Figure 5.3. Schematic of a laboratory tunable diode laser system: L1 and L2 are the lenses used to focus the beam onto the White cell entrance and the detector, respectively, and PM1–PM5 are gold-coated mirrors used for beam alignment.
Lock-In-Verstärker

\[ U_{out} = U(\Delta) = \frac{ab}{2} \cos(\Delta) \]
Lock-In-Verstärker

Consider the case where a noise-free sinusoidal signal voltage $V_{\text{in}}$ is being detected, where

$$V_{\text{in}} = A \cos (\omega t)$$

$\omega$ is the angular frequency of the signal which is related to the frequency, $F$, in hertz by the equality:

$$\omega = 2 \pi F$$

The lock-in amplifier is supplied with a reference signal at frequency $F$ derived from the same source as the signal, and uses this to generate an internal reference signal of:

$$V_{\text{ref}} = B \cos (\omega t + \theta)$$

where $\theta$ is a user-adjustable phase-shift introduced within the lock-in amplifier.

The detection process consists of multiplying these two components together so that the PSD output voltage is given by:

$$V_{\text{psd}} = A \cos (\omega t) \cdot B \cos (\omega t + \theta)$$

$$= AB \cos \omega t (\cos \omega t \cos \theta - \sin \omega t \sin \theta)$$

$$= AB(\cos 2\omega t \cos \theta - \cos \omega t \sin \omega t \sin \theta)$$

$$= AB((\frac{1}{2} + \frac{1}{2}\cos 2\omega t)\cos \theta - \frac{1}{2}\sin 2\omega t \sin \theta)$$

$$= \frac{1}{2}AB((1 + \cos 2\omega t)\cos \theta - \sin 2\omega t \sin \theta)$$

$$= \frac{1}{2}AB(\cos \theta + \cos 2\omega t \cos \theta - \sin 2\omega t \sin \theta)$$

$$= \frac{1}{2}AB \cos \theta + \frac{1}{2}AB(\cos 2\omega t \cos \theta - \sin 2\omega t \sin \theta)$$

$$= \frac{1}{2}AB \cos \theta + \frac{1}{2}AB \cos(2\omega t + \theta)$$

If the magnitude, $B$, of the reference frequency is kept constant, then the output from the phase-sensitive detector is a DC signal which is:

- proportional to the magnitude of the input signal $A$
- proportional to the cosine of the angle, $\theta$, between it and the reference signal
- modulated at $2\omega t$, i.e. it contains components at twice the reference frequency.

The output from the PSD then passes to a low-pass filter which removes the $2\omega t$ component, leaving the output of the lock-in amplifier as the required DC signal.

In a practical situation the signal will usually be accompanied by noise, but it can be shown that as long as there is no consistent phase (and therefore by implication frequency) relationship between the noise and the signal, the output of the multiplier due to the noise voltages will not be steady and can therefore be removed by the output filter.
TDLS: Tunable Diode Laser Spectroscopy

Wavelength Modulation Spectroscopy

<table>
<thead>
<tr>
<th>Input signal</th>
<th>Modulation controls</th>
<th>Output</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intensity</td>
<td>Tune Amp Gain Phase</td>
<td></td>
</tr>
<tr>
<td>3.80</td>
<td>-1.20 1.00 1.0 0.00</td>
<td></td>
</tr>
<tr>
<td>Noise</td>
<td></td>
<td>Output voltage 0.505</td>
</tr>
<tr>
<td>0.00</td>
<td></td>
<td>Output noise 0.0872</td>
</tr>
<tr>
<td>Background</td>
<td></td>
<td>Signal-to-noise ratio 6</td>
</tr>
<tr>
<td>0.00</td>
<td></td>
<td>Relative Std. Dev. 17.27%</td>
</tr>
</tbody>
</table>

- Pause
- Run (1f mode)
- Run (2f mode)

- Spectral peak profile
  - red line = modulation interval

- Output of photodetector

- Output of synchronous detector
TDLS: Tunable Diode Laser Spectroscopy

\[ S(n\Omega) = a L \left[ \frac{a}{4} \frac{d^2}{d\omega^2} + \frac{d\alpha}{d\omega} \sin(\Omega t) - \frac{a}{4} \frac{d^2}{d\omega^2} \cos(2\Omega t) \right. \\
\left. - \frac{a^2}{24} \frac{d^3}{d\omega^3} \sin(3\Omega t) + \ldots \right]. \] (6.7)
Figure 5.7. The NO₂ spectrum in the region 1604.13–1604.65 cm⁻¹. AM detection (top) and 2f detection (bottom) schemes are shown for a 1% mixture of NO₂ in air in an 11-cm cell. Total pressure = 10 torr.
DOAS: Differential Optical Absorption Spectroscopy
Figure 3.5. $\text{SO}_2$ DOAS measurement: (a) the raw recording of the lamp intensity observed over a 2000-m absorption path; (b) a magnified spectral region with a fitted polynomial (dashed line); (c) the recorded intensity divided by the polynomial; finally, in (d) the logarithm of the curve has been formed and a fit to a laboratory spectrum (dashed line) has been made, yielding a mean $\text{SO}_2$ concentration of 11 $\mu\text{g/m}^3$ (4 ppb). From Edner et al. (1992a, 1993b).
DOAS: Differential Optical Absorption Spectroscopy

Diagram showing the components and setup of a DOAS system.
Figure 2.8. (a) Outline of the optics of a typical long-path spectrometer. (b) Relative sizes of receiving telescope focal spot and spectrometer entrance slit.

<table>
<thead>
<tr>
<th>Optical Element</th>
<th>Loss Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lamp into beam, $x_1$</td>
<td>0.08</td>
</tr>
<tr>
<td>Geometric losses, $x_2$</td>
<td>$3.0 \times 10^{-4}$</td>
</tr>
<tr>
<td>($a = 10^{-3}$ rad; $R_b = 17$ m)</td>
<td></td>
</tr>
<tr>
<td>Atmospheric attenuation</td>
<td>0.2</td>
</tr>
<tr>
<td>(Mie and Rayleigh scattering)</td>
<td></td>
</tr>
<tr>
<td>Entrance slit</td>
<td>1.0</td>
</tr>
<tr>
<td>Spectrograph losses</td>
<td>0.2</td>
</tr>
<tr>
<td>Dispersion</td>
<td>$5.0 \times 10^{-3}$</td>
</tr>
<tr>
<td>Multiplex losses (400 channels)</td>
<td>$2.5 \times 10^{-3}$</td>
</tr>
<tr>
<td>PMT$^d$ quantum efficiency</td>
<td>0.2</td>
</tr>
<tr>
<td>Total loss factor</td>
<td>$1.2 \times 10^{-12}$</td>
</tr>
</tbody>
</table>

$^a$ 10-km light path.
$^b$ See Eq. (2.13) in text.
$^c$ See Eq. (2.16) in text.
$^d$ PMT = photomultiplier tube.
Figure 2.5. Overview of UV–visible spectral ranges usable for the detection of atmospheric trace gases. Vertical scale: log of absorption cross section of the molecule (10^{-20} to 10^{-17} cm^2/molecules); also approximate detection limit at 10 km light path length (1 ppt to 1 ppb, see insert). Molecules exhibiting strong rotational structure at atmospheric pressure are denoted by an asterisk (*).
DOAS: Differential Optical Absorption Spectroscopy

Figure 2.13. Deconvolution process of an air spectrum with overlapping NO$_2$, O$_3$, and CH$_2$O absorptions. This example shows an atmospheric absorption spectrum from 325 to 350 nm taken at Jülich, Germany (top trace). The most dominant absorption features are due to NO$_2$ (NO$_2$ reference spectrum, second trace from top). Three reference spectra due to NO$_2$, O$_3$, and CH$_2$O, respectively, were simultaneously fitted to the atmospheric spectrum. Using the coefficients thus determined, one can subtract the suitable scaled logarithms of the NO$_2$ and CH$_2$O reference spectra, leaving a residual spectrum clearly showing O$_3$ absorption features (two center traces). An analogous operation with the NO$_2$ and O$_3$ reference spectra shows that CH$_2$O absorption features are also present in the spectrum (two bottom traces). Adapted from Platt and Perner (1983).
DOAS Tomographie
On the right side, the "eye" of the DOAS is shown. With this telescope, stray light from the sky is guided by an optical fiber into the spectrometer inside the observatory.
PAS: Photoacoustic Spectroscopy
PAS: Photoacoustic Spectroscopy

PAS: Photoacoustic Spectroscopy

Longitudinal
$n_z = 0, 1, 2, ...$

Azimuthal
$m = 0, 1, 2, ...$

Radial
$n = 0, 1, 2, ...$