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STUDY OF THE H_2CO PRESSURE LINESHIFT USING A MILLIMETER-WAVE RAD SPECTROMETER WITH A SOLID-STATE REFERENCE-FREQUENCY SYNTHESIZER

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A 4-mm-wave RAD spectrometer with a solid-state reference-frequency synthesizer (a microwave synthesizer) is described. The use of a microwave synthesizer allows one to construct a compact, easily automatized system for control and measurement of the frequency of a radiation source and covers all basic needs of microwave spectroscopy in the 4-mm-wave band. The spectrometer was used for measuring the pressure lineshift and broadening of the H_2CO $1_{01}-0_{00}$ line. The parameters obtained are equal to $\Delta\nu_C = +4.8 \pm 0.3$ MHz/tor for the line shift and $\Delta\nu_Y = 27 \pm 3$ MHz/torr for line broadening. Some possible applications for the spectrometer are discussed.

Microwave spectroscopy in the millimeter- and submillimeter-wave regions is used for investigating the structure and properties of molecules [1-4]. Systems for precise control and measurement of the frequency of spectroscopic radiation sources in millimeter- and submillimeter-wave microwave spectrometers allow one to determine the exact position of spectral lines with high resolution (10^{-8} or better), but such systems are very complex and are the least reliable element of these spectrometers. Further development of microwave spectroscopy requires the construction of a compact, easily automatized system for precise control and measurement of the frequency of radiation sources in the millimeter- and submillimeter-wave regions. This study describes a 4-mm-wave microwave spectrometer with a solid-state reference-frequency synthesizer (a microwave synthesizer) and presents the initial results obtained using the spectrometer.

1. Description of the System. The schematic of a 4-mm-wave RAD spectrometer with a microwave synthesizer is given in Fig. 1. Radiation from a 4-mm-wave backward-wave tube (BWT) passes through a cell filled with gas, and an acoustic detector receives the signal from the power absorbed by the gas at line absorption frequencies [3]. The frequency of the BWT is stabilized at the harmonic of the reference signal obtained at a mixer-multiplier through a phased frequency autotuner (PFAT). The reference signal is created by a solid-state microwave synthesizer. For convenience, the amplitude or frequency of the BWT is modulated, and only the variable component of the gas pressure with a modulation frequency of 180 Hz is taken. The spectrometer cell, the acoustic detector, and the PFAT for the BWT are similar to those devices used in [5]. The centimeter-wave microwave synthesizer is a new element of the system and is briefly described below.

The microwave synthesizer generates an electrical signal with a highly stable frequency in the range of 1.0-17.85 GHz and consists of a primary block and several auxiliary microwave blocks which cover the indicated range. The primary block is used for controlling the signal input into the microwave blocks and forms a spectrally pure oscillation centered at a frequency of 100 MHz with an oscillation range of 80-120 MHz which is changed in steps of 40 kHz or 4 Hz, depending on the modifications used. The microwave blocks consist of solid-state microwave generators which are stabilized by PFATs. In this study, we will use a microwave block which operates in the range of 8-12 GHz. The features of the synthesizer include a wide frequency range, fine-tuning of the frequency, a low level of phase noises which is

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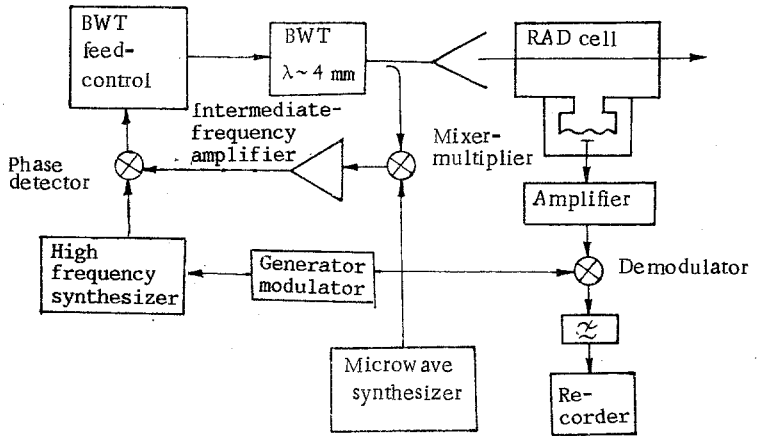

Fig. 1

independent of the output frequency, and the possibility of controlling the basic parameters through a computer. A simplified block diagram of the microwave synthesizer is given in Fig. 2, its basic characteristics are shown in Table 1, and the general form of the microwave synthesizer is illustrated in Fig. 3.

The microwave synthesizer consists of three basic blocks, as indicated in the schematic of Fig. 2 by dashed lines.

In the reference frequency block, the reference signal generator puts out two reference oscillations with frequencies of 2 and 100 MHz. The reference generator consists of either an internal 5 MHz quartz generator or an external source of stable oscillations with frequencies of 1, 5, or 10 MHz (a quartz or quantum mechanical frequency standard). For improving the spectrum of the oscillation at 100 mHz, a synchronous quartz generator is used whose frequency is synchronized with the harmonic of the reference generator by a narrowband PFAT (with a bandpass of 100 Hz). For preserving the coherence of the oscillations at 5 and 100 MHz the spectrum of the reference generator at 100 MHz is determined only by the spectrum of the quartz generator's phase noises at 100 MHz, which are substantially less than those obtained by directly multiplying the oscillation frequency at 5 MHz. The technique for optimizing such a PFAT system was considered in [6]. Oscillations with a 2-MHz frequency are obtained by dividing a signal with a 100-MHz frequency using a digital frequency divider.

The shortwave synthesizer block has two modifications, which differ in their frequency stepping, and consists of a PFAT with ChFDs [7] and "sample-memorize" phase detectors. For a 100-kHz frequency step one PFAT with a phase detector is used which operates on the fifth harmonic of the reference frequency. Finer tuning is obtained by including three PFATs (see Fig. 2). The PFAT with the phase detector operates in the range of 120-160 MHz in steps of 40 kHz. The frequency of the output signal is divided by 100 times and is used for interpolation in the summation PFAT of the output generator. The third PFAT for 78.8-118.4 MHz permits frequency steps of 400 kHz through the use of a divider with a preprogrammed division coefficient. The bandpasses of the shortwave block's PFATs are in the range of 5-20 kHz, i.e., at frequencies which are more than 20 kHz away from the carrier, and the noise spectrum of the output signal only contains the noises of the synchronous generator at 80-120 MHz.

The microwave synthesizer block contains two Gann diode PFATs which are tuned by changes in the frequency of an iron-yttrium garnet generator (an IYG generator). There are two oscillations at the output of the Gann PFAT: one from a generator with a frequency of 80-120 MHz, and the second with a frequency which is a multiple of the 100 MHz reference frequency. Selection of the necessary number of 100 MHz harmonics, suppression of unwanted harmonics, and frequency transmission in the microwave region are done using the auxiliary PFAT of the second Gann generator with a stroboscopic phase detector and a digital integrator [8].

The high Q-factor of the IYG generator's resonator allows one to obtain an almost constant level of phase noises at frequencies up to 18 GHz. At frequencies off of the carrier (by about 100 kHz), the phase noises are not functions of the multiplication coefficient for the 5 MHz reference frequency. The bandpasses of the PFATs in the microwave synthesizer are selected to optimize the noise characteristics of the signal [6].

TABLE 1. Basic Microwave Synthesizer Characteristics

Parameter	Parameter values	Remarks
Frequency range, GHz	1 — 2 2 — 4 4 — 8 8 — 12 12 — 18	With interchangeable blocks
Tuning step, kHz	100 0,01	Depends on modification
Frequency instability, $\delta\nu/\nu$		
after 1 sec	$4 \cdot 10^{-11}$	With an internal reference frequency generator at 5 MHz
0,1 sec	$4 \cdot 10^{-10}$	
0,01 sec	$1 \cdot 10^{-9}$	
0,0001 sec	$6 \cdot 10^{-8}$	
Output power, mW	from 2 to 10	Depends on range
Output power regulation, dB	from 0 to 70	
The level of spurious components relative to the carrier, dB		
Harmonic	20	
Non-harmonic	60	
The level of phase noises relative to the carrier, dB/Hz, for tuning at		The spectral power profile for the synthesizer oscillation is close to Lorentzian
100 Hz	40	
1 kHz	75	
10 kHz	90	
100 kHz	95	
Transfer time, msec		
across 1 MHz	18	
across 100 MHz	50	

The microwave synthesizer described above can be used in many different radio electronic systems as a calibration source.

The microwave synthesizer is connected to the PFAT of a 4-mm-wave BWT through a mixer-multiplier. The microwave synthesizer's output power is on the order of a few milliwatts in the 3 cm region, which is more than sufficient for obtaining signal beats between the seventh or eighth synthesizer harmonic and the oscillations of the 4-mm-wave BWT.

The BWT oscillations must be modulated for observing spectral lines with such a spectrometer. Figure 4 shows the spectral line 1_{01}-0_{00} for H_2CO obtained using amplitude modulation induced by a mechanical interrupter mounted on the axis of a synchronous motor. The frequency stepping was selected as 800 kHz for clarity. Discrete tuning of the frequency was done with a microwave synthesizer. The smallest frequency stepping was obtained by replacing the 80-120-MHz source with a discrete high frequency synthesizer or by returning the reference frequency oscillation in the 4-mm PFAT.

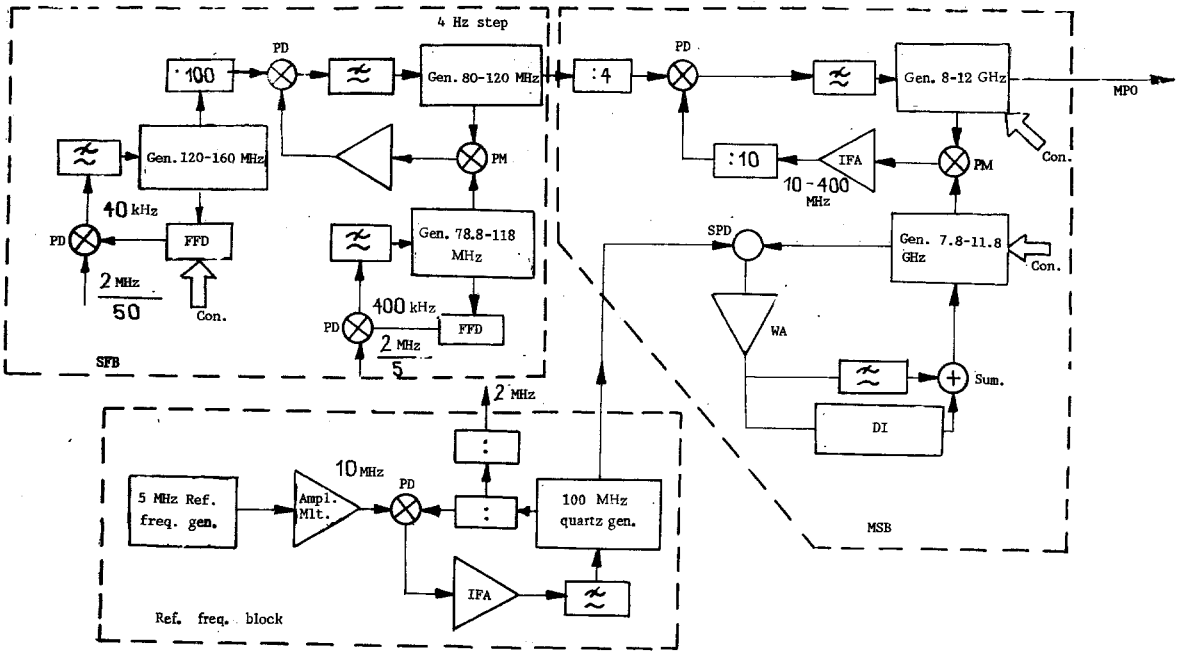

Fig. 2. SPD) stroboscopic phase detector; MSB) microwave synthesizer block; MPO) microwave power output; IFA) intermediate frequency amplifier; PD) phase detector; FFD) fixed frequency divider; SFB) shortwave frequency block; PM) power mixer; WA) wideband amplifier; DI) digital amplifier; Con.) control; Sum.) summator.

Frequency modulation was also used in place of the 80-120-MHz source for determining the center frequencies of the spectral lines.

Measurements for the frequencies of the known lines of N_2O were made for calibrating the system. These measurements indicate that the measured and calculated frequencies of the lines coincide with an accuracy of 0.2 MHz. The sensitivity of the RAD spectrometer using the BWT control system described above is normal.

These measurements also show that the accuracy in controlling the BWT frequency is greater than the accuracy in measuring the frequencies of the spectral lines. The chief source of errors in measuring the frequencies of lines in the 4-mm-wave region is the frequency dependences of the BWT output power and the microwave waveguide characteristics, including the cell. Observation of spectral lines on the sloped sections of the waveguide and BWT frequency dependences naturally leads to shifts in the observed center of the spectral line. The quantity of this error for wide lines is on the order of hundreds of kilohertz, but is substantially less between the horn of the BWT and the cell of the microwave filter and can be further decreased by using an absorber for preventing reflections from the flanges of the absorbing cell. For increasing the accuracy in measuring the spectral lines, the frequency characteristics of the microwave waveguide and the BWT must be uniform.

The spectrometer discussed above was used for studying pressure line shifts for molecules.

2. A Study of Pressure Line Shifts. One application of an RAD spectrometer with a compact, automatized system for precise control of the frequency of a spectroscopic radiation source is to measure the pressure frequency shifts of "test" spectral lines. The lineshifts are in the first approximation determined by the average dipole moment of the gas molecules and are for higher approximations specified by the highest moments of the molecules, by their isotopic composition, etc. (e.g., see [9, 10, 11]). An instrument which can measure the average dipole moment of gas molecules [9] can be used for studying intermolecular interactions and for "integral" analysis of gases with polar or nonpolar impurities, of different molecular combinations, etc. Such a technique is related to refractometric analysis, where the integral characteristics of the investigated substance are also determined. One must also find suitable spectral lines which can be used as "test" lines. A "test" line must possess a sufficiently large shift parameter with high enough intensity, which specifies its "sensitivity," and it must be positioned at a convenient frequency. Hence, we chose the line

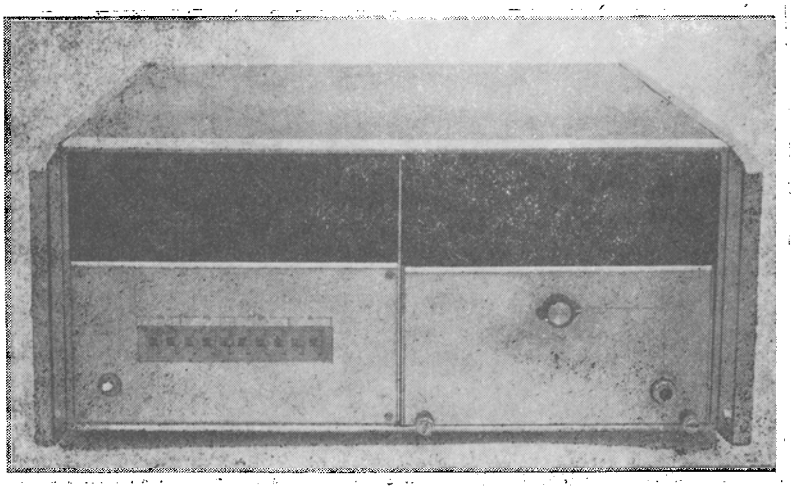

Fig. 3

for the lower rotational transition 1_{01}-0_{00} of H_2CO, which is positioned in the 4-mm-wave region. Study of shifts in this line is pertinent for understanding the phenomenon of pressure shifts.

The molecule H_2CO is a weakly asymmetric top with a large dipole moment μ_a = 2.331(30) [12]. The frequency of the lower rotational transition J + I ← J(1_{01}-0_{00}) for the molecule $H_2{}^{12}C^{16}O$ is equal to ν_0 = 72837.974(24) MHz [12]. The pressure shifts of the H_2CO millimeter-wave lines have been investigated in [13], where several families of transitions with K_{-1} = 0 (J = 2 − 1, J = 3 − 2), K_{-1} = 1 (J = 2 − 1, J = 3 − 2, J = 4 − 3), and K_{-1} = 2 (J = 3 − 2) were considered along with several individual transitions with higher values of J. Substantial pressure line shifts (up to 2.47 MHz/torr) were observed by [13] in H_2CO for the transition 2_{12}-1_{11}. The data in [13] indicate the general increase in the quantities of the shifts for each family of transitions with a decrease in the quantum number J. Therefore, the transition 1_{01}-0_{00} is of special interest because it is the rotational transition with smallest quantum numbers. The shift for the transition 1_{01}-0_{00} was not studied in [13].

We will consider the possible quantity for the pressure shift parameter of the transition 1_{01}-0_{00}. Unfortunately, the calculations in [13] gave only theoretical values for the shifts, which differ even in sign from the experimental values. In general, pressure line-shift calculations for transitions in a molecule similar to an asymmetric top are complicated (e.g., see [14]). Nevertheless, one would at least like a rough estimate of the expected effect, and, therefore, we made semiempirical estimates for the shifts of these lines. We started with the assumption that for "rough" and short term processes, such as the interactions of molecules during collisions (which leads to broadening and shifting of lines), one can apply the results obtained in previous studies of broadening and shifting of similar lines for symmetric molecules to weakly asymmetric molecules such as H_2CO. The criterion for using such an approach [10] must be the triviality in the changes of the molecular dipole moment orientations after collisions. Estimates for a series of asymmetric molecules are given in [10]. For H_2CO the collision time is about $\tau \approx 2.4 \cdot 10^{-12}$ sec. This time is less than the period of rotation for an absorbing molecule $1(B + C) \approx 1.4 \cdot 10^{-11}$ sec. The rate of change in the orientations of the perturbing molecules, i.e., in contrast to symmetric molecules, is determined by the quantity of K-splitting of the rotational levels, which sharply decreases with an increase in the quantum number K_{-1} [12-15]. When averaging the populations of the H_2CO rotational levels at room temperature, the fraction of levels with noticeable K-splitting is extremely small, and one can, therefore, use previous results obtained for symmetric molecules [10, 11]. The J = 1–0 transition investigated in a number of other molecules in [10, 11] is similar to the 1_{01}–0_{00} transition of H_2CO in symmetric-top molecules. A reliable method for making estimates is to extrapolate the quantity of the shifts to the smallest values of J and K for the experimental shifts of other H_2CO lines [13] using data for the lineshifts of symmetric molecules as functions of the quantum numbers J and K [10, 11]. Using the data in [13] for the transitions with the largest shift parameters (2_{02}-1_{01}, 2_{12}-1_{11}, 2_{11}-1_{10}), one can estimate the self-shift parameter of 1_{01}-0_{00} to be $\Delta\nu_C$ = +5.2 MHz/torr with an average spread of about 12%. One should note the substantial errors in the measurements of the shift parameters in [13], which undoubtedly contribute to the high spread in the data. The expected shift parameter for the line 1_{01}-0_{00} is significant; shifts in this parameter for the millimeter-wave region were not observed earlier.

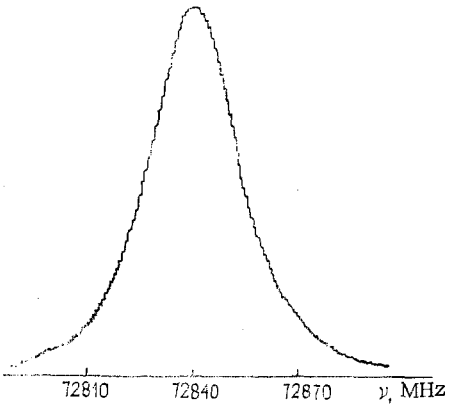

Fig. 4

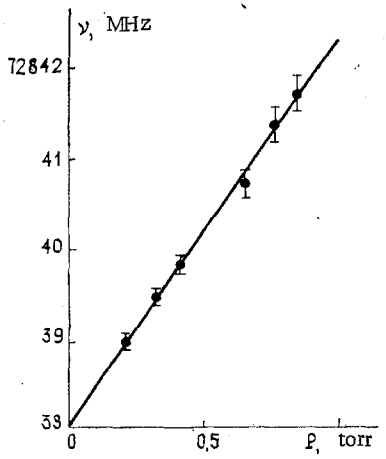

Fig. 5

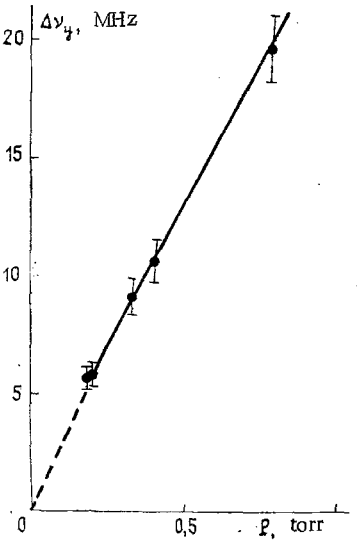

Fig. 6

The experimental dependence for the pressure lineshift of 1_{01}-0_{00} for H_2CO using the spectrometer described in the previous section is shown in Fig. 5, the corresponding dependence for pressure broadening is given in Fig. 6, and the experimental quantities for the self-shift and self-broadening of the spectral line 1_{01}-$0_{00}H_2^{12}C^{16}O$ are indicated in Table 2.

The results show that the experimental quantity for the self-shift parameter agrees with previous estimates to an accuracy (for the experiment in this study and in [13]) of 8%, which indicates the reliability of the results in [10, 11, 13] and the correspondence between the various representations of the mechanism behind the line shifts.

In summary, this study has described a microwave RAD spectrometer with a solid-state reference frequency synthesizer (a microwave synthesizer). The high stability of the frequency and spectral purity of the oscillations from the microwave synthesizer allow one to use the device in microwave molecular spectroscopy for high resolution in the 4-mm-wave region. The use of a microwave synthesizer sharply reduces the size of the system and increases the capacity for conducting spectroscopic research. The spectrometer can be used for regular spectroscopic investigations, and can also serve as a basis for perfecting the industrial RAD spectrometer in [16] and creating a specialized spectrometer for measuring pressure lineshifts in gases for studying the properties of molecules and intermolecular interactions. In the future, we hope to increase the frequency range of our spectrometer to the submillimeter range.

Pressure broadening and lineshifts in H_2CO were studied using our spectrometer. The study allowed us to relate the regularities in the shifts observed in symmetric molecules to those observed in asymmetric molecules such as H_2CO. The predicted sign of the shift parameter for the transition 1_{01}-0_{00} coincides with the measured value. The predicted quantity of the shift parameter for the same transition also coincides with the measured values within

TABLE 2

$\Delta\nu_c$	$+4{,}8\pm0{,}3$ MHz/ torr
$\Delta\nu_y$	27 ± 3 MHz / torr

($\Delta\nu_y$ is the half-width of the line at half the intensity.)

the experimental error tolerances. These results indicate that the basic representations of the mechanism behind pressure lineshifts are correct. The measured value for the shift parameter of the line 1_{01}-0_{00} is the largest of those obtained in the millimeter-wave region, which makes it useful as "test" line for studying molecular properties and intermolecular interactions and for integral analysis of gases through pressure shifting of frequency.

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