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Published in:
Optics Letters

DOI:
[10.1364/OL.7.000221](https://doi.org/10.1364/OL.7.000221)

1982

[Link to publication](#)

Citation for published version (APA):

Aldén, M., Edner, H., & Svanberg, S. (1982). Remote Measurement of Atmospheric Mercury Using Differential Absorption Lidar. *Optics Letters*, 7(5), 221-223. <https://doi.org/10.1364/OL.7.000221>

Total number of authors:
3

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Remote measurement of atmospheric mercury using differential absorption lidar

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Received January 4, 1982

Atomic mercury in the atmosphere was detected by the differential-absorption lidar technique. Laser light at the mercury resonance wavelength of 253.65 nm was generated by anti-Stokes shifting in H_2 of the frequency-doubled output from a Nd:YAG-pumped dye laser. The measurements demonstrate that a concentration of 4 ng/m³, corresponding to a typical background value, can be detected if a path length of 2×1 km is used.

Introduction

The first reported lidar measurements on atomic mercury in the atmosphere are given here. A differential-absorption lidar system was used on and close to the resonance transition of mercury at 253.65 nm ($6s^2 \ ^1S_0-6s6p \ ^3P_1$). The remote-sensing measurements were supported by laboratory absorption studies, and estimates of sensitivity and detection limits are given.

During recent years the sources, mechanisms of transport, transformations, and sinks of mercury in the environment have received considerable attention (see, e.g., Ref. 1). The toxic properties of mercury and its compounds are well known, and the expected increase in environmental mercury resulting from a more widespread use of coal for heating and power generation is a matter of increasing concern. Mercury is the only pollutant present as a free atom in the lower atmosphere, which makes it special with regard to detection by optical techniques. The background concentration of atomic mercury is about 2–6 ng/m³ and corresponds to 0.25–0.75 ppt by volume (1 ppt = 1:10¹²). Atomic vapor normally dominates over water-soluble mercury compounds. The latter are deposited in the water, in which methyl mercury is an important compound. In the global mercury cycle it is believed that mercury is reemitted into the atmosphere as atomic vapor.² Increased concentrations of atmospheric mercury are obtained locally from industrial activities, particularly chloralkali plant operation. Clearly, powerful measuring methods for mercury are of great interest in assessing the impact of anthropogenic mercury and for investigations of the global mercury cycle. Remote-sensing techniques offer unique possibilities for atmospheric monitoring, and in this Letter we show how these can be extended to atomic mercury.

Laser-radar techniques have been used for remote sensing of a large number of molecular atmospheric pollutants, especially NO₂, SO₂, and O₃ (for reviews see, e.g., Refs. 3 and 4). The technology in this field in some cases is approaching operational status.^{5,6} The preferred technique is the differential-absorption lidar approach (DIAL), in which the change in range-resolved

particle backscattering is monitored for on- and off-resonance wavelengths. Laser-induced fluorescence is less suitable for tropospheric use because of the strong collisional quenching of the fluorescence but is quite attractive for probing hydrospheric conditions.^{3,4} On the other hand, fluorescence is the best method for monitoring low concentrations of stratospheric atoms,^{7,8} as quenching is absent at such altitudes. The few emission lines of atoms as compared with molecules favor atomic over molecular fluorescence monitoring because of easier background rejection in narrow-band detection systems. In our experiments on mercury, absorption as well as fluorescence was observed. Because of the few electronic states in atoms compared with the multitude of rotational-vibrational levels in molecules, the sensitivity for atomic detection is favored by several orders of magnitude, of which we critically take advantage for monitoring of the extremely low atmospheric-mercury number densities.

Experimental Arrangement

A scheme of the setup used in the mercury experiments is shown in Fig. 1. We have used a frequency-doubled Quanta-Ray DCR-1A Nd:YAG laser, which produced 230-mJ pulses at 532 nm at a repetition rate of 10 Hz. The green beam pumped a Quanta-Ray PDL-1 tunable dye laser, yielding pulse energies of about 100 mJ with the dye rhodamine 6G. The linewidth was about 0.3 cm⁻¹ but could be narrowed to about 0.07 cm⁻¹ by using an intracavity étalon.

In order to reach the mercury absorption line at 253.65 nm, we tuned the dye laser to 567.06 nm and used a KD*P crystal to frequency-double the visible light to UV radiation at 283.54 nm. The angle tuning of the doubling crystal was servo controlled, which made it possible to make continuous UV-frequency scans.^{9,10} The tunable-laser output at 283.53 nm with a pulse energy of 25 mJ was directed into a Quanta-Ray RS-1 Raman shifter, operating with 8 atm of H₂. With a Raman shift in H₂ of 4155 cm⁻¹, the desired mercury wavelength, i.e., 253.65 nm, was reached by anti-Stokes shifting. The pulse energy in this first anti-Stokes

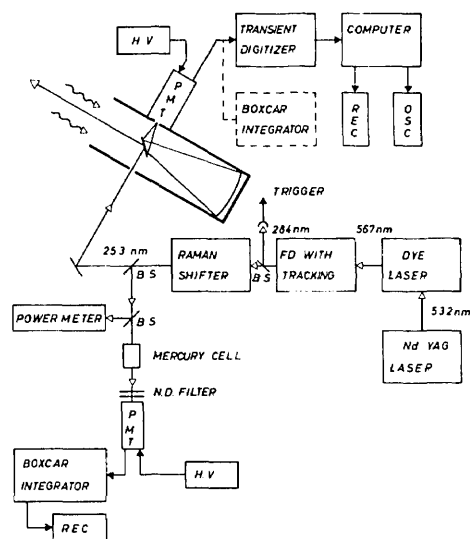


Fig. 1. Schematic diagram of the measurement system.

beam was typically 0.7 mJ. After the Raman shifter a quartz plate was inserted in the beam to split off a small part of the light for reference purposes. The main part of this light was directed into a power meter for setting a constant laser power, whereas a smaller part was directed through a reference cell containing atmospheric-pressure air and a droplet of mercury. The absorption from mercury in the reference beam served as our reference signal in all the subsequent measurements. The reference signal was detected with an EMI 6256 photomultiplier tube (PMT) and was processed with a PARC Model 162 boxcar integrator equipped with Model 165 gated integrators.

The main beam from the Raman shifter was sent into the atmosphere by using a Newtonian telescope with a 25-cm mirror and a focal length of 100 cm. The backscattered light was detected with an EMI 9558 QA PMT through an interference filter. No optimal filter was available, and the experiments reported here were performed with a filter of 20-nm full half-width and a transmission of 3%. The signal from the PMT was fed to a fast transient digitizer, Biomation 8100, which was used to convert the signal to time-resolved digital data. The transient digitizer was interfaced to a specially constructed computer, which averaged a large number of lidar curves. Further details of the lidar optical and electronic systems have been published.¹¹ In the frequency-scanning experiments the PMT signal was fed into one channel of the boxcar integrator, as indicated by the dashed line in Fig. 1, while the reference signal from the power meter was fed to the second channel.

Measurements

Measurements were made on absorption cells with various path lengths and different mercury-vapor pressures. The experiments yielded an absorption coefficient of $2.7[(\text{mg}/\text{m}^3)\text{m}]^{-1}$ with the laser linewidth achieved with the étalon in the dye laser. Vapor-pressure data from Ref. 12 were used. With an estimated detection limit of 2% absorption this indicates

a sensitivity of about $8(\mu\text{g}/\text{m}^3)\text{m}$, or an average concentration of $4 \text{ ng}/\text{m}^3$ over a path length of $2 \times 1 \text{ km}$. Whereas this is a typical background value, more than 10-times higher concentrations could occur close to chloralkali plants.

Remote detection of atomic mercury was made on a larger open chamber at a distance of about 100 m. The sample chamber had a path length of 2 m along the lidar direction and was open at each end. Three small vessels with mercury inside the chamber provided the mercury vapor. The openings could be closed, thus allowing the vapor pressure to increase before the measurements. The laser beam was directed through the chamber and backscattered light detected from either a target or the atmosphere behind the chamber. Figure 2 shows the signal versus wavelength when the boxcar integrator was gated to the echo from a board placed just behind the chamber. The relative absorption at the mercury line depended a great deal on how soon after the opening the measurement took place. A better stability of the mercury concentration could be achieved by using the closed back door as target.

The lidar approach was demonstrated to be quite feasible in this wavelength region. With only 0.2 mJ of output from the telescope a good atmospheric backscatter signal was registered out to 1–2 km with signal averaging during good atmospheric conditions. The range was, however, sensitive to haze and dust in the path. Figure 3 shows that the lidar curves in a DIAL measurement on the distant open-ended cell averaged over 50 laser shots. The on- and off-resonance wavelengths were 253.65 and 253.68 nm, respectively. The attenuation that is due to absorption in the chamber is clearly noticeable in the on-resonance curve and in the ratio curve. In this divided representation of the signal, the slope of the curve corresponds to the mercury content. The on-resonance curve also shows a peak before the attenuation, which is caused by resonance fluorescence from the mercury atoms. The peak at the beginning of each of the two curves comes from scattered light when the laser pulse emerges from the telescope, and it serves as a zero-time reference. The data in Figs. 2 and 3 were taken without the étalon, and simultaneous reference measurements in the laboratory indicate a mean concentration of $0.1 \text{ mg}/\text{m}^3$ in the chamber. This is, as expected with the open chamber used, much lower

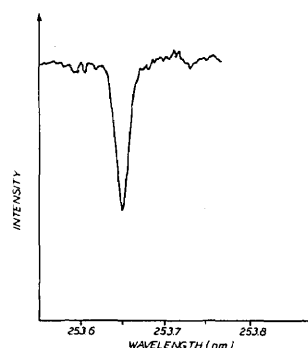


Fig. 2. Intensity of backscattered light versus wavelength from a fixed target behind a remotely positioned sample chamber.

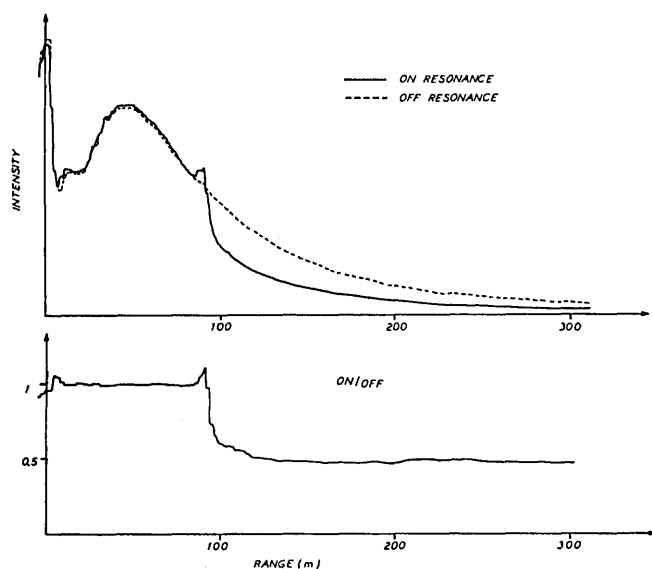


Fig. 3. A DIAL measurement of the mercury-vapor content in the distant chamber. The two upper curves show the intensity of atmospheric backscattering on and off mercury resonance, respectively; the lower curve displays the divided DIAL signal.

than the 4 mg/m^3 concentration calculated from a saturated-vapor pressure at the ambient temperature. With a better interference filter in the detection system and with high-reflectance mirrors in the beam-handling system, the signal intensity could be increased by a factor of 20.

Discussion

We have demonstrated the feasibility of measuring atmospheric mercury with the lidar technique. A detection limit of $8 (\mu\text{g/m}^3)\text{m}$ was achieved with a laser linewidth of about 0.15 cm^{-1} . The remote measurements were, however, performed without an étalon since the étalon reduced the pulse energies at 254 nm by a factor of 4. There are other methods for reaching the mercury absorption line than by using Raman shifting. One possibility is to double a coumarin-dye output directly, but the doubling has a poor efficiency in this wavelength region and we did not consider this approach. Yet another option would be to use frequency mixing of a doubled DCM-dye output and the residual $1.06\text{-}\mu\text{m}$ beam in another KD^*P crystal. This approach would probably not yield substantially higher pulse energies than we achieved and would also result in a larger linewidth without line narrowing of the Nd:YAG laser.

Remote monitoring of mercury using atmospheric backscattering is quite applicable to measurements of plumes, as simulated in our experiments. Typical levels of mercury at the outlet of a coal-fueled power-plant stack should be about $10 (\mu\text{g/m}^3)\text{m}$,¹³ resulting in a lidar-curve attenuation of about 2.5%. Corresponding values for refuse-destruction plants could be about 10

times higher. The range-resolved detection of low concentrations distributed over a longer path could be hampered by the occurrence of resonance fluorescence and has to be investigated more thoroughly. In this application the employment of a topographic target for average-concentration measurements should be a more useful method. We intend to do more specific field tests using the mobile lidar system,⁵ when comparisons with point monitors for mercury and its compounds will be made.

The authors are grateful to B. Nilsson and P. Norrman for assistance in the measurements.

Interesting communications with C. Brosset and B. Galle at the Swedish Water and Air Pollution Research Institute, Göteborg, are acknowledged.

This work was supported by the Swedish Board for Space Activities.

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