RESONATOR SPECTROSCOPY AS A NEW METHOD OF INVESTIGATION OF UNCONVENTIONAL MILLIMETER-WAVE ATMOSPHERIC ABSORBERS

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Abstract Principles of millimeter wave resonator spectroscopy of broad lines are presented. Block-diagram and parameters of high sensitive resonator spectrometer are described. Results of investigations of millimeter water and oxygen rotation lines in laboratory atmosphere demonstrate great potential of this technique for the measurements both broad atmospheric absorption lines and continuum absorption.

Keywords: millimeter wave absorption of water vapor and oxygen / resonator spectroscopy / millimeter waves / water dimer / rotational lineshape / collision-induced absorption spectra

1. Introduction

Water vapor and molecular oxygen are among main species in the Earth's atmosphere absorbing radiation in the millimeter and submillimeter wave ranges. They have strong rotational transitions over broad spectral region. In the gaps between these lines, called atmospheric windows, the absorption is due to the sum of the line wings and continuum. Conventional lineshapes, describing an isolated resonant transmission are the Van Vleck-Weisskopf (VVW) lineshape and the kinetic lineshape (Gross) rewritten by Zhevakin-Naumov (ZN). It is recognized, however, that the absorption far from the centers of lines, where the impact approximation fails, cannot be accounted for by the above lineshapes. Physical mechanisms leading to the formation of a continuum are still a matter of controversies. Several mechanisms have been proposed besides that of far line wings contribution. Excess absorption

C. Camy-Peyret and A.A. Vigasin (eds.),
Weakly Interacting Molecular Pairs: Unconventional Absorbers of Radiation in the Atmosphere, 239–246.

may arise from the water dimer H_2O–H_2O and/or from such weakly-bound molecular complexes as H_2O–N_2 and H_2O–O_2. It could also be caused by collision-induced absorption. The measurements of absorption were made in different atmospheric windows both in the field and in the laboratory environments, see for example [1]. The amount of measurements in the mmw and sub-mmw atmospheric windows is still very limited and no agreement is achieved as to the origin of anomalous temperature and water vapor pressure dependence. Our belief is that significant new perspectives in the solution of this problem could be offered through the use of broadband resonator spectrometry. This method is especially suitable for investigations of broad line shapes, in particular continuum absorption, under high and normal atmospheric pressure.

There are two main classes of resonator spectrometry, depending on the ratio of absorption linewidth to the cavity resonance width: (i) the line is narrower than the cavity resonance and (ii) the line is much broader. The first case includes high-resolution spectroscopy while the second one relates to highly pressure-broadened and atmospheric spectral lines as well as to absolute measurements of absorption at one fixed frequency. Our paper deals with the spectrometers belonging to the second class only.

2. A principle of the wide range microwave resonator spectroscopy

Resonator spectrometer consists of an open high quality Fabry-Perot resonator, precisely controlled and powerful source of radiation, and sensitive detector. Fabry-Perot resonator uses the fundamental TEM($00q$) mode, where q is the longitudinal mode number, i. e. the number of half-wavelengths between mirrors. The sample to be studied is placed inside the cavity. In case of atmospheric measurements the cavity is filled with a gas. The measurements of absorption in this version of resonator spectroscopy reduces to comparison of the quality factors Q characteristic to the empty and loaded resonator. The sensitivity of resonator spectroscopy increases with an increase in both the resonator quality factor and in the accuracy of the measuring the resonance width. The resonator quality factor Q is defined as the ratio of the frequency of the resonance f_0 to the width of the resonance (FWHM) Δf

$$\Delta f = \frac{c\,P_t}{2\,\pi\,L}, \tag{1}$$

where c is the velocity of light in a substance, L is the resonator length, and P_t stands for the total relative losses of radiation energy during one traversal in the resonator. We can evaluate the total resonator losses by measuring the width of the resonance curve. Total relative losses in the Fabry-Perot cavity P_t consist of

$$P_t = P_r + P_c + P_d + P_a. \tag{2}$$

The reflection P_r, coupling P_c, and diffraction P_d losses can be calculated or evaluated experimentally. The absorption coefficient γ and the atmospheric losses P_a are related by

$$P_a = 1 - e^{-\gamma L}. \tag{3}$$

Such measurement can be performed at any resonator mode under constant resonator length. If the resonator length is about some tens of a cm, the distance between two consecutive longitudinal modes correspond approximately to some hundreds MHz. The measurement of γ reduces to finding the resonance width. Techniques and instruments for such measurements are described below.

3. Experimental set-up

The block-diagram and parameters of the real broad band resonator spectrometer developed at the Institute of Applied Physics RAS [2] are shown in Fig. 1. The Fabry-Perot resonator used the fundamental TEM($00q$) mode. The quality factor of a Fabry-Perot resonator having 25–42 cm length, spherical silver-plated mirrors 12 cm in diameter and 24 cm in curvature radius, coupled with a source and detector by 6-mm Teflon film placed at 45° to the resonator axis, is determined by unavoidable reflection losses and equals approximately 600 000. Expressions for all the losses are known more or less accurately. Diffraction losses can be calculated as a fraction of total energy accumulated inside the resonator which is cut by the resonator mirrors' aperture and can be done much smaller than all other losses; coupling losses and reflection losses can be calculated from the coupling film parameters and from the *dc* conductivity of bulk silver, respectively.

The synthesized frequency radiation source employs a backward wave oscillator (BWO) [3] which is stabilized by a phase lock-in loop (PLL) with the use of two reference synthesizers in this case: one microwave (MW) synthesizer (8–12 GHz) defining the central frequency of the BWO, and one fast radio frequency (RF) synthesizer (20–40 MHz)

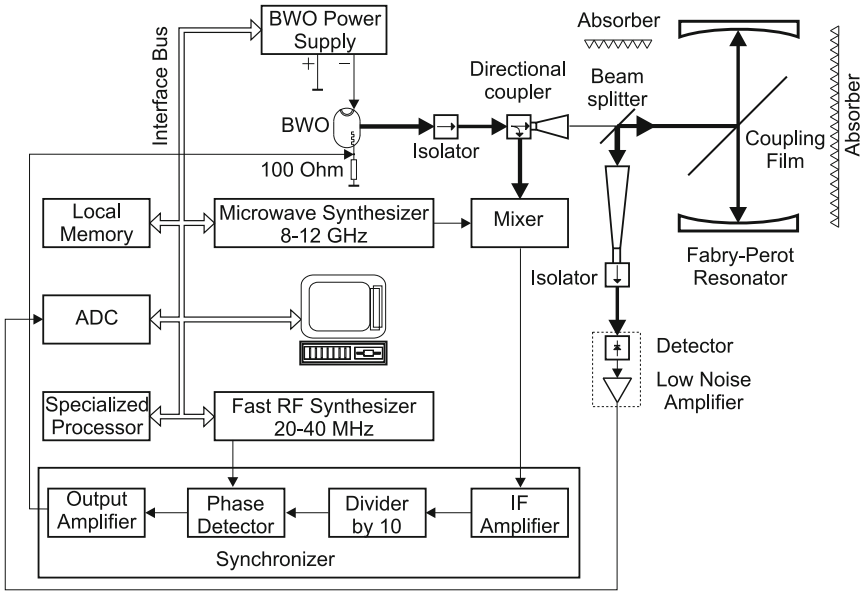

Figure 1. Block-diagram of the millimeter-wave broad band resonator spectrometer.

for precision fast scanning of the BWO frequency around the chosen central frequency. The radio frequency synthesizer provides frequency scanning without loss of the phase of oscillations (without phase jumps). Both synthesizers are computer-controlled. As a result, the BWO frequency is defined as

$$f_{\mathrm{BWO}} = n\, f_{\mathrm{MW}} - 10\, f_{\mathrm{RF}}, \tag{4}$$

where n varied from 4 to 20, and a factor of 10 before f_{RF} appears because phase detection was done at 10 times the digitally divided intermediate frequency (IF), which was 350 MHz. The main source of uncertainty in the measurement of the resonance width is the drift of the central frequency of a resonance during the time of measurement. To minimize this error one has to measure the resonance curve as fast as physically possible. Response time of the resonator itself equals $\tau \sim 1/\pi\Delta f$. In our case it amounts $\sim$ 2 ms. For precision measurement the observation time should be increased, say, 10 times, i. e. up to $\geq$ 20 ms. The microwave and the millimeter-wave synthesizers commonly used in spectroscopy employ indirect frequency synthesis and have therefore $\sim$ (10–50) ms switching time, thus preventing fast scanning of the resonance curve. A fast direct radio frequency synthesizer

with switching time 200 ns and time between switching 58 ms was used in this work as a source of a reference signal for the phase detector in the lock-in loop. Thus both precision and fast scanning of the BWO radiation frequency within 200 MHz around the central frequency defined by the microwave frequency synthesizer were reached. Scanning without loss of a phase permits the physical limits of the resonance observation time to be approached and reduces the source phase noise. The passed-through resonator radiation was received then by a low-barrier Schottky diode detector. The precision frequency control, signal acquisition, and processing were done by a computer. The results of each scan were recorded and processed separately. The automation system consisted of an IBM PC and a module containing an RF synthesizer and a data acquisition system. The main part of the module is a microprocessor with external memory. The RF synthesizer is based on direct digital synthesizer (DDS) and is able to generate a harmonic signal in the 20–40 MHz range with 0.03 Hz discreteness and without phase jumps at the switching.

A microprocessor controls the frequency of the synthesizer and synchronizes the data-acquisition process with the frequency steps. The frequency was changed by a triangle law, meaning forward and backward scan. The maximum number of points per one scan was 512. At each frequency point, the microprocessor collected the data several times from the ADC, averaged the obtained results, and stored the average into data memory. In such a way 32 of the 512 point triangle scans may be put into a local memory. The data were transferred then to a PC for further processing.

4. Procedure and results of the measurements

The basic procedure in resonator spectroscopy is to measure the width of the resonance. The experimentally observed resonant curve of the Fabry-Perot resonator at 85 GHz is presented in Fig. 2, as an example. The curve is a combination of 500 scans with a duration of 30 ms each, i. e. corresponding to the total averaging time 15 s. Each fast scan was processed separately, then resonant curves were combined so that their centers coincided to allow for obtaining the averaged curve in Fig. 2. The residual of the fit, shown in the lower part of the figure, indicates the adequacy of the fitting model. The increased noise on the line slopes corresponds to transformation of the phase noise of radiation into the amplitude noise. The width of the resonance (FWHM) was defined then as $\Delta f = 164728(20)$ Hz. The actually achieved accuracy of the resonance width measurements is 20 Hz. It corresponds to

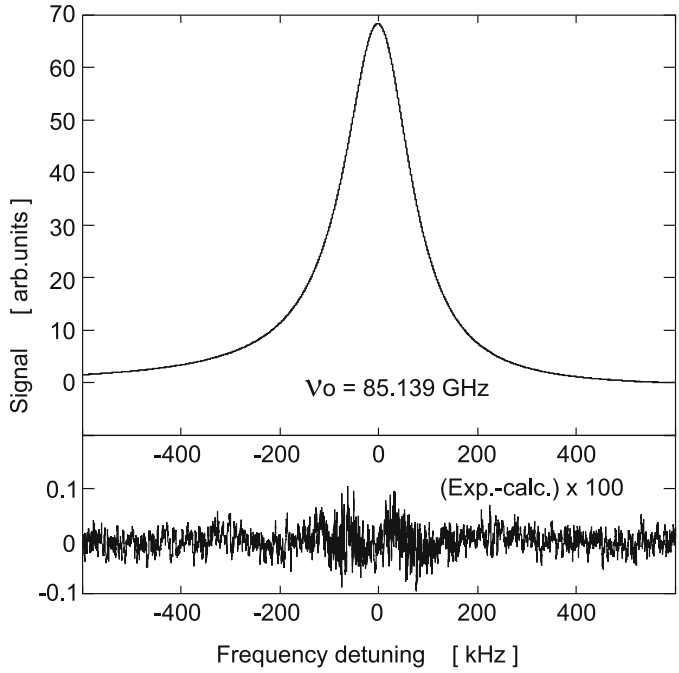

Figure 2. Observed Fabry-Perot resonator curve and its fitting to Lorentzian profile.

$4 \times 10^{-9}\,\mathrm{cm}^{-1}$ or 0.002 dB/km sensitivity limit (in absorption coefficient) of the spectrometer that exceeds by an order of magnitude the values characteristic to previously known analogous schemes [4].

The capabilities of the spectrometer were demonstrated with in *in situ* analysis of the laboratory air. Scans covering 44–98 GHz and 113–200 GHz were recorded in experiment for each range. The results are shown in Fig. 3. The spectra shown are the absorption band in atmospheric oxygen produced by magnetic dipole transitions between fine structure rotational energy levels [6] and [5], and electric dipole transition between rotational energy levels of water [2]. Broad scanning in these experiments was produced by jumping from one longitudinal mode to another without mechanical tuning of the resonator. The circles in Fig. 3 represent experimental points (after subtraction of the calculated resonator losses); solid line in the low frequency range corresponds to calculation according to [4]; residuals of the fit multiplied by 10 is presented at the bottom. The solid line in the higher frequency range is the Van Vleck-Weisskopf profile with an addition of the linear and quadratic frequency terms fitted to the experimental points to

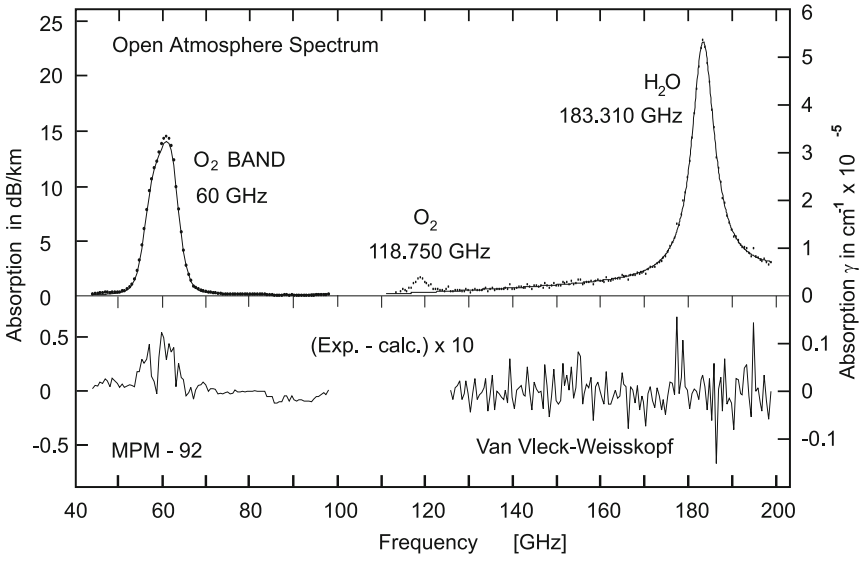

Figure 3. Experimental and calculated spectra of laboratory atmosphere.

account for the possible inaccuracy of the calculated resonator losses, nonresonance absorption in the air filling the resonator, and the wings of strong higher frequency water lines.

The departure of the calculated profile from the observed one is clearly seen in the residuals in Fig. 3 in the range of atmospheric oxygen band absorption. The nature of these regular deviations is not obvious as for now. It was found that the 183 GHz water line profile at atmospheric pressure fits the Van Vleck-Weisskopf shape with experimental accuracy over twenty halfwidths down and six halfwidths up from the line center. The measured integrated absorption coefficient for the water line coincides with the calculated one within 2%. Dry air broadening parameter for this line was found equal 3.985(40) MHz/Torr. This result is more accurate than those previously reported in the literature. First measurement of the 119 GHz oxygen line allowed for obtaining the air broadening parameter of 2.14(9) MHz/Torr. Within 10 halfwidths the line profile can be fitted nicely by the VVW lineshape [5].

5. Conclusion

Millimeter-wave resonator spectrometer have the highest presently available sensitivity among similar devices operating in that region.

The spectrometer allows for very wide frequency tuning range provided the BWO is used a radiation source. Similar techniques apply to the frequency range in excess of 1 THz and the submillimeter-wave resonator spectrometer can be constructed soon. Such instruments could be very useful for investigations of millimeter and submillimeter lines of conventional molecules under elevated pressure. These may play an important role in the studies of broad spectral features appropriate to unconventional atmospheric absorbers like dimers and other weakly-bound complexes.

Acknowledgments

The authors are thankful to Svetlana Tretyakova for her assistance in producing the camera-ready typescript and to the organizer of the NATO Advanced Research workshop "Weakly Interacting Molecular Pairs: Unconventional Absorbers of Radiation in the Atmosphere" for their interest to our work. Present work was supported in part by the Russian Foundation for Basic Research (RFBR) Grant and the Contract from the Ministry of Industry, Science and Technology of Russian Federation. The authors express their deep gratitude to these sources of support.

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