MODERN POSSIBILITIES OF WATER VAPOUR MICROWAVE SPECTROSCOPYIN NIZHNY NOVGOROD

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Pure rotational spectrum of water widely spreads from centimeter wave-lengths up to middle infrared reaching maximum of intensity near 6 THz. HITRAN database list contains about 2000 lines. But assuming upper frequency limit of modern microwave spectroscopy as about 1 THz and reasonable absorption coefficient sensitivity of spectrometers of 10^{-8} cm^{-1} we've got about few dozens of water lines left available in principal for analysis by the method. The list can be slightly extended by lines in exited lowest vibrational states. About the same number of lines is in microwave spectra of $H_2{}^{17}O$ and $H_2{}^{18}O$. The number of lines of deuterated water as a heavier molecule is in a few times bigger. Center frequencies are quite well known for most of lines belonging to $H_2{}^{16}O$, $D_2{}^{16}O$ and $HD^{16}O$ but about order of magnitude in accuracy could be gained for other water isotopes. Intensity of water lines can be quite well calculated. However in view of fast growing number of microwave instruments used for Earth atmosphere and interstellar media remote sensing, the list of precisely known line parameters should be extended by parameters responsible for visualization of intermolecular interactions. Among such parameters required for various spectroscopic applications as well as for further developments of theoretical description of water spectrum in conditions of real atmosphere are line shape parameters i.e. pressure broadening, pressure shifting of line center including broadening and shifting by foreign gases, line mixing, and their temperature dependencies. These data are rare in spectroscopic databases and even for most common molecular lines used for remote sensing experimental values of these parameters are not known. Systematic pressure broadening studies including broadening by foreign gases using different spectroscopic techniques and methods had been undertaken only for three microwave water lines at 22, 183 and 380 GHz. Cases when parameters measured in some papers differ much more than errors quoted by authors are quite common. Self-broadening and pressure shifting parameters has been measured once for the 439 GHz line and estimated for the 556 GHz water line. Line mixing effect of microwave water lines had been never studied. Evident cause of lesser abundance of precise data of that kind is difficulty of accurate measurement of parameters associated with shape of lines.

Recent developments of spectroscopic experimental technique and methods allowing precision measurements of spectral line shape parameters in our laboratory are presented. Two spectrometers in their modern versions are described. Both spectrometers are based on MM/SubMM backward-wave oscillator tubes phase-locked against harmonic of frequency standard. The first one is automated spectrometer with radio-acoustical detection (RAD) of radiation absorption operating in pressure range from hundreds of milliTorr to ten Torr. Combination of high sensitivity, precision frequency setting and use of amplitude modulation of radiation makes the spectrometer very well suitable for study of shape of absorption lines. High signal to noise ratio of observed lines permits accurate determination of the line parameters. Among examples the study of temperature dependences of the 439 GHz water line pressure broadening and shifting is presented. In the second spectrometer the studied sample is placed inside Fabry-Perot resonator and the sample absorption is measured through broadening of resonance curve of the resonator. Thus many problems associated in other kind of spectrometers with amplitude-frequency characteristics of radiation source are considerably eliminated. This feature allows using the spectrometer for investigation of molecular lines in a pressure range up to atmosphere. Specialties of our resonator spectrometer are employ of fast digital forth and back frequency scanning (~ 60 microseconds per step) and broad – band BWO. These advantages allow us to achieve absorption sensitivity in about factor of 10 higher than in other known analogs, and to make broad spectral records (up to hundred of GHz) in one experiment. Abilities of the spectrometer are demonstrated on example of study of highly important for remote atmosphere sensing water line at 183 GHz. The resonator spectrometer can be also used for precision studies of continuum kind of absorption usually associated with influence of molecular complexes and far wings of regular molecular lines.