

# Absorption spectrum of nitrogen dioxide (NO<sub>2</sub>) in the region of 3900–8000 Å

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We describe a grating spectrometer developed using a linear CCD array as a photoelectric recording system. The spectrometer provides spectral resolution of 0.3 Å in the visible region. The signal-to-noise ratio is  $2 \cdot 10^4$  at summing 1000 pulses (each of  $3 \cdot 10^{-2}$  s). A portion of the NO<sub>2</sub> absorption spectrum in 390–850 nm region was recorded with the spectrometer.

## Introduction

Nitrogen oxide plays an important role in atmospheric photochemistry; it is one of the greenhouse gases and one of the ubiquitous gaseous pollutants produced by the industry. The natural concentration of NO<sub>2</sub> in the atmosphere is about 10 ppb; therefore, to measure its content in the air one is forced to use its strongest absorption bands, such as, for example, the electronic bands in the visible region. The NO<sub>2</sub> absorption spectra in the visible region are extremely complicated, being formed by transitions among four interacting electronic states.

In Ref. 1, 407 rotational-vibrational bands in the frequency region of 12117–24563 cm<sup>-1</sup> were recorded at the low rotational temperature obtained through adiabatic cooling of molecules in a supersonic jet. At room temperatures, the rotational structure of the bands overlaps and becomes irresolvable.

In the experiment described, the NO<sub>2</sub> absorption spectrum was recorded in the visible spectral region with the resolution of 0.3–0.4 Å.

## 1. Experimental setup

To record the NO<sub>2</sub> absorption spectrum, we used a spectrophotometer, the functional diagram of which is shown in Fig. 1.

A 50-W quartz-halogen bulb was used as a source of radiation. In our experiment, we have employed a

single-channel spectrophotometer; therefore, for correct usage of the Bouguer–Lambert–Beer law, it was very important to eliminate the effect of cell windows. For this purpose, we used a 5-cm long empty quartz cell identical to the cell filled with NO<sub>2</sub>. The focal length of quartz lenses was 7.5 cm. The DFS-452 grating spectrometer used is equipped with the objectives of 1-m focal length with the grating of 1200 grooves/mm operated in the first-order of diffraction. Pigmented glasses (Russian State Standard 9411-66) were used to suppress the multiple diffraction orders and to decrease scattering in the spectrograph.

The recording system used was assembled based on a Sony ILX511 linear CCD array.

### 1.1. Photoelectric recording system based on a Sony ILX511 linear CCD array

The use of a multielement photodetector allows recording of spectra in wide spectral ranges desired. Below we present specifications of the photoelectric recording system based on the Sony ILX511 linear CCD array.

Signal build-up (exposition) time, ms . . . . .	from 30 to 10000
Total number of cells . . . . .	2088
Total number of working cells . . . . .	2048
Total length of the photosensitive part of the linear array, mm . . . . .	28
Element dimensions, μm . . . . .	14×200
Operating temperature, °C . . . . .	from -30 to + 60°C
Working readout frequency, no higher than, MHz . . . . .	2

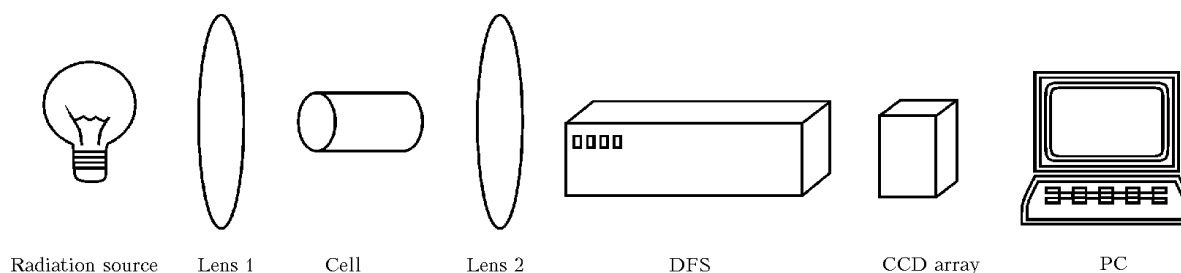


Fig. 1. Functional block-diagram of the spectrophotometer.

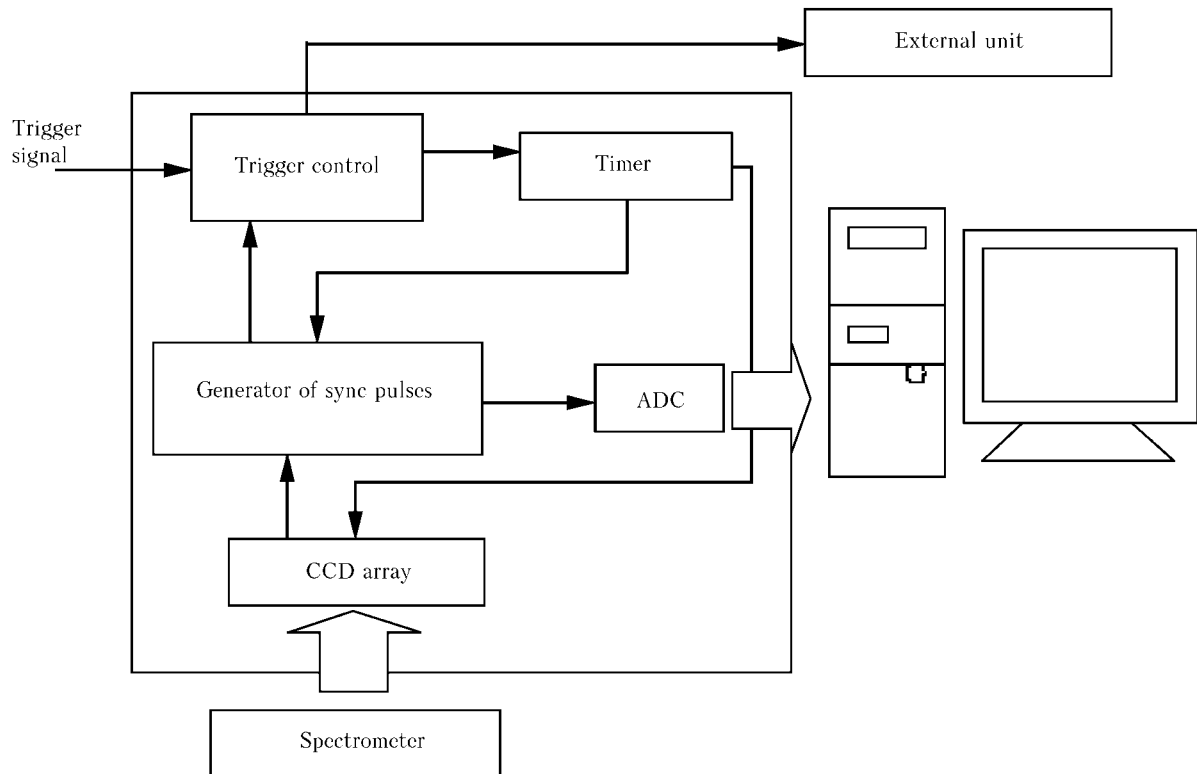


Fig. 2. Functional layout of the recording system.

The structure scheme of the ILX511 control unit is shown in Fig. 2. The trigger signal comes at the input of a timer, which keeps the needed time and specifies the build-up time for the optical signal. The actual optical build-up (exposition) time is equal to the sum of the timer period and the time for information readout from the linear array in the previous operating cycle. After the execution of the timer job, the data readout mode starts, that is, the generator of sync pulses of CCD readout turns on. No less than 2088 pulses with the pulse repetition frequency no higher than 2 MHz are needed for normal operation of a SONY ILX511 linear CCD array. Among 2088 pulses, 2048 pulses are working. During the readout mode, these pulses come, simultaneously with the analog signal from the array, to the computer through a 12-bit ADC. The first 32 and last 8 elements bear no information, thus being dark, and they allow the zero level to be taken into account. All the elements from 33rd to 2080th are informative.

The spectrophotometer developed provides for a possibility of controlling startup of the external devices (pulsed sources, lasers, etc.) in both single and cyclic modes. In both of the cases, the signal is generated at the start of the working cycle. With an external startup (generator, startup button, etc.), the single pulse mode and the use of an external timer are allowed. The information is entered into the computer at the finishing stage of the working cycle.

The data are transmitted to a computer by two signals. The first signal is analog and transmits the

image from the CCD array. The second signal is a set of pulses synchronized with output of the analog signals from every element of the CCD array. The time chart of the working cycle is shown in Fig. 3.

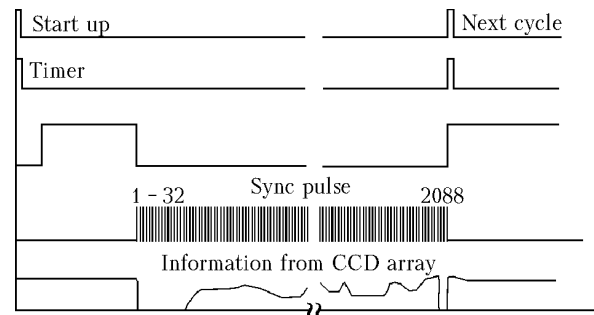


Fig. 3. Time chart of the working cycle of a Sony ILX511 linear CCD array.

## 1.2. Frequency scale calibration

The spectrometer was calibrated against mercury and neon emission lines. For this purpose, a DRGS-12 mercury lamp and a TN-0.5 neon lamp were used. These lamps were selected, because their spectra include well-known emission lines in the region from 2200 to 10000 Å and overlap the whole Sony ILX511 spectral sensitivity range.

Since a linear CCD array simultaneously spans a spectral range about 200-Å wide, to calibrate the frequency scale, we had to divide the whole range into

subranges, each including no less than two known Hg or Ne lines. Initially, we have selected a subrange with a large number of emission lines for they can be then interpreted. A necessary condition for complete calibration of the frequency scale was overlapping of all spectral subranges. Figure 4 depicts a combined spectrum of Hg and Ne emission in the range of 2950 to 9100 Å consisting of 35 subranges.

The emission spectra are shown so that they give the overall picture of the entire working spectral range. The width of the subranges varied from 190 to 240 Å for the 2.8-cm long linear array with the diffraction grating of 1200 grooves/mm. The signal-to-noise ratio achieved 0.0005 for 1000 signals with the systematic error subtracted in every spectral range at different exposures.

#### Spectrometer parameters

Spectral range, Å .....	2950–9100
Spectral subrange for record of one frame, Å .....	190–240
Spectral resolution, Å .....	0.1
Accuracy of the frequency scale calibration, Å .....	within 0.15
Signal-to-noise ratio at 1000 signals .....	20000

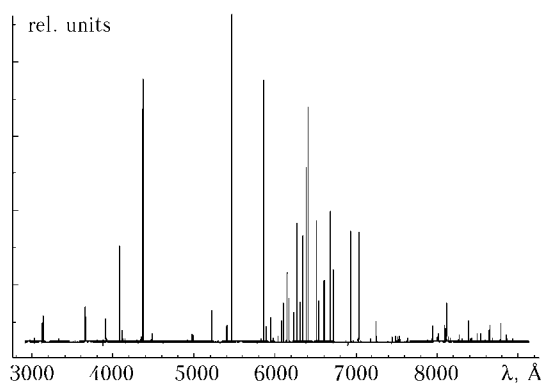


Fig. 4. Combined Hg and Ne emission spectrum in the region of 2950–9100 Å.

## 2. Recording of NO<sub>2</sub> absorption spectrum

The NO<sub>2</sub> absorption spectrum was recorded at 293 K in a 5-cm long quartz cell at the gas pressure of several Torr. The total path length of a beam in the atmosphere, including the path inside the spectrometer, was 5 m. The NO<sub>2</sub> absorption spectrum was recorded in the region from 3900 to 8000 Å with the resolution of 0.3–0.4 Å.

Nitrogen dioxide was produced from thermal decomposition of lead nitrate:



First, the noise of the linear CCD array was recorded at the chosen exposure time with the radiation source off. Then this noise can be subtracted from the

spectra as a systematic error to increase the signal-to-noise ratio.

The next stage was recording the radiation from the quartz-halogen bulb passing through an empty cell to eliminate the cell effect. Once the spectrum of incident radiation is recorded, the noise of a linear array used and the background (zero) are subtracted from it. The signal obtained presents the incident radiation  $I_0$  in the Bouguer–Lambert–Beer law

$$I(\nu) = I_0(\nu) \exp [-\kappa(\nu) CL],$$

where  $I_0$  is the intensity of the incident radiation,  $I$  is the intensity of the transmitted radiation;  $\kappa(\nu)$  is the absorption coefficient;  $C$  is the gas concentration;  $L$  is the length of the absorbing layer.

Then, the empty cell is replaced by a cell filled with nitrogen dioxide. Once the spectrum of incident radiation is recorded, the noise of a linear array used and the background are subtracted from it. In this case, the signal obtained is proportional to the intensity of transmitted radiation  $I$  in the Bouguer–Lambert–Beer law.

The recorded NO<sub>2</sub> absorption spectrum is characterized by extremely high absorption in the visible region. Radiation extinction in the region of 4000–5000 Å achieves 95% even with the 5-cm long cell (Fig. 5), and then the absorption decreases smoothly in the longwave region. The spectrum is strongly indented, and rather regular intervals between vibronic polyads facilitate its separation against the background of absorption by other gases and aerosol absorption in the case of atmospheric observations.<sup>2</sup> The comparison of the experimental results obtained with the results published in Ref. 3 demonstrates similar spectral pattern, that is, identical spectral shapes. In Ref. 3, the Fourier transform spectrometer with the path lengths of 20.8 and 60.7 m was used. We employed the spectrophotometer with 5-cm long cell, but high signal-to-noise ratio (2000) allowed us to record the same weak absorption lines. Our resolution of 0.3 Å in place of 1 Å in Ref. 3 provided for recording of the fine spectral structure (see Fig. 5).

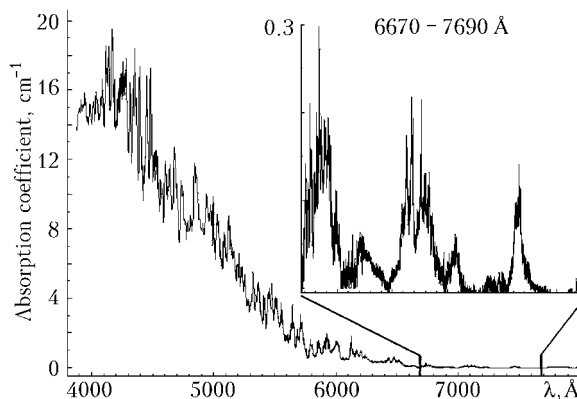


Fig. 5. NO<sub>2</sub> absorption spectrum in the region of 3900–8000 Å.

The spectrum recorded allowed us to refine the NO<sub>2</sub> concentration in the cell. For the line at 7105.73 Å,

we took the absorption coefficient  $\alpha = 0.07 \cdot 10^{-19} \text{ cm}^2/\text{mol}$  from Ref. 3. Known the optical density and the absorbing cell length  $L$ , from the Bouguer–Lambert–Law we found the concentration

$$C = \ln \frac{I_0}{I} / (L\alpha),$$

which turned out to be  $1.45 \cdot 10^{18} \text{ mol}/\text{cm}^3$ .

Analysis of the  $\text{NO}_2$  absorption spectrum showed that for a 5-cm long absorbing cell the lowest measurable concentration is about 380 ppm. If we increase the optical path up to 100 m, then the minimum measurable concentration is 160 ppb (the maximum permissible atmospheric concentration is 170 ppb).

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