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Monitoring Cl₂ 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.¹² 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 H₂O, NO₂, SO₂, and O₃. In this Letter we report on the use of a DIAL system to test the remote sensing of Cl₂.

The gaseous forms of chlorine most frequently encountered in polluted atmospheres include Cl₂, HCl, and the vapers of a number of chlorinated organic solvents, pesticides, and herbicides.³ Except in the vicinity of major pollution sources, the atmospheric concentrations of the chlorine compounds are very low. Elemental chlorine Cl₂ is a heavy greenish-yellow colored gas with a strong pungent odor. It is very reactive and highly irritating to the mucous membranes. Cl₂ 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 Cl₂ make the ability to monitor sensitively its presence in the atmosphere very important. A variety of point measuring Cl₂ 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/m³. Many other gases (NH₃, NO₃, SO₂, 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/m³.

The DIAL measurements were made with a mobile lidar system constructed in 1979. This system has been presented in detail.⁴ 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 Cl₂ 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 Cl₂ 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 ¹Σg⁺ to a repulsive ¹Πu⁺ state. The maximum absorption cross section at 328 nm is σₐ = 2.7 × 10⁻²³ m² at room temperature.⁵ 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 Δσₐ = 7.5 × 10⁻²⁴ m² 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 Cl₂/N₂ reference gas. Figure 1 shows the spectrum obtained with a laser linewidth of 1 cm⁻¹. No significant fine structure could be observed. Unfortunately, in this area other molecules, especially SO₂, have absorption bands. The absorption of SO₂ can be considerable, which means that care has to be taken to choose wavelengths with equal absorption cross sections for SO₂ if both gases are encountered in the atmosphere. This was not a problem in the present measurements on a simulated Cl₂ source.

The remote monitoring of Cl₂ was performed at an open site. To simulate a source an open-ended box of plywood, 200 × 50 × 50 cm³, 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 chlorine plume without spreading large amounts of chlorine in the atmosphere. During the measurement, the box was placed...
plume was scanned vertically in different horizontal direc-
A small Cl
2
flow was let out from the top of a tall tube. The
gas fell very rapidly to the ground, normally within a
few seconds.

The curves are the average of 140 shots at each wavelength,
and the chlorine concentration was calculated to be 1.8 g/m
3

The peak in the lidar curves is due to scattering from the box.
The curves are the average of 140 shots at each wavelength,

Similar recordings with other wavelengths and other absorp-
tion cross sections on the same chlorine flow showed good
consistency.

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 curves 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 pro-
file. 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 direc-
tions downwind from the tube to monitor the spread of the
chlorine plume. The gas fell very rapidly to the ground,

The sensitivity of a DIAL measurement on chlorine can be
calculated from an estimated detectable differential absorp-
tion of half a percent for distances up to 1 km. With the
large separation of 10 nm this results in a sensitivity of 85 mg/
m2 corresponding to 170 μg/m3 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/m2 or 20 μg/
m3 with a 2 × 250 m absorption path.6 The detection limit
for chlorine could be lowered to 25 mg/m2 if a larger wave-
length separation is used. However, a large wavelength sepa-
ration can cause problems. The difference in the atmo-
spheric 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 possi-
ble 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.,7 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 dis-
distributed over a large atmospheric volume. This correction
can, according to Ref. 7, be divided into a molecular extinc-
tion correction and an aerosol extinction correction, where
the molecular extinction is due to Rayleigh scattering. Us-
ing Elterman's9 values the latter offset is calculated to be
0.32 mg/m3, independent of the meteorological conditions.
The aerosol extinction coefficient varies with the visibility
with a wavelength dependence of λ
0.3
. Using α = 1 and
Elterman's values9 the coefficient can be estimated for dif-
ferent visibilities. The values will vary greatly. For a visi-
bility 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/m3 (0.7 km
-1
), 0.91 mg/m3 (1.79 km
-1
), and
1.8 mg/m3 (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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Swedish Environmental Protection Board.

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**Wind and C₄₅² profiling by single-star scintillation analysis: erratum**

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We recently noticed a printer's error in our paper: Eq. (1) should read

\[
W(f, f') = 1.54 \lambda^{-2} \left( \frac{f^2 + f'^2}{2} \right)^{11/6} \times \int_{h_0}^{h_0 + \Delta h} C_4 \left( \frac{h}{\Delta h} \right) \sin^2 \frac{\lambda}{h} t' \left[ f^2 + f'^2 \right] dh.
\]

Reference


**Use of LOWTRAN in transmission calculations**

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Atmospheric transmission from ground to space may be calculated using the AFGL/LOWTRAN 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

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

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.

Fig. 1. Nominal LOWTRAN transmission vs wavelength (mid-latitude winter haze).

Fig. 2. Modified LOWTRAN transmission vs wavelength (mid-latitude winter haze).