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Monitoring Cl<sub>2</sub> using a differential absorption lidar system

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The single-ended differential absorption lidar (DIAL) technique has proved to be a powerful method for remote measurements of source emissions and ambient air quality. DIAL systems working in the UV and visible spectral regions are often based on Nd:YAG and dye laser technology. The readily accessible molecules with such a system are H<sub>2</sub>O, NO<sub>2</sub>, SO<sub>2</sub>, and O<sub>3</sub>. In this Letter we report on the use of a DIAL system to test the remote sensing of Cl<sub>2</sub>.

The gaseous forms of chlorine most frequently encountered in polluted atmospheres include Cl<sub>2</sub>, HCl, and the readily accessible molecules with such a system are H<sub>2</sub>O, NO<sub>2</sub>, SO<sub>2</sub>, and O<sub>3</sub>. In this Letter we report on the use of a DIAL system to test the remote sensing of Cl<sub>2</sub>.

The readily accessible molecules with such a system are H<sub>2</sub>O, NO<sub>2</sub>, SO<sub>2</sub>, and O<sub>3</sub>. Except in the vicinity of major pollution sources, the atmospheric concentrations of the chlorine compounds are very low. Elemental chlorine Cl<sub>2</sub> is a heavy greenish-yellow colored gas with a strong pungent odor. It is very reactive and highly irritating to the mucous membranes. Cl<sub>2</sub> is widely used in, e.g., the chemical and plastics industries, water and sewage treatment plants, and swimming pools. Normal industrial emissions are not excessively high, but accidental releases of the gas, which is shipped in large barge and railroad tank car quantities, can be very dangerous to a community. This risk and acute toxicity of Cl<sub>2</sub> make the ability to monitor sensitively its presence in the atmosphere very important. A variety of point measuring Cl<sub>2</sub> monitors can be found on the market. A common method is to absorb the sample on a semiconductor detector. The diffusion of the gas in the detector gives rise to a current that is proportional to the concentration. The time constant is some seconds, and the sensitivity is 0.3–0.6 mg/m<sup>3</sup>. Many other gases (NH<sub>3</sub>, NO<sub>x</sub>, SO<sub>2</sub>, etc) may interfere, and some monitors provide a scrubber to remove the interference. Another method is to dissolve the sample in a liquid and determine the concentration with a colorimeter. Here a reference cell is needed. For liquids containing chlorine a third measurement possibility exists. It is based on the reaction of chlorine with iodide, producing iodine, and the sensitivity is 0.003 mg/m<sup>3</sup>.

The DIAL measurements were made with a mobile lidar system constructed in 1979. This system has been presented in detail. The laser source consists of a Nd:YAG laser and a dye laser. The wavelength of the dye laser is calibrated using an optogalvanic method based on a hollow-cathode discharge lamp filled with neon. Results from the detected lines (5–7) are fitted using linear regression, and the correct grating position for the desired wavelengths is then calculated.

The dye laser output is frequency-doubled with two KD*P crystals, one for each of the two wavelengths in the DIAL measurement, and the beam is directed into the atmosphere using two right-angle prisms and a large plane mirror. The mirror can be rotated around two axes and thus determines the direction of the outgoing beam. The same mirror reflects the backscattered light to a 30-cm diam Newtonian telescope. An interference filter selects the proper wavelength, and the light is detected by a photomultiplier. The signal is digitized by a transient recorder with a 100-MHz sampling frequency. Signal averaging takes place in a multi-channel memory, and the results are finally stored on computer disks. A computer controls laser triggering, wavelength settings, and beam steering during a measurement. In the Cl<sub>2</sub> experiments the dye laser was operated with rhodamine 640 at wavelengths around 605 nm. The dye solution was tuned to a maximum at these wavelengths by adding some sulfuric acid. The dye tuning broadens the peak of the dye, which was favorable in these measurements. At the desired UV wavelengths the output energy was ~2 mJ.

The Cl<sub>2</sub> molecule has a broad absorption profile extending from 250 to 430 nm with the peak at 328 nm with no significant structure. The continuum is usually attributed to transitions from the ground state (1Σ<sub>u</sub><sup>-</sup>) to a repulsive (1Π<sub>u</sub>) state. The maximum absorption cross section at 328 nm is σ<sub>a</sub> = 2.7 × 10<sup>-23</sup> m<sup>2</sup> at room temperature. To obtain a large differential absorption cross section the two DIAL wavelengths must be as far apart as possible on the slope of the absorption profile. With the rhodamine 640 dye a wavelength difference of up to 10 nm could be obtained in the UV region with sufficient output power. The investigated region was 298–308 nm yielding a maximum differential absorption cross section Δσ<sub>a</sub> = 7.5 × 10<sup>-24</sup> m<sup>2</sup> estimated from Ref. 5. To make sure that there are no finer details in the spectrum, the dye laser was scanned in the 298–308-nm region, and the absorption spectrum was recorded through a 30-cm quartz cell filled with a Cl<sub>2</sub>/N<sub>2</sub> reference gas. Figure 1 shows the spectrum obtained with a laser linewidth of 1 cm<sup>-1</sup>. No significant fine structure could be observed. Unfortunately, in this area other molecules, especially SO<sub>2</sub>, have absorption bands. The absorption of SO<sub>2</sub> can be considerable, which means that care has to be taken to choose wavelengths with equal absorption cross sections for SO<sub>2</sub> if both gases are encountered in the atmosphere. This was not a problem in the present measurements on a simulated Cl<sub>2</sub> source.

The remote monitoring of Cl<sub>2</sub> was performed at an open site. To simulate a source an open-ended box of plywood, 200 × 50 × 50 cm<sup>3</sup>, was constructed. The box was filled with gas from a chlorine tube, and the laser beam was directed through it. This constituted a way of simulating a chlorline plume without spreading large amounts of chlorine in the atmosphere. During the measurement, the box was placed...
on the roof of a building 350 m away, and the beam was aimed through the end openings. The openings were about the same size as the beam diameter at this distance. Therefore, the alignment had to be very carefully performed so that no attenuation of the beam due to the box occurred. This was possible to check since there was ~800 m of free air behind the box before the beam hit the ground. To verify the alignment a DIAL measurement was performed without chlorine before each chlorine injection.

The measurements were performed in two different ways. First, a constant inflow of chlorine was established, and the measurement was performed. The gas flow was maintained during the measurement. Figure 2 shows a DIAL recording of this kind taken with a wavelength separation of 5.8 nm. The lidar signals are displayed together with the ratio curve. The peak in the lidar signal is due to scattering from the box. The curves are the average of 140 shots at each wavelength, and the chlorine concentration was calculated to be 1.8 g/m$^3$. Similar recordings with other wavelengths and other absorption cross sections on the same chlorine flow showed good consistency. An apparent feature of Fig. 2 is that absorption in both the individual lidar curves is larger than the resulting differential absorption because of the broad absorption profile. Experiments where the flow was stopped showed that the gas blew out of the box very quickly, normally within a few seconds.

Another experiment was performed on a spreading plume. A small Cl$_2$ flow was let out from the top of a tall tube. The plume was scanned vertically in different horizontal directions downwind from the tube to monitor the spread of the chlorine plume. The gas fell very rapidly to the ground, since the molecular weight of chlorine is more than twice the mean molecular weight of air. Figure 3 shows an example of a measurement of this kind. As the absorption on any of the on or off wavelengths was great it was sufficient to use just one wavelength to detect and localize the chlorine plume.

The sensitivity of a DIAL measurement on chlorine can be calculated from an estimated detectable differential absorption of half of a percent for distances up to 1 km. With the large separation of 10 nm this results in a sensitivity of 85 mg/m$^3$ corresponding to 170 μg/m$^3$ with an absorption length of 2 × 250 m. This can be compared, for example, with the sensitivity for NO$_2$ monitoring, which is 10 mg/m$^3$ or 20 μg/m$^3$ with a 2 × 250 m absorption path. The detection limit for chlorine could be lowered to 25 mg/m$^3$ if a larger wavelength separation is used. However, a large wavelength separation can cause problems. The difference in the atmospheric transmission may be so large that it gives rise to a concentration offset. In Cl$_2$ monitoring using the short-wavelength slope of the absorption profile the offset will be negative; i.e., the concentration is underestimated. A possible correction can be separated into a backscatter term and an extinction term. The backscatter correction will be large only for a case with strong variation in backscatter with range, e.g., a dense plume or cloud. As shown by Browell et al., it is possible to obtain the correction if the aerosol backscattering profile is calculated from the lidar return signal. It can be difficult to apply this method to the case where chlorine is present in industrial areas with interfering local particle plumes. The atmospheric extinction has to be corrected for in measurements of lower concentrations distributed over a large atmospheric volume. This correction can, according to Ref. 7, be divided into a molecular extinction correction and an aerosol extinction correction, where the molecular extinction is due to Rayleigh scattering. Using Elterman's values the latter offset is calculated to be 0.32 mg/m$^3$, independent of the meteorological conditions. The aerosol extinction coefficients vary with the visibility with a wavelength dependence of $\lambda^{-\alpha}$. Using $\alpha = 1$ and Elterman's values the coefficient can be estimated for different visibilities. The values will vary greatly. For a visibility of 10 km the aerosol extinction is 0.7 km$^{-1}$. For 4-km visibility it is 1.78 and 3.58 km$^{-1}$ when the visibility is down to 2 km. These extinction values yield the concentration offsets 0.36 mg/m$^3$ (0.7 km$^{-1}$), 0.91 mg/m$^3$ (1.79 km$^{-1}$), and 1.8 mg/m$^3$ (3.58 km$^{-1}$) with a wavelength difference of 10 nm. Clearly there is great uncertainty involved in any attempt to estimate the offset. The best way to check the offset is probably to make a zero measurement before the lidar is pointed at the chlorine source. An offset should then be seen as a slope on the DIAL curve where it should be horizontal.

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References

Use of LOWTRAN in transmission calculations

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Atmospheric transmission from ground to space may be calculated using the AGNLLOWTRAN 6 model as a function of height above sea level. The results are shown in Fig. 1 for a mid-latitude winter rural haze (5-km visibility) condition. The five curves correspond (from top to bottom) to five transmitter altitudes: 2, 1.5, 1.0, 0.5, and 0 km (sea level). This figure comes from a naive use of LOWTRAN and shows a severe altitude dependence. However, LOWTRAN treats the ground as being located at sea level. We have manipulated the LOWTRAN output, defining the transmission as

\[ T(H) = T_0(H)T_A(0)/T_A(H), \]

where \( T_0(H) \) = LOWTRAN value for transmission from \( H \) to space; \( T_A(H) \) = LOWTRAN value for transmission due to aerosols from \( H \) to space, and \( H \) = ground elevation above sea level. Thus in effect we have defined the transmission from ground to space as \( T(H) = T_M(H)T_A(0) \), where \( T_M(H) = \) LOWTRAN value for transmission due to molecular interactions from \( H \) to space. This is consistent with the statement that visibility is correlated to aerosol phenomena and that visibility conditions can be stated at any altitude with a similar aerosol content independent of altitude. (This ignores the effect of the humidity profile vs altitude, which is used by LOWTRAN in evaluating aerosol extinction.)

The results of the manipulation according to Eq. (1) are shown in Fig. 2 and show a far less severe dependence on ground elevation.