavities generally require smaller sample volumes and have longer effective pathlengths through the sample. Cavity ring-down spectroscopy (CRDS), which measures the decay time of photons in the cavity, was the first technique to exploit optical cavities for absorption measurements.[4] CRDS systems attain very high sensitivity but have the drawback of a complex and expensive experimental system. A more straightforward approach is to directly measure the light intensity transmitted through the cavity, a technique variously known as cavity-enhanced absorption spectroscopy (CEAS)[5] or integrated cavity-output spectroscopy (ICOS).[6,7]

Because the cavity mirrors act as an efficient band rejection filter, it is desirable that the light source be extremely bright. Lasers are ideal in this respect, and a wide range of reliable, tuneable and affordable diode lasers is available with output at visible and near-IR wavelengths. Using such near-IR lasers, CEAS systems targeting vibrational overtone absorption bands have provided excellent selectivity and sensitivity to numerous small molecules, and devices for monitoring CH_4, CO_2, H_2O and other compounds are now commercially available. Impressively, off-axis ICOS is now fully competitive with traditional isotope ratio-MS for measuring H_2O isotope ratios.[8]

As yet, these inexpensive lasers do not extend below 300 nm to the deep-ultraviolet. Nevertheless, absorption measurements at these wavelengths are suited to a wide range of chemical and biological samples and applications. For instance, absorption detectors for liquid chromatography and other techniques target electronic transitions such as the $n \rightarrow \pi^*$ transitions of carbonyls and the strong $\pi \rightarrow \pi^*$ transitions of aromatic compounds. Although CRDS has been performed down to 197 nm,[9] and CEAS down to 308 nm,[10] the high power laser systems and non-linear processes used to generate deep-UV light are too costly and complex for widespread adoption. A robust and inexpensive light source is therefore required to extend the benefits of optical cavities to this spectral region.

In 2003, Fiedler and co-workers made an important conceptual advance by demonstrating that incoherent light sources can be used with optical cavities.[5] Several groups have subsequently used broadband light sources such as arc-lamps[5] and LEDs[11] for trace gas detection, and supercontinuum sources[12] for analysis of liquid samples.[13] To our knowledge, atomic line sources have not been used for cavities. As low vapour pressure mercury (Hg) lamps are known for the intense 253.7 nm emission line of Hg, corresponding to the $^3P_1 \rightarrow {}^1S_0$ transition, these lamps have practical potential as light sources for use with optical cavities.

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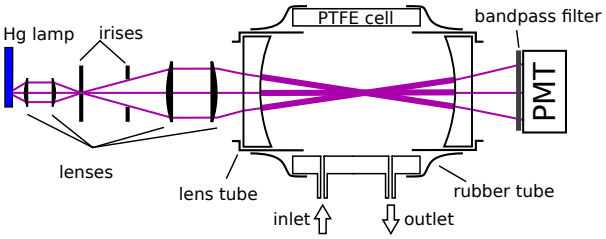


Fig. 1 Diagram of the atomic line CEAS system

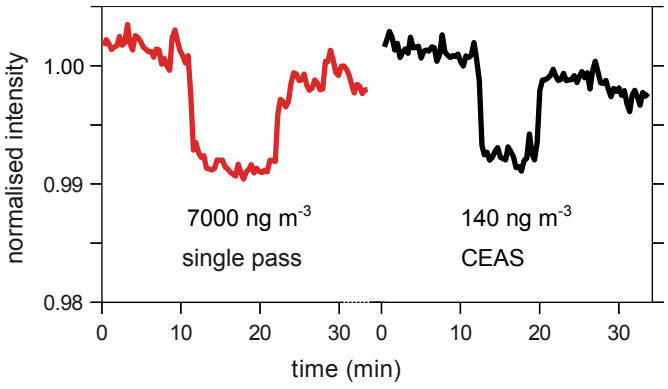
In this paper, we demonstrate the first use of a low vapour pressure Hg lamp as a robust and inexpensive light source for CEAS measurements at 253.7 nm. We show that a path-length enhancement of about two orders of magnitude over the single-pass configuration is achievable in a straightforward experimental configuration. The system is applied to measure the absorption of gaseous Hg and ozone (O_3), both important environmental pollutants. Potential improvements and limitations of the approach are discussed.

1 Experimental

Figure 1 shows a diagram of the setup. The output of a Hg-Ne pencil lamp (Oriel 6034) was focussed into an optical cavity formed by two dielectric mirrors (Laseroptik) separated by 252 mm. The cavity mirrors had a 200 mm radius-of-curvature and were approximately 98% reflective between 254 and 320 nm. These mirrors were housed in lens tubes held by mirror-mounts and sealed to the PTFE detection cell (i.d. = 33 mm, volume = 190 cm^3) with a thin rubber tube. Light transmitted through the cavity was measured using a CsTe photomultiplier tube (Hamamatsu H10784 with a C9744 pulse discriminator unit). The counter was a DAQ board (Measurement Computing USB-1208HS-4AO) read with a LabVIEW program every 5 s, and averaged over 10 s in post-processing. Other atomic emission lines and out-of-band wavelengths were removed by a Schott 254 nm bandpass filter. The intensity was adjusted with irises to around 3×10^6 counts over the 5 second interval, including the 10-fold downscaling by the discriminator.

One of the problems of diode laser CEAS is that cavity mode-structure must be removed, usually through averaging.[5,6] The free spectral range of our cavity was 595 MHz and we calculate that the 253.7 nm Hg emission line would excite around 30 longitudinal cavity modes as well as numerous transverse modes. No evidence of mode structure was observed in our experiments. The system was stable to knocks and vibration, but a drift of a few percent was observed over several hours, probably due to changes in the lamp output. Temperature and humidity were monitored with a Vaisala DM70 meter.

Fig. 2 Comparison of the intensity changes arising from different concentrations of Hg in the single pass and CEAS configurations.



2 Results and Discussion

When a beam is focussed into an optical cavity formed by mirrors with a reflectivity of R, the intensity of light transmitted through the cavity in the presence (I) and in the absence (I_0) of a single absorbing species are related:

$$N = \left(\frac{I_0 - I}{I}\right)\left(\frac{1-R}{d\sigma}\right) \qquad (1)$$

where d is the length of the cavity, N is the number density of molecules and σ is the absorption cross-section.[5] The enhancement factor — the increase in observed absorption over the single pass configuration — is defined for small absorptions as $(1-R)^{-1}$. For the mirrors used here ($R = 0.98$), an enhancement factor of approximately 50 is expected. To compare the cavity-enhanced and the single-pass absorption directly, the cavity mirrors were replaced by fused silica windows and the intensity was attenuated to a similar value to that found with the cavity to avoid saturating the PMT. As Figure 2 shows, in the CEAS configuration a moderate Hg concentration of 140 ng m^{-3} (equivalent to a mixing ratio of 18 pptv under ambient conditions) produces a comparable absorption to that by a much higher Hg concentration of 7000 ng m^{-3} in the single-pass setup. In this example, the cavity increases the fractional intensity change by around 30 – 50 times without affecting the baseline noise.

Calibration curves were produced for O_3 and Hg, to determine the enhancement factor more precisely. O_3 was introduced into a 2.2 m^3 atmospheric simulation chamber[14] with an Ozone Services O_3 generator. The chamber air was continuously extracted (600 cm^3 min^{-1}) to the CEAS cell and then to an O_3 monitor (2B Technologies model 202). We assumed that our cell was at atmospheric pressure. Figure 3 shows the intensity changes with varying concentrations of O_3 in the cell. At several times laboratory air was sampled

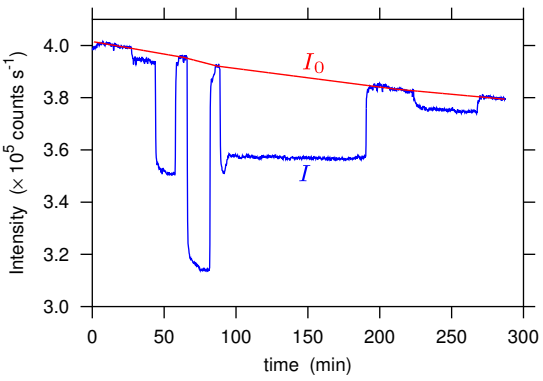


Fig. 3 Time profile of the CEAS intensity at different O_3 concentrations. The estimated baseline, I_0, is shown in red.

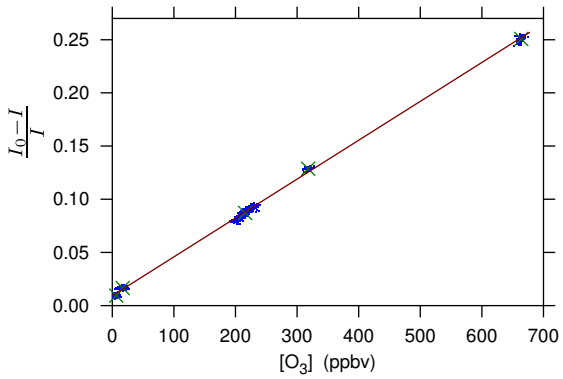


Fig. 4 Calibration curve of CEAS absorption against O_3 in a flowing sample stream. O_3 concentrations were measured using the commercial monitor.

through an O_3 scrubber to determine the baseline. The overall baseline, I_0, was estimated by linear interpolation, and shows that the lamp output decreased about 5% over a period of 5 hours. The CEAS absorption rose linearly with the O_3 mixing ratio (Pearson correlation coefficient $R_P^2 = 0.9995$, Figure 4). The slope of the linear regression through the centroid of each concentration cluster is proportional to the product of the O_3 absorption cross-section (1.15×10^{-17} cm^2 molecule^{-1} at 253.7 nm,[15]) and the enhancement factor. For our cavity the slope gives an enhancement factor of 50.5 ± 0.6, corresponding to a mirror reflectivity of 0.9802 ± 0.0003 at a relative humidity of 38.6%. The small non-zero intercept arose because air for the baseline was taken from outside the chamber where the humidity was slightly higher (40.6%). Water vapour adsorbed to the mirror coating reduces both the absorption and, to a lesser extent, the reflectivity of the mirror,[16] so that a change in humidity causes a change in cavity transmission. In the O_3 calibration the small difference resulted in the baseline signal (I_0) being too high. This is accounted for in the calibration as an offset equivalent to 25 ppbv O_3. Drying the mirrors with a flow of dehumidified air (0.4% RH) reduced the signal by 12%, corresponding to about 360 ppbv O_3. Many practical applications will require either the mirrors to be kept dry by heating, purging with dry gas (already common in atmospheric applications[1]) or a different mirror coating.

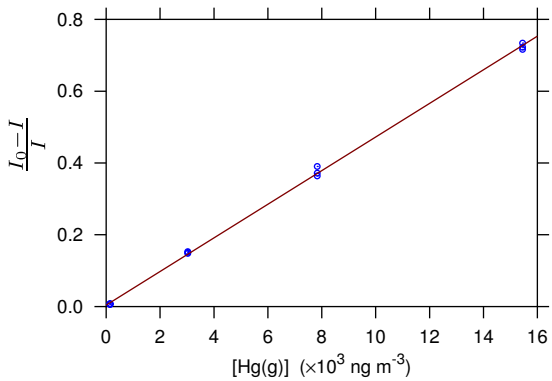


Fig. 5 Calibration curve of CEAS absorption against Hg vapour in a static cell. Hg concentrations were obtained from injections of known volumes of saturated vapour.

The calibration curve for Hg vapour was obtained by injecting aliquots of between 2 and 200 μL from an Hg containing vessel (thermally equilibrated with the room and the gas-tight syringe) into the static volume of the cavity. The Hg concentration was calculated from the Dumarey equation.[17] I and I_0 were estimated as previously. The relationship between the absorption and the concentration was again linear ($R_P^2 = 0.9993$, Figure 5). Radiation trapping and saturation effects by the Hg atoms were assumed to be negligible at the low concentrations and lamp intensities in these experiments, and no dependence of the absorption on the optical power was observed.

Using the enhancement factor from the O_3 calibration (50.5) gives an Hg cross-section of 1.23×10^{-14} cm^2 molec^{-1}. This value is instrumentally-defined because it depends on the precise overlap of the emission profile of the lamp and the pressure-broadened and pressure-shifted absorption of Hg in the sample cell. Nevertheless, this cross-section value is in fair agreement with prior measurements, although we note that there is a considerable spread in literature values.[18,19]

Based on the smallest detectable change in signal (around 0.003 at 3σ, Figure 2), the estimated limits of detection to Hg, O_3, and several other compounds are presented in Table 1.

Our detection limit for Hg in a single pass is 3300 ng m^{-3} compared to 66 ng m^{-3} in the cavity. Although Faïn *et al.*[19] have achieved a much better detection limit with cavity ring-down spectroscopy, they did so using powerful pulsed lasers and 99.895% mirror reflectivities. They attained a detection limit of about 0.10 ng m^{-3} in the same averaging time of 10 s.

Table 1 Estimated LOD of our system to several species based on their absorption cross-sections, obtained via the MPI Spectral Database [20]

Species	cross-section ($cm^2\,molec^{-1}$)	LOD ppbv	reference
mercury	1.2×10^{-14}	0.0081	this work
ozone	1.15×10^{-17}	8.4	[15]
xylene	5.9×10^{-19}	160	[21]
toluene	3.9×10^{-19}	250	[21]
benzene	2×10^{-19}	350	[21]
acetone	3×10^{-20}	3300	[22]

On the other hand, the CEAS detection limit is already better than commercial optical absorption based devices for monitoring elevated Hg levels (e.g., LOD = 100 ng m^{-3} for the Mercury Tracker 3000IP). Such commercial instruments use highly stabilised light sources and electronics, which our instrument does not. Nevertheless, our detection limit is significantly better than the 0.1 ppbv (800 ng m^{-3}) detection limit reported by Anderson *et al.* [23], using sum-frequency generation and two diode laser systems, or the 200 ng m^{-3} estimated by Thiebaud *et al.* [24] with a Hg vapour lamp combined with a UV LED. Both of these systems were designed for the high Hg levels of continuous emission monitoring and made use of additional spectral information to discriminate the absorption of Hg from background absorption. Finally, the CEAS approach could potentially be combined with Hg pre-concentration on a gold substrate to lower the detection limit to below average global atmospheric Hg concentrations (ca. 2 ng m^{-3}), as is currently done in Hg monitors based on cold vapour atomic fluorescence and atomic absorption spectroscopy.

Further applications include O_3 monitoring, acetone in breath analysis, and use as a nonspecific detector in chromatography. For O_3, the detection limits of the system are 420 ppbv (single pass) against 8.4 ppbv in the cavity. Commercial absorption instruments (such as our O_3 monitor, LOD = 3 ppb, 2σ) already attain this level of sensitivity in a single-pass measurement. The dual beam version of the same monitor (model 205) attains a LOD better than 1 ppbv, and therefore stands to improve its sensitivity using the cavity approach.

Acetone concentrations in breath are of interest as a biomarker for diabetes, lung cancer, dietary fat loss, congestive heart failure, and brain seizure. [25] The estimated limit of detection for acetone is higher than the range found in healthy breath (390 to 850 ppbv), but further improvements in sensitivity could make this approach practical for breath analysis. Other applications include detectors for chromatography, for which both CRDS [26,27] and CEAS [28] have previously been proposed. Although this work has focussed on gases, the approach is also feasible for liquid samples. In this case, scattering by the liquid limits the performance, although useful enhancements are still possible. [13]

These multiple applications of a single wavelength absorption measurement highlight the low specificity of the detector and the need to account for confounding absorptions. Possible strategies include pre-concentrating the target analyte or selectively removing or quantifying interferences at another wavelength or by other means, such as Zeeman correction or a deuterium lamp as in traditional AAS. In continuous emission monitoring, for example, a UV LED could be used to quantify the background absorption following the approach of Thiebaud *et al.* [24]. In some samples, interfering absorptions are likely to be negligible, as in breath analysis where acetone concentrations are much higher than other absorbing components of breath.

The sensitivity of the approach can be improved in a number of ways. Use of a heat-stabilised Hg electrodeless discharge lamp, which is significantly more stable than the pencil lamp used here, would improve the signal-to-noise ratio. Other straightforward solutions are to average for longer or to use longer cavities. [29] As our system sampling time is already around the minimum of the Allan deviation at 5 s, longer averaging is not advantageous. A more broadly applicable approach would be to use cavity mirrors of higher reflectivity. This is feasible for our system because it is still far from the shot-noise regime where the enhancement factor improves more modestly as $\sqrt{2/(1-R)}$. [13] Extremely high mirror reflectivities are probably not feasible in the deep-ultraviolet owing to increased scatter and absorption by the dielectric mirror coatings. The cavity mirrors in our system were fabricated using electron-beam evaporation coating because it produces less absorbing coatings than alternative methods. These coatings are, however, porous and sensitive to humidity changes as illustrated above. Incorporating features such as alternative mirror coatings, or heated or gas-purged mirrors in the system design, would minimise the issue. It is important to maintain the cleanliness of the mirrors and to calibrate the system periodically. Care is also necessary to reject unwanted wavelengths, particularly light outside the reflectivity range of the mirrors, which is transmitted very efficiently through the cavity.

In summary, this work demonstrates that CEAS is feasible with an atomic line source and greatly improves the absorption sensitivity over a single-pass configurations. The low vapour pressure Hg lamp allowed us to extend the approach into the deep-ultraviolet without requiring a complex laser system. The deep-UV wavelength region is particularly attractive for a number of compounds of environmental, analytical, and medical importance. The same approach is feasible with other atomic line sources, such as sodium vapour lamps and hollow cathode lamps, although alternative light sources should have a high radiance to offset the large losses to the op-

tical cavity. As our results with Hg demonstrate, the combination of an atomic line source with an optical cavity is useful for elemental analysis and may have potential to enhance the sensitivity of atomic absorption spectroscopy. Further improvements to the cavity sensitivity are possible, although some care is necessary to maintain a stable mirror reflectivity. Owing to poorer mirror reflectivities and to larger losses to Rayleigh scattering in the UV, the attainable sensitivity of this approach will not match the impressive sensitivities of optical cavities at longer wavelengths. Nonetheless, this work demonstrates a practical approach to exploit the large absorption enhancement of such cavities in the deep-UV.

References

1 S. S. Brown, H. Stark, S. J. Ciciora, R. J. McLaughlin and A. R. Ravishankara, *Rev. Sci. Instrum.*, 2002, **73**, 3291–3301.

2 T. Gherman, D. S. Venables, S. Vaughan, J. Orphal and A. A. Ruth, *Environ. Sci. Technol.*, 2007, **42**, 890–895.

3 O. J. Kennedy, B. Ouyang, J. M. Langridge, M. J. S. Daniels, S. Bauguitte, R. Freshwater, M. W. McLeod, C. Ironmonger, J. Sendall, O. Norris, R. Nightingale, S. M. Ball and R. L. Jones, *Atmos. Meas. Techniq.*, 2011, **4**, 1759–1776.

4 G. Berden, *Cavity ring-down spectroscopy: techniques and applications*, John Wiley and Sons, 2009.

5 S. E. Fiedler, A. Hese and A. A. Ruth, *Chem. Phys. Lett.*, 2003, **371**, 284–294.

6 R. Engeln, G. Berden, R. Peeters and G. Meijer, *Rev. Sci. Instrum.*, 1998, **69**, 3763.

7 A. O'Keefe, J. J. Scherer and J. B. Paul, *Chem. Phys. Lett.*, 1999, **307**, 343–349.

8 G. Lis, L. I. Wassenaar and M. J. Hendry, *Anal. Chem.*, 2007, **80**, 287–293.

9 M. Sneep, S. Hannemann, E. J. van Duijn and W. Ubachs, *Opt. Lett.*, 2004, **29**, 1378–1380.

10 G. Méjean, S. Kassi and D. Romanini, *Opt. Lett.*, 2008, **33**, 1231–1233.

11 S. M. Ball, J. M. Langridge and R. L. Jones, *Chem. Phys. Lett.*, 2004, **398**, 68–74.

12 S. Kiwanuka, T. Laurila and C. F. Kaminski, *Anal. Chem.*, 2010, **82**, 7498–7501.

13 S. E. Fiedler, A. Hese and A. A. Ruth, *Rev. Sci. Instrum.*, 2005, **76**, 023107.

14 E. Ashu-Ayem, U. Nitschke, C. Monahan, J. Chen, S. B. Darby, P. D. Smith, C. D. O'Dowd, D. B. Stengel and D. S. Venables, *Environ. Sci. Technol.*, submitted.

15 K. Bogumil, J. Orphal, T. Homann, S. Voigt, P. Spietz, O. Fleischmann, A. Vogel, M. Hartmann, H. Kromminga, H. Bovensmann, J. Frerick and J. Burrows, *J. Photochem. Photobiol., A*, 2003, **157**, 167–184.

16 P. Baumeister, *Optical coating technology*, SPIE Press, 2004.

17 R. Dumarey, R. J. C. Brown, W. T. Corns, A. S. Brown and P. B. Stockwell, *Accreditation and Quality Assurance*, 2010, **15**, 409–414.

18 D. L. Donohoue, D. Bauer and A. J. Hynes, *J. Phys. Chem. A*, 2005, **109**, 7732–7741.

19 X. Faïn, H. Moosmüller and D. Obrist, *Atmos. Chem. Phys.*, 2010, **10**, 2879–2892.

20 H. Keller-Rudek and G. K. Moortgat, *MPI-Mainz-UV-VIS Spectral Atlas of Gaseous Molecules*, www.atmosphere.mpg.de/spectral-atlas-mainz, 2012.

21 T. Etzkorn, B. Klotz, S. Sørensen, I. V. Patroescu, I. Barnes, K. H. Becker and U. Platt, *Atmos. Environ.*, 1999, **33**, 525–540.

22 J. D. Koch, J. Gronki and R. K. Hanson, *J. Quant. Spectrosc. Radiat. Transfer*, 2008, **109**, 2037–2044.

23 T. Anderson, J. Magnuson and R. Lucht, *Appl. Phys. B: Lasers Opt.*, 2007, **87**, 341353.

24 J. Thiebaud, M. J. Thomson, R. Mani, W. H. Morrow, E. A. Morris and C. Q. Jia, *Environ. Sci. Technol.*, 2009, **43**, 92949.

25 C. Wang and P. Sahay, *Sensors*, 2009, **9**, 8230–8262.

26 H. Waechter, K. Bescherer, C. J. Dürr, R. D. Oleschuk and H. Loock, *Anal. Chem.*, 2009, **81**, 9048–9054.

27 L. van der Sneppen, F. Ariese, C. Gooijer and W. Ubachs, *Ann. Rev. Anal. Chem.*, 2009, **2**, 13–35.

28 L. N. Seetohul, Z. Ali and M. Islam, *Anal. Chem.*, 2009, **81**, 4106–4112.

29 R. M. Varma, D. S. Venables, A. A. Ruth, U. Heitmann, E. Schlosser and S. Dixneuf, *Appl. Opt.*, 2009, **48**, B159–B171.