

Diagnostics of ortho and para water isomers with tunable diode lasers

E.V. Stepanov, V.I. Tikhonov, V.A. Milyaev

Abstract. A spectrometer based on tunable diode lasers intended for determining the relative content of ortho and para water isomers is described. A double-heterostructure GaInAsP laser is used as a source of tunable IR radiation in the 1.37- μm region. The spectrometer was used for the diagnostics of spin-selective absorption in water isomers.

Keywords: ortho and para water isomers, laser spectroscopy, application of semiconductor lasers.

It is known that the spin isomers of water molecules have vibrational–rotational levels of different symmetry [1, 2]. For this reason, the rotational and vibrational–rotational spectra of ortho and para water isomers are different [2], which makes it possible to distinguish these isomers by their high-resolution spectra. Because the probability of a change in the total nuclear spin in collisions of water molecules is very small, ortho and para water isomers in a gas phase behave as two different modifications of water, whose relative content under normal conditions is 3:1 [1]. The difference in the energy structure can also result in a small difference in the physicochemical properties of ortho and para water isomers and is manifested, for example, in interactions with sorbents [3].

Spin-selective processes in H_2O , which can be in principle used for isotope separation, have been studied so far only by measuring the rotational spectra of H_2O by the methods of backward-wave tube submillimetre spectroscopy [3, 4]. The complexity of this method and the actuality of studying such processes require the development of simpler approaches that would confirm the possibility of separation of ortho and para isotopes by other physical methods [3]. This problem can be solved by the method of laser spectral analysis, for example, diode laser spectroscopy [5], which allows precision measurements of the parameters of individual vibrational–rotational molecular absorption lines in the near- and mid-IR regions.

We have developed a spectrometer for measuring the relative content of water isomers, which uses tunable diode lasers (TDLs) as radiation sources. We employed a double-

structure GaInAsP TDL emitting in the 1.37- μm region where the $\nu_1 + \nu_3$ combination band of the absorption spectrum of H_2O is located. The resonance absorption in ortho and para water isomers was detected simultaneously on the adjacent absorption lines of these isomers with the frequencies 7368.848 and 7368.392 cm^{-1} and intensities 2.6×10^{-21} and 7.7×10^{-21} cm mol^{-1} , respectively [6]. They correspond to the transitions from the ground vibrational (000) state to the excited (101) state with the vibrational quantum numbers (J, K_a, K_c): (606) \rightarrow (707) for para isomers and (616) \rightarrow (777) for ortho isomers (K_a and K_c are the rotational quantum numbers to the a and c axes of the molecule, respectively).

The transmission spectra of H_2O were recorded using the repetitively pulsed regime of the TDL, when the laser was tuned during each of the pulses due to heating the laser crystal by the pump current. Pumping was performed by $\sim 2800\text{-}\mu\text{s}$ current pulses with a pulse repetition rate of ~ 120 Hz. The current amplitude at the beginning of each pulse was 100–150 mA and linearly increased to the pulse end by 10%–20%, which provided the linear frequency tuning in time [7].

The spectral region of the laser tuning was selected by varying the laser temperature and pump current amplitude [7]. The laser used in the spectrometer emitted in the required spectral range at temperature $\sim 57.3^\circ\text{C}$, this temperature being maintained by the electronic stabilisation system with an accuracy of $\sim 10^{-3}^\circ\text{C}$ [8]. The frequency tuning rate was $\sim 400 \text{ cm}^{-1} \text{ s}^{-1}$, which provided the recording of the spectral range of $\sim 1.2 \text{ cm}^{-1}$ during one pulse. The TDL output power was ~ 0.5 mW, $\sim 90\%$ of the power being in the fundamental mode. According to our estimate, the laser linewidth was smaller than 10^{-3} cm^{-1} , while the relative noise of the output power was at a level of 10^{-4} . Due to a high pulse-to-pulse reproducibility of the amplitude and tuning curve of the laser, the spectral resolution was better than 10^{-3} cm^{-1} .

The TDL radiation was collimated with a parabolic mirror, transmitted through a gas cell of length ~ 12 cm, and focused on an uncooled germanium photodiode. The detected electric signal was amplified within the 0–3-MHz bandwidth and was fed to the input of the digital system for recording the laser pulse shape [8], which provided, in particular, the signal accumulation (up to 256 accumulations). The discreteness of the digital amplitude recording of the laser spectra was $\sim 10^{-5}$ of the incident power [9], and the temporal discreteness was 0.8 μs , corresponding to $\sim 3 \times 10^{-4} \text{ cm}^{-1}$ in the frequency scale. The measurement of the shape of a 2800- μs laser pulse took ~ 20 s. Weak

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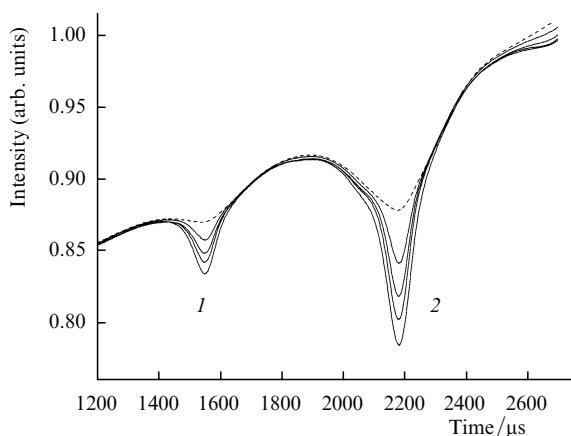


Figure 1. Fragment of the transmission spectra of water vapours in the 7368.5 cm^{-1} region demonstrating the absorption lines of para (1) and ortho water isomers (2).

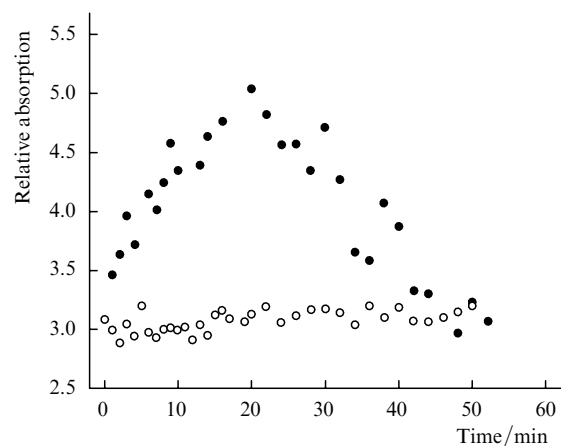


Figure 2. Dynamics of the relative absorption of ortho and para water vapours in an empty evacuated cell (○) and in a cell with a sorbent (●) disconnected from the vacuum system.

absorption was measured by recording the derivative of the transmission spectrum.

Figure 1 shows a part of the transmission spectrum of water vapours recorded near 7368.5 cm^{-1} . The spectrum exhibits the lines of ortho and para water isomers. Note that the TDL of this type is tuned in the regime used in our experiments toward lower wavenumbers. The spectrum shown by the dashed curve was recorded in an analytic cell continuously evacuated with a backing pump and corresponds to the transmission in a part of the optical path open to atmosphere (of length $\sim 15\text{ cm}$). After the analytic cell was disconnected from the vacuum system, the resonance absorption in water gradually increased due to the desorption of water molecules for the cell walls. The transmission spectra obtained after 10, 15, 20, and 30 min after the cell disconnection are shown in Fig. 1 by solid curves. The absorption lines of water in the cell are narrowed down to $\sim 0.022\text{ cm}^{-1}$, which corresponds, within the experimental error, to the Doppler broadening of the H_2O lines in this spectral range at room temperature. Absorption of the order of 10% for the recorded ortho water isomer line of such width in a cell of length $\sim 12\text{ cm}$ corresponds to the total water vapour pressure $\sim 3\text{ Torr}$.

Such spectra (or their derivatives) were used to calculate the relative content of ortho and para water isomers in the cell. The spectra were processed by using the methods and algorithms developed earlier for precision laser analysis of the relative content of isotopic isomers $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ [10]. Our experiments have shown that, when the optical density of substances under study is ~ 1 , the accuracy and sensitivity of measurements of their relative content with the help of TDLs can be a few hundredths of percent.

We tested the laser spectrometer described above in the diagnostics of spin-selective adsorption of water molecules by some sorbents. Figure 2 shows the relative contents of ortho and para water isomers measured in two experiments. In the first case (open circles), we studied a gradual increase in the content of water vapour in a preliminary evacuated cell, which occurred due to the desorption of water from the cell walls after the cell disconnection from the vacuum system. In the second case (black circles), we studied the same process but in a cell with a sorbent, which provided the selective binding of the ortho and para water isomers [3]. One can see that in the first case, the absorption ratio of the

isomers determined by the concentration ratio of ortho and para water isomers, was virtually invariable for an hour. At the same time, in the presence of a sorbent in the cell, during the first 20 min the content of ortho water isomers is higher than the equilibrium value. During the following 30 min, the relative content of ortho and para water isomers returns to its equilibrium value. One can see that in the case of the maximum enrichment of a medium by ortho water isomers, their relative content is more than half as much as its equilibrium value.

Thus, our results demonstrated the reproducibility of spin-selective adsorption of ortho and para water isomers, which were earlier observed only by the methods of submillimetre spectroscopy [3]. The method of laser analysis of the relative content of ortho and para water isomers developed in our paper can be used for studying spin-selective interactions of H_2O with surfaces, sorbents, and polyatomic biological molecules, as well as for the development of methods and technologies for separating the spin isomers of water.

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