# High-vacuum system for spectroscopic studies of water vapor

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The high-vacuum system for spectroscopic studies of water vapor is described and its main parameters are presented.

## Introduction

Water vapor absorption in the region of rotational-vibrational transitions (the visible and IR spectral ranges) is actively studied, that is reflected in a number of specialized monographs.[1] However, for many years the measurements of the water vapor absorption coefficient in the region of electronic transitions have been limited to the region of 106–198 nm.[2,3]

In 1980, in the experiment on sensing the atmosphere excited by the near-UV radiation in the region up to 3000 $cm^{-1}$, the effect of re-emission from the exciting line was found,[4] and the re-emission magnitude correlated with the atmospheric humidity and the presence of precipitation. Direct measurements in artificial mixtures have shown that the signals, earlier discovered in the atmosphere, are caused by water vapor. Further experimental investigations with the use of various laser spectroscopic methods yielded voluminous information about the absorption and fluorescence of water vapor in the region of 213–425 nm and allowed the signals due to ionization to be recorded. Some experiments were conducted at the increased (up to 70°C) temperature. The available results are indicative of a complex mechanism of transformation of the UV energy absorbed by the Í$_2$Î molecule.[5]

The obtained data on the spectral characteristics of water vapor do not always agree. Thus, for example, spectral dependences of the fluorescence excitation and the photoacoustic signal determined in different experiments are directly opposite: in the first case there is a peak nearby 270 nm,[6] while in the second case there is a dip.[7] A serious disadvantage of the conducted measurements is the absence of control for the composition of initial gases and vapors, as well as for the purity of the measuring system itself, which is especially important when using high-sensitive fluorescent and photoacoustic methods and increased temperatures, when the measuring system itself emits gases, contributing to the absorption or fluorescence spectrum.

The discrepancy between the spectral behavior of the fluorescence and the photoacoustic signal[6,7] can be eliminated (or its nature can be found) through simultaneous combined measurements at the same system with the use of different methods, which would allow a more comprehensive study of the interaction of water molecules with each other and with buffer gases. Thus, simultaneous measurements of spectral characteristics of the fluorescence, photoacoustic, and ionization signals of water vapor in air and in mixtures with other atmospheric gases will allow us to determine both radiative and nonradiative channels of relaxation of the energy absorbed by water molecule and their dependence on the measurement conditions: composition, temperature, and pressure of the gas medium. Combination of sensors ensuring simultaneous obtaining of information about these relaxation channels in one experimental system will open, in our opinion, the possibility of judging more correctly the processes proceeding in the molecule absorbing optical radiation, as well as the redistribution of the contributions from these channels under varying conditions.

This paper is devoted to description of the experimental system; the results of testing and the measured characteristics of water vapor will be considered in next publications.

## Schematic of the measuring system

The measuring system should provide for preparation of the gas mixture with high reproducibility of the conditions and the composition, which can be achieved only with the use of a high-vacuum heated system. Dealing with water vapor at increased temperatures requires a heated pressure sensor to avoid the uncontrolled condensation of water. The optical channel of the system should provide for molecular exciting in the range 213–355 nm (3rd–5th harmonics of the Nd:YAG laser, harmonics of the copper vapor laser) and recording the fluorescence in the UV and visible spectral ranges, therefore, all its elements must be made of the nonfluorescing KU-1 fused silica.

The described system (Fig. 1) includes a high-vacuum heated gas subsystem, ensuring the operation with water vapor in mixture with other gases in a wide temperature (15–250°C) and pressure ($5 \cdot 10^{-7}$–1000 Torr) ranges, the fluorescent, photoacoustic, and ionization sensors, and a computerized recording system.

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**Fig. 1.** General view of the system developed.

## Gas subsystem

The principal layout of the gas subsystem is shown in Fig. 2, and the general view of the high-temperature heated block is shown in Fig. 3. All the components placed in heated compartments are connected by ConFlat flanges with copper gaskets.

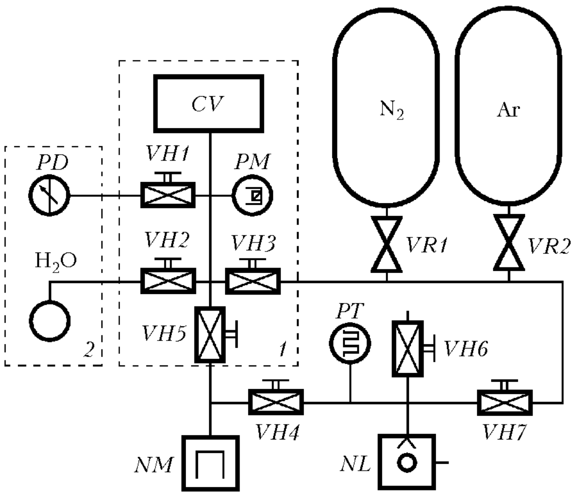


**Fig. 2.** Vacuum subsystem: optical chamber *CV*; 3NVR-1D diffusion pump *NL*; NMD-0.16-1 ion pump *NM*; PMM-32-1 high-vacuum sensor *PM*; PDTK-0.1M quartz deformation pressure and temperature transducer *PD*; PMT-2 thermocouple sensor *PT*; VV-10U heated valves *VH1*–*VH4*; VV-32 heated valve *VH5*; Du-16 vacuum diaphragm valves *VH6* and *VH7*; valves on gas cylinders *VR1* and *VR2*.

The dashed line in Fig. 2 marks the parts heated (*1*) up to 250°C, where the optical chamber is placed, and (*2*) up to 80°C, where the flask with water and the pressure sensor are placed. The temperature in the both parts is maintained automatically; a gr.21 resistance thermometer serves a sensor in the first part, and a contact thermometer is employed in the second part. The temperature of the optical chamber is determined by an individual resistance thermometer. The maximal temperature of the high-temperature heated compartment is 285°C, and the time of heating up to this temperature from the room one is about 4 hours.

The parameters of the working gas mixture are determined by the quartz pressure and temperature transducer. The PDTK-0.1M transducer, specially modified for the system requirements in the EIPA design office (Uglich, Russia), measures the temperature and pressure in the ranges 0.6–800 mm Hg and −40 – +5°C accurate to, respectively, 0.25 mm Hg and 0.02°C. The information is carried by two signals, whose frequency is connected functionally with the measured pressure and temperature of the mixture.

The interaction between radiation and water vapor (both pure and in mixtures with other gases) can be studied in two modes. At the temperature of the optical chamber below 80°C, the valves *VH1* and *VH2* are open and the mixture pressure is determined by the pressure transducer *PD*. At higher temperatures, to prevent the condensation of water vapor in the elements of the low-temperature heated compartment, these valves are closed, and the gas pressure in the optical chamber is determined through calculations.

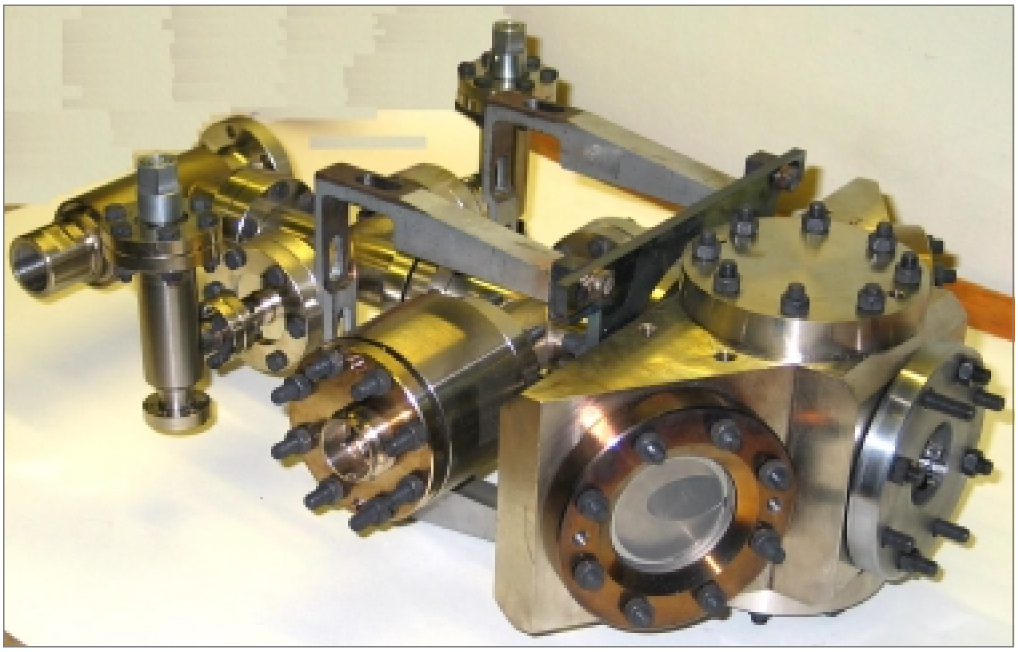

**Fig. 3.** Components of the heated high-temperature block of the system.

## Optical arrangement

The optical arrangement is shown in Fig. 4 (top view).

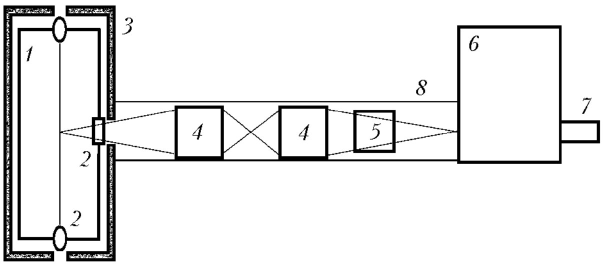


**Fig. 4.** Principal optical arrangement for fluorescence measurements: optical chamber *1*, fused silica windows *2*, heat-insulating case *3*, condensers from MDR-23 monochromator *4*, Pechan prism *5*, MDR-6 double monochromator *6*, photomultiplier tube *7*, light-intercepting case *8*.

When designing the optics, we faced two problems: manufacturing windows operable under above conditions and matching the monochromator with the optical chamber.

The existing market of optical elements for operation in the UV spectral region under high-vacuum and high-temperature conditions is very limited and practically beyond the reach of Russian researchers. To complete the system developed, the Institute of Nuclear Physics SB RAS has restored the earlier developed technology of manufacturing the fused silica windows for operation at temperatures up to 300°C. By this technology, the titanium ring of the adapter is connected by means of the diffusion welding to a stainless steel flange, and a fused silica window is welded by pure lead to this ring (Fig. 5). The tests have shown that the window ensures the vacuum within $5 \cdot 10^{-8}$ Torr at temperatures up to 285°C.

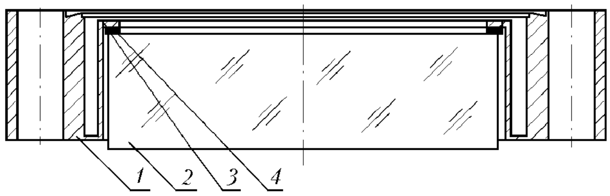


**Fig. 5.** Design of the window: flange *1*, fused silica plate *2*, titanium ring *3*, lead layer *4*.

The elements are arranged in such a way that the laser radiation is transmitted through the optical chamber horizontally, while the monochromator slits are set vertically. Under such conditions, the monochromator "sees" the illuminated area, the length of which is approximately equal to the slit width (at the roughly unit transfer factor of the condenser system). If the image of the illuminated area is turned through 90°, then the monochromator receives the radiation from the area having the length equal to the slit height. The gain is 15–50 times in this case.

We used the Pechan prism made of the KU-1 fused silica as an inverting element of the optics. This prism has the larger angular field of view than the traditional inverting Dove prism.[8]

## Microphone and ionic sensor

The microphone unit is shown schematically in Fig. 6. Two types of the microphones are used: the EK-3024 microphone fabricated by Knowles Electronics and the microphone fabricated in the Institute of Atmospheric Optics SB RAS.[9] The elements of the ionic sensor are made of stainless steel and capable of operating at temperatures up to 250°C. The presence of three independent electrodes allows analyzing both positive and negative ions and studying the dependence of the ion yield on the laser radiation power density.

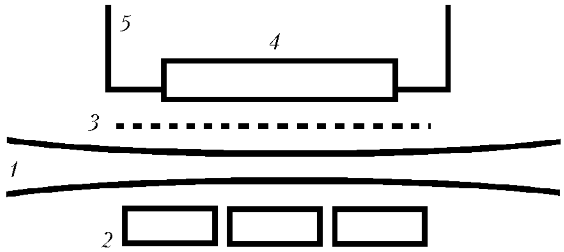


**Fig. 6.** Schematic layout of the microphone unit (side view): laser beam *1*; electrodes of the ionic sensor *2*; mesh electrode of the ionic sensor *3*; microphone *4*; mounting parts *5.*

## Data acquisition and processing system

The data acquisition and processing system consists of five independent channels (Fig. 7).

An AMD Duron-650 personal computer is used as a central element for processing, acquisition, and displaying the obtained data. Data link controllers specially developed for this system are connected to the PC through standard ports.

All information about the state of the vacuum system from its sensors is pre-processed by an independent device developed based on Atmel microcontroller. This allows us to unload the central computer and to make convenient its connecting with sensors.

The channel for data input from the photon counter system, operating in the charge integration mode, is made based on elements of the Vektor standard, which ensures a high metrological reliability of measurements.[10]

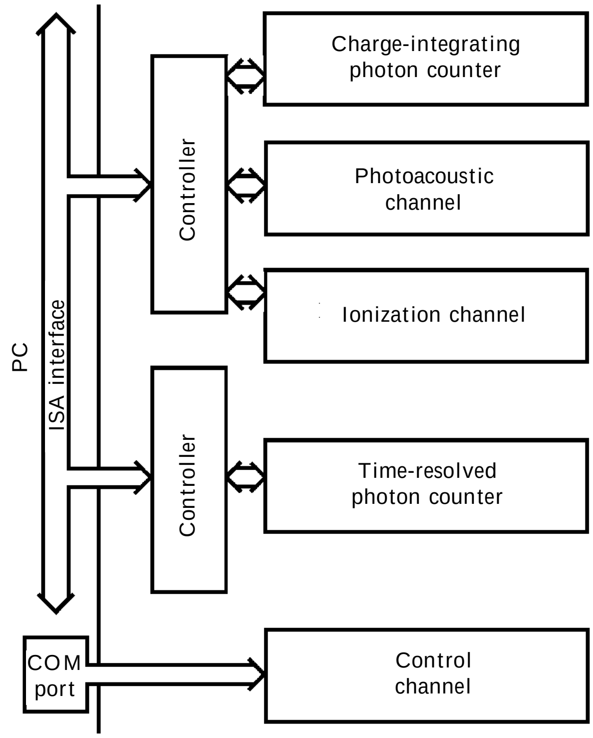


**Fig. 7.** Structure of the data acquisition and processing system.

| Evacuation system | | |
|---|---|---|
| Stage | 1 | 2 |
| Residual vacuum, mm Hg | $10^{-2}$ | $5{\cdot}10^{-7}$ |
| Pumping time, h | 0.5 | 0.5–12 |
| Heating system | | |
| Maximum temperature, °Ñ | 285 | |
| Heating time, h | 4 | |
| Temperature of the medium under study, °C | | |
| | Fluorescent and ionic sensors | Photoacoustic sensor |
| | 285 | 60 |
| Parameters of measuring channels | | |
| *Fluorescence channel* | | |
| Spectral range, nm | 200–2000 | |
| Spectral resolution, nm | 0.06–0.26 | |
| *Charge-integrating photon counter* | | |
| Threshold sensitivity*, photon / pulse | 0.01 | |
| Dynamic range | 200 000 | |
| *Time-resolved photon counter* | | |
| Digitizing rate, MHz | 500 | |
| *Photoacoustic channel* | | |
| Sensitivity, $cm^{-1}$ / J | $3 \cdot 10^{-8}$ | |
| *Ionization channel* | | |
| Threshold sensitivity*, ion / pulse | 0.1 | |

* With averaging over 100 laser pulses.

The time-resolved photon counter is constructed based on the LA-n02 DAQ board made in the Rudnev–Shilyaev Center.

To control the whole system, as well as the data input and preprocessing, we have developed a unique software. It allows us to control the operation of lasers and to work in the lock mode. The software controls for the temperature distribution in the heated compartment and the temperature in the optical chamber, determines the pressure of the studied gas mixture, and inputs the data from the photon counting system operating in the charge integration mode. The main parameters of the system are summarized in the Table.

The trial tests of the system with excitation of the water vapor molecules by the 4th harmonic of the Nd:YAG laser have demonstrated the presence of all signals and the normal operation of the system as a whole.

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## References

1. A.D. Bykov, Yu.S. Makushkin, and O.N. Ulenikov, *Rotational-Vibrational Spectroscopy of Water Vapor* (Nauka, Novosibirsk, 1989), 296 pp.; A.D. Bykov, L.N. Sinitsa, and V.I. Starikov, *Experimental and Theoretical Methods in Spectroscopy of Water Vapor Molecules* (SB RAS Press, Novosibirsk, 1999), 376 pp.
2. K. Watabene and M. Zelikoff, J. Opt. Soc. Am. **43**, No. 9, 753–755 (1953).
3. B.A. Thompson, P. Harchek, and R.R. Reeves, Jr., J. Geophys. Res. **68**, No. 24, 6431–6436 (1963).
4. Yu.G. Vainer, L.P. Malyavkin, P.M. Nazarov, Sh.D. Fridman, and V.D. Titov, Meteorol. Gidrol., No. 12, 39–47 (1980).
5. M.M. Makogon, Atmos. Oceanic Opt. **14**, No. 9, 696–706 (2001).
6. V.M. Klimkin and V.N. Fedorishchev, Atm. Opt. **2**, No. 2, 174–176 (1989).
7. B.A. Tikhomirov, V.O. Troitskii, V.A. Kapitanov, G.S. Evtushenko, and Y.N. Ponomarev, Acta Phys. Sin. Oversias Ed. **7**, No. 3, 190–195 (1998).
8. Yu.G. Kozhevnikov, *Optical Prisms* (Mashinostroenie, Moscow, 1984), 148 pp.
9. Yu.N. Ponomarev, B.G. Ageev, M.V. Sigrist, V.A. Kapitanov, D. Courtois, and O.Yu. Nikiforova, *Laser Photoacoustic Spectroscopy of Intermolecular Interactions in Gases* (Rasko, Tomsk, 2000), 200 pp.
10. S.E. Karmazin, A.N. Kuryak, M.M. Makogon, and A.L. Tsvetkov, Atmos. Oceanic Opt. **8**, No. 11, 937–939 (1995).