HIGH POWER MICROWAVE SPECTROSCOPY

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Abstract: Sources of coherent radiation, tunable over millimeter and sub-millimeter wavebands are successfully used in the absorption spectroscopy of molecules; the high sensitivity being provided by the Radio Acoustic Detector (RAD) with backward wave oscillator (BWO) as a radiation source[1]. However, as the RAD sensitivity is proportional to the applied microwave power, new opportunities can be provided by using a gyrotron. Demonstration experiment to detect the 6_{15}–6_{16} transition of HCOOH molecule had been already performed with a ~1 kW gyrotron[2]. In the future, fine-frequency-controlled gyrotrons are promising to observe highly exited vibration states of molecules, forbidden transitions of non-polar molecules and very weak lines of rare species in natural abundance[3].

Key words: molecular spectroscopy, nonlinear spectroscopy, radio acoustic detector, BWO, gyrotron, fine frequency control.

1. MICROWAVE RADIO ACOUSTIC SPECTROSCOPY

The RAD spectrometer (*www.appl.sci-nnov.ru/mwl/*) has been developed as a general-purpose laboratory spectrometer for study of high-resolution spectra in the mm and sub-mm wave regions. It has an excellent resolution; an extremely high accuracy of frequency measurements, a very good sensitivity and can operate in THz frequency region[1,4,5].

Fig. 1 presents a traditional block-scheme of the experimental setup (see also Fig. 3). A BWO tunable within a 30% frequency-range is phase locked against a harmonic of fundamental frequency of 78–118 GHz reference synthesizer (KVARZ, Nizhny Novgorod). BWOs cover 30–1200 GHz range), deliver tens of mW at 200–600 GHz and about 1 mW at 1.1 THz; they are produced by the ISTOK Microwave Inc. (*www.istok.com*). The line-width of a phase-locked BWO is about 1 kHz at 100 GHz and depends upon the

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BWO frequency, spectral purity of the reference synthesizer signal and the phase noise of a phase-lock loop (PLL) electronic circuits.

The synthesizer frequency itself, is stabilized against a rubidium standard (5 MHz, $\Delta f/f = 10^{-11}$) and controlled via computer. Microwave radiation incident on a cell with a gas sample is absorbed by molecules and the subsequent variation in pressure, due to heat energy released by the molecule upon return to the ground state, is detected by an acoustic cell (RAD spectrometer). The sensitivity of the technique arises from the inherently high efficiency of thermal conversion that occurs in microwave absorption processes. This is combined with a similar efficiency in a highly sensitive microphone that converts the acoustic wave into a voltage signal.

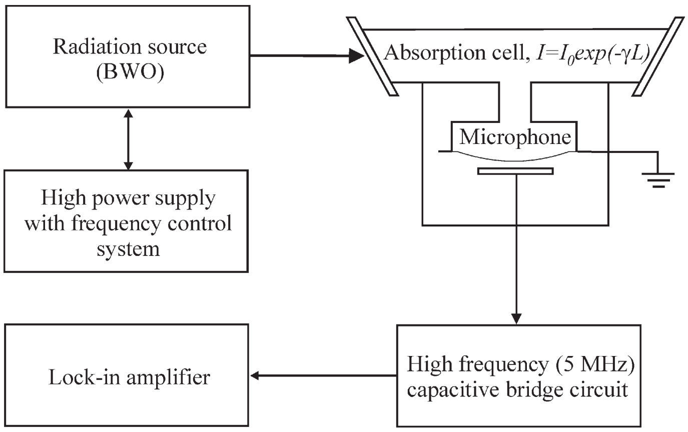

Figure 1. Block–diagram of experimental setup with RAD spectrometer.

The main advantages of the acoustic detection technique are as follows:

- the zero base line detection – the radiation power is practically unabsorbed apart from a spectral line;
- the sensitivity comparable with sensitivities of cryogenic detectors (but much less cost if to compare with the liquid-He InSb bolometer);
- the signal-to-noise ratio (SNR) proportional to the radiation source power;
- the extremely broadband detection from microwave to optic range (that depends on cell windows transparency only);
- sample under study and detector itself are combined in one unit.

The small size of the acoustic cell (our cells are about 10 cm length, and 2 cm diameter) also permits better temperature stabilization of the sample and provides easier studying; for example, a molecule such as oxygen[6] being sensitive to Earth magnetic field. Acoustic cell could be also used for measurements of radiation power[7] with max speed of response 1-10 kHz.

As an example, the line profile measurements of weak (N, J) = (7, 6) – (5, 6) rotational transition of oxygen ($^{16}O_2$) molecule at 1.12071484(5) THz are presented in Fig.2 (at the left) together with the fit to Voigt line profile[6]. Another example of line-widths of 118.75-GHz oxygen line, retrieved from the line shape measurements, broadened by pressure of different foreign gases[6b] are presented as part of Fig. 2. Very small deviations of the line widths from the linear pressure dependence (see residue in Fig. 2, below at the right) have demonstrated the high accuracy of the line shape measurements with RAD spectrometer. Such data are very important for earth observation systems.

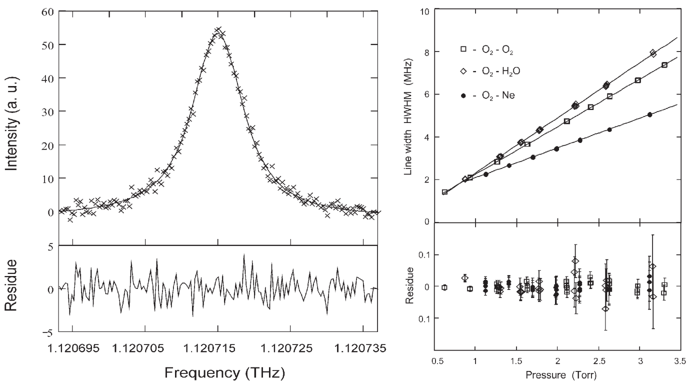

Figure 2. Record of the (N, J) = (7, 6) – (5, 6) of $^{16}O_2$ rotational line. (central frequency is 1.12071484(5) THz). Experimental points are denoted by cross (+), the line (—) represents the fit to Voigt line profile; bottom trace is residuum of the fit. *(Left*). The 118.75-GHz self-broadened line widths (boxes), broadened by Ne (circles), and by water (diamonds); linear regression fits to the data are shown by solid lines, the residua of the fits are shown below. *(Right*).

2. OPPORTUNITIES TO USE GYROTRONS IN SPECTROSCOPY

Gyrotrons capable of delivering $10^3 - 10^6$ W power in the millimeter and sub-millimeter wavebands are very attractive for molecular spectroscopy. A free running, non-stabilized, ~1 kW gyrotron in combination with the RAD has already been used to detect the 6_{15}–6_{16} transition of HCOOH molecule[2]. The SNR was about ~6000. The relatively broad line of formic acid HCOOH was chosen to eliminate noticeable power broadening effect of the line and as a result, the possible changing of the line intensity.

However, advantages of the gyrotron can be demonstrated in a full scale system, e.g., for measurements of the spectral line profile and line center shift versus power that is very important for studying non-rigid molecules similar to the water. However this is only possible when fine frequency control is available, that can be done by using a phase-locking loop (PLL) scheme (Fig.3) similar to that used to control BWO frequency. A fraction of the gyrotron radiation split off by a directional coupler is combined in a harmonic mixer with the output of a frequency synthesizer. The frequency difference between the gyrotron and a harmonic of the frequency synthesizer is constrained to 350 MHz by a PLL synchronizer. The error signal produced by synchronizer is then amplified and applied to the gyrotron as additional high voltage power supply. Electrical frequency tuning could be done during a few microseconds. The only difference from the BWO case is the use of a high voltage video amplifier of sufficient power.

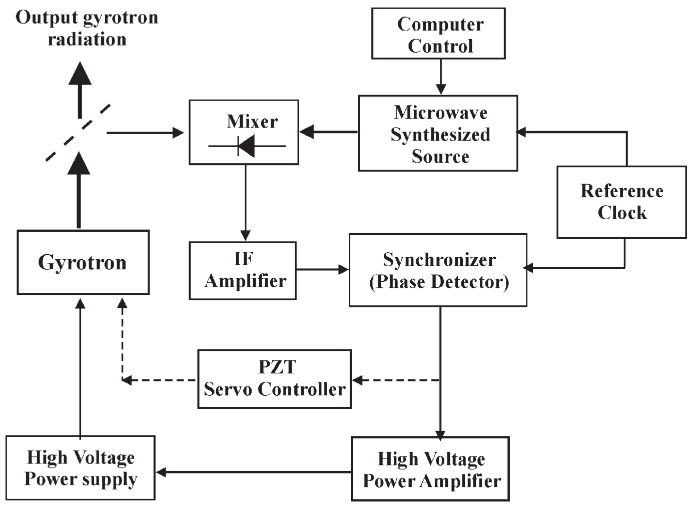

Figure 3. Block-diagram of the gyrotron frequency stabilization system.

This scheme provides the electrical tuning within the gyrotron cavity bandwidth $\Delta\omega \sim \omega / Q$, where the quality factor Q is usually around 1000 and can be specially reduced to some hundreds. This natural cavity bandwidth can be expanded by using two, coupled cavities[8]. In an X–band gyrotron, the frequency was tuned within 1%.

A slow broadband tuning of the gyrotron can be provided by changing the magnetic field in the solenoid and by changing parameters of the cavity, by changing the separation between mirrors in a two-mirror cavity, or by the position of conical rod in a coaxial cavity.

3. POTENTIALS OF HIGH POWER MICROWAVE SPECTROSCOPY

A thorough review of high power spectroscopy can be found in a book by *Letokhov and Chebotayev*[9]. Compared to the optical case, the spectroscopy at microwave frequencies is featured with a very low probability of spontaneous emission between quantum levels. At the sub-millimeter waveband, such a nonlinear effect as power saturation, or power line broadening, in addition to collision broadening of Lorentzian lines, of rotational transition of dipole molecules, reveals itself at power only of a few milliwatts. It could be observed in the form of so-called Lamb dip[10] in

Doppler broadened line, which favors increasing the frequency resolution. The absolute value of the Lamb dip is usually quite small to observe it directly[1] in a spectral line. To enhance the observation of this effect, the frequency modulation technique is used for waves traveling in opposite directions (standing wave). High power could allow observing it directly as effect of nonlinear transparency.

The saturation mechanism of nonlinearity was used for experimental demonstration of phase conjugation of gyrotron radiation by degenerate four-wave mixing in gaseous carbonyl sulfide[12] (OCS). A phase-conjugate signal restores the initial wave front automatically when it propagates backward through an optically inhomogeneous medium (real atmospheric conditions could be an example).

Another application of high power in molecular spectroscopy was considered[3] in the form of inducing the electric dipole moment in non-polar molecules by strong microwaves to detect forbidden transitions. As distinct from the dynamic Stark effect, the molecule acquires asymmetry or induced dipole moment via non-resonant enhancing of one of the vibrational states of this molecule. Here is also an advantage of the RAD technique to bring out such a little effect against a powerful background signal.

High microwave power allows Doppler-free two photon transitions, as it has been shown by Surin et al.[13] in 150 GHz region. There, it used a millimeter wave generator called OROTRON, together with intracavity-jet technique. The generator power was estimated to be approximately 1 W/cm^2. Such a power level was enough to detect two photon absorption signals of OCS and CHF_3 rotational transitions. So, kilowatt power level of gyrotrons could increase observable frequency range of molecular transitions by the multi-photon absorption technique.

It is well known that the upper frequency limits of sub-millimeter microwave spectroscopy is gained by using both frequency multiplication from powerful microwave radiation sources and primary sub-millimeter wave radiation sources are around 1 THz[7,14]. But, the extension of radiation frequency into THz range by employing moderate power (~1 kW) gyrotrons for frequency multiplication looks very promising for further development of this technique. Such systems look expensive, but nevertheless they are competing in price with laser sideband systems used for generation in the THz range.

The high sensitivity which can be obtained with high power gyrotrons would give opportunities to detect very weak lines of rare species in natural abundance. For example, the lines of oxygen isotopes and especially less

[1] The direct observation of the power saturation effect in sub-Doppler rotational line of water vapor (at 183 GHz) was first demonstrated by Fabry-Perot resonator technique[11] in form of a peak at resonance curve.

populated higher energy vibrational/electronic states in atmosphere such as oxygen $a^1\Delta_g$ state, having importance for supersonic jet traces detection, and for understanding stratosphere ozone photochemistry. Gyrotrons with frequency-control could be used for monitoring the water contamination in chemical processes[15], for detection of some toxic pollutants such as SO_2, NO_2, N_2O, CO, ClO, H_2O_2, HNO_3, HCN, CH_3CN species; etc[2].

4. ACKNOWLEDGEMENTS

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[2]We hope that gyrotrons with frequency stabilization give new possibilities and widen their application making impacts not only in spectroscopy, but in such areas as radar and plasma research**.**

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