DEVELOPMENT OF A PHASE-LOCK SYSTEM UP TO TERAHERTZ FREQUENCIES IN MICROWAVE OSCILLATORS

A. F. Krupnov UDC 537.86; 621.37

The development of a phase-lock system up to the highest frequencies greater than one terahertz in microwave oscillators is considered. Applications of such systems for physical and technical measurements are discussed.

1. INTRODUCTION

The phase locking (PL) was proposed by De Bellescize [1] in 1932 as a method for reception of weak signals. Afterwards, the advantages of a PL system were recognized as being of primary importance for the frequency stabilization of oscillators by the reference signal with complete exclusion of frequency error. As the frequency range of the radio methods was broadened in the fifties, the PL systems began to master microwaves [2]. Phase locking of microwave oscillators by the reference frequency harmonic is virtually a unique method for transfer of the stability of frequency standards to an arbitrary point in the wave range used by modern radio methods and provides a basis for high-precision microwave frequency synthesizers. Frequency synthesizers are closest to a "tunable but stable in frequency" coherent source, which is ideal for radio engineering, and are an important characteristic of assimilation of the wave band. Besides the absence of frequency error in PL systems, which is exactly the factor that provides for the creation of large systems of high-precision digital frequency control, we will also mention the fineness of the PL method. The author of this method understood that the beats of reference and stabilizing signals themselves possess the properties of a phase disciminator and the beat voltage, if large enough, can represent the control signal itself in the simplest version of a PL circuit. Closing the PL circuit requires only the use of a voltage-controlled oscillator (VCO). The technique of frequency synthesizers with digital control is fully compatible with the modern computer technique used for the control of experiment and collection and processing of data.

Modern PL systems were considered in tens or even hundreds of books, mainly written by foreign authors (in Russian, see, e.g., [3]). Only the last catalogue (November-December 1997) issued by one publishing house includes at least ten books devoted to phase locking [4].

In 1958, Bershtein and collaborators implemented, for the first time in the USSR, a PL system for microwave oscillators (3-cm wavelength klystrons) by the harmonic of a quartz oscillator (with frequency about 75 MHz) [5]. As follows from the description, this system had considerable advantages over the previous construction proposed by Peter and Strandberg [2]. The reasonable design of the new system, including the tuning procedure, ensured its easy mass production.

Obviously, the consequences of their study were even greater than those known to the author of the present paper. In particular, I think that the advent of a PL system of microwave oscillators in Nizhny Novgorod and the appearance of a microwave frequency synthesizer for the first time in Russia (developed at Kvarts, Scientific and Production Association of Nizhny Novgorod, former Instrumental Research Institute) were not a mere coincidence.

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We were privileged to use the version of PL system developed immediately by Bershtein and collaborators [6] in our work at improvement of high-resolution beam spectrometers described in [7, 8]. In this version, the frequency of a 10-cm klystron was stabilized by the generation frequency 1.25 cm of an ammonia maser. A spectroscopic result was the resolution of the splitting of the maser line J=3, K=3 of ammonia $^{14}NH_3$ [9] due to the difference between inversion levels equal to one-thousandth of the quadrupole constants (earlier, only the quadrupole splitting itself was resolved). A "technical" result of this work, which remains unsurpassed, was the obtaining of a 240-Hz width of one component of the molecular spectral line. Besides the two-meter length of the molecular beam reached in our studies, the observation of such a narrow line also required high quality of the transition-inducing microwave signal provided by the PL system fed from an individual molecular oscillator. This result was also mentioned by Laine in his latest review [10].

The objective of the present paper is narrower. We only follow the development of the high-frequency branch of PL to the highest frequencies of the existing electron oscillators, which exceed one terahertz at present, and mention some physical and engineering applications of such systems. A large contribution in this field was given by specialists from Nizhny Novgorod. Microwave spectroscopy was first in the radio-engineering mastering of increasingly shorter wavelengths (see, e.g., [11, 12]). Our goal was to assimilate the submillimeter wave range by the methods of microwave spectroscopy, using primary sources of the radiation (see [12, 13]) in which PL systems were very important. The results were published mainly in spectroscopic journals. However, the development of PL systems is also of general physical importance, and the results obtained in this field also apply in other areas of science and engineering. Hence, it seems reasonable to use this opportunity, which coincided with the completion of a certain stage, for writing a miniature review. Without going into the details, we will give references for the reader willing to gain more information on the subject.

2. MASTERING MILLIMETER AND SUBMILLIMETER-WAVE BANDS

In mastering these wave bands by frequency methods, we chose the way of active high-precision control of the source frequency, which gives one considerably greater opportunities than the easier way of passive measurement of the frequency; of course, the problem of frequency measurement is also solved in this case. Moreover, unlike many other methods, we used continuous covering of the frequency range. In the seventies, the idea and scheme of PL were common knowledge. However, the transition to higher frequencies also meant the transition to a different type of electron oscillators. The reflecting klystrons employed in the first microwave PL circuits were closest to being defined as "voltage-controlled oscillators." Backward-wave oscillators (BWO) were and still are an exceptional type of oscillators which cover the millimeter (mm) and submillimeter (submm)-wave bands continuously. They have even a broader band for electron frequency control through the high voltage of the decelerating system; however, this required the development of control elements with bands broad enough for provision of stable operation of the PL system in a BWO. This also required the creation of a reference signal source for continuous covering of such a high-frequency range and efficiency of the PL system of BWOs over a large dynamic range.

The operation of the first PL system for mm and submm-wave BWOs of type [14] at up to $\sim 350~\mathrm{GHz}$ frequencies was demonstrated by us in 1970 [15]. Later, the frequency range of PL systems in BWOs was extended to 500 GHz in 1976 [16], 600 GHz in 1979 [13, 17], and 820 GHz in 1984 [18]. The development of PL systems for submm-wave BWOs was also started in France [19] on the basis of Thomson-CFS submm-wave BWOs (400-500 GHz). The next significant step, which allowed us to master a wide terahertz region for PL systems, was made after the development of a mm-wave commercial synthesizer. In 1994, together with the University of Cologne, we mastered at first a range of up to 970 GHz [20] (see also [21]) and demonstrated the possibility of a single scan with a length of up to 200 GHz in the PL mode of a BWO. The scheme of installation of a BWO PL system in a spectrometer [20] is given in Fig. 1. This scheme shows the main features of the setups operated at present in Cologne and Lille over a range of up to 1.2 THz (improved in [22]). The operations with the setups created together with the University of Lille are described in [22-25]. In 1997, such a terahertz apparatus was transferred from Cologne to Japan [26].

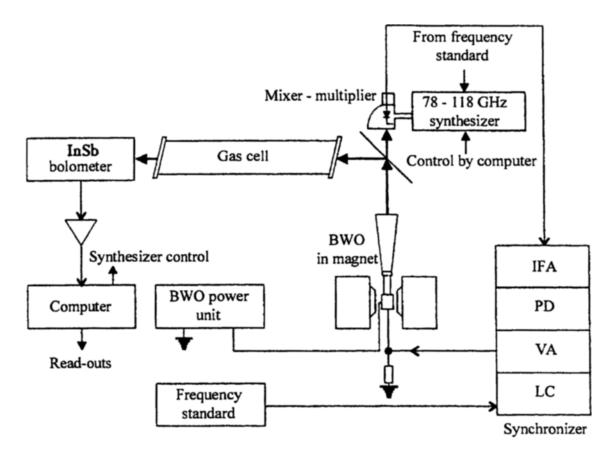


Fig. 1.

The main features of a modern BWO PL system for stabilization of all BWOs, including the highest frequencies (Fig. 1) [20], are as follows. The master oscillator is a computer-controlled mm-wave synthesizer of type [27], which is often stabilized by the quantum frequency standard. The wideband mixer is a multiplier which most often has the quasioptical construction with a planar Schottky diode developed at the IAP RAS and operated in BWO PL circuits at frequencies from 200 GHz to 1.2 THz [20, 22, 26]). * The system also includes an intermediate-frequency amplifier (IFA) in the 350 MHz region, which often has HEMT uncooled preamplifier ($T_{\text{noise}} \sim 40 \text{ K}$) and an effective automatic manual control (AMC) system, and a digital phase detector (PD) operated at a ten-times divided frequency (35 MHz), † as well as a final video amplifier (VA) with bandwidth about 3 MHz (and control of currents of up to 50 mA). The synchronizer is controlled by logical circuits (LC). High voltage at BWOs is usually varied from 500 to 5 500 V. The steepness of the BWO characteristic is 50–100 MHz/V on the average (and sometimes reaches 150 MHz/V).

The development of laboratory BWO PL systems also led to their "technical" improvement and the creation of frequency synthesizers on their basis. The history of development of mm-wave frequency synthesizers from laboratory to commercial ones is seen from [32, 33, 27]. The first mutual work with Kvarts, which contained the main features of a mm-wave synthesizer (a microwave synthesizer of 10–12 GHz, a mixer-multiplier, and a PL ring of a mm-wave BWO) was published in 1985 [32]. In 1990, we described the above-mentioned mm-wave commercial synthesizer and a laboratory BWO PL system of up to 370 GHz, which had the same construction but was closer to a synthesizer [33]. At a later time, the efficiency of such

^{*}A similar construction is also operated as a frequency multiplier at up to 1.5 THz [28, 29] and as a mixer-multiplier in a FIR laser spectrometer at side frequencies of up to 2.5 THz [30, 31].

[†]A pulsed phase-frequency detector [3] combines the properties of phase and frequency detectors in one device (without transfer of control), which facilitates phase locking and increases the stability of BWO PL systems.

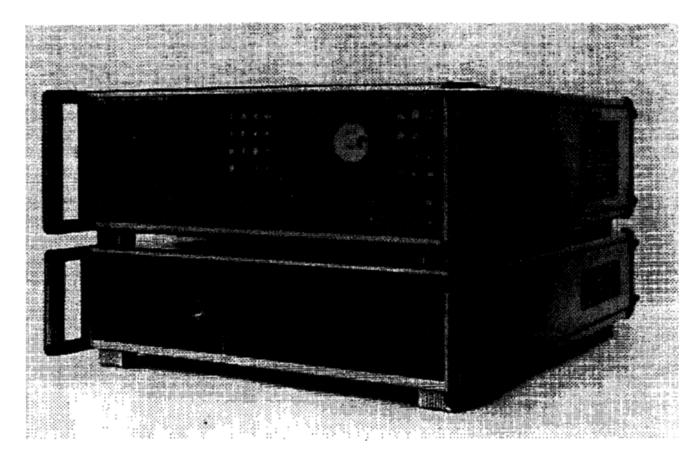


Fig. 2.

a scheme was demonstrated at frequencies of up to 500 GHz. In 1994, the researchers of Kvarts finished the development of a family of commercial frequency synthesizers with continuous covering of frequencies from 53 to 178 GHz (units 53–78, 78–118, and 118–178 GHz) with the least frequency step of 100 Hz and digital control by a computer [27]. These synthesizers do not have foreign analogues and are used in many countries of the world (USA, Germany, Japan, France, Italy, China, etc.). The appearance of a mm-wave synthesizer of 118–178 GHz is presented in Fig. 2 [27]. Synthesizers operated at still higher frequencies on the basis of BWO PL systems are also being developed at present.

3. SOME APPLICATIONS OF PL SYSTEMS AND FREQUENCY SYNTHESIZERS

3.1. Spectroscopic applications

Here, we consider only the role of the increased accuracy of measurement and possibilities of high-precision wideband scanning in the broadening of the range of accessible studies. The principles of spectroscopic methods and investigations were published in a large number of original papers, and some particular aspects were considered in reviews and books [12, 16, 34–36]. However, even the latest (and most complete) review of 1996 [37] does not include about two tens of recent papers.

3.1.1. First of all, the methods described there were focused on the examination of molecular spectra. Microwave spectroscopy is mainly the spectroscopy of rotational spectra of molecules. The use of high-precision coherent radiophysical methods in microwave spectroscopy makes it possible to reach high resolving power, high accuracy, and high sensitivity of spectrometers, i.e., this gives ample high-precision information on the structure and properties of atoms and molecules (see, e. g., [38]). There is a number of

molecular spectra which cannot be observed at the lower frequencies. The high-frequency region is also the region of strong nonrigidity effects. In combination with high accuracy of measurement, this permits one to examine new qualitative nonrigidity effects and many properties of molecules which are difficult for study in other spectral regions. We have the possibility of giving only a few examples.

An important "classical" object is the spectrum of ammonia NH₃: the rotational spectrum, whose study was initiated even before the development of PL circuits and was continued by more exact methods [39], and the spectrum inverted in the excited state ν_2 , which we considered in a series of papers. We measured these spectra for the first time in the submm-wave region using microwave methods *.

The observation of an anomalously low-frequency vibrational-rotational spectrum of the nonpolar molecule C₃O₂ solved the mystery of its infrared spectrum which had long resisted decoding [41]. The history of study and the importance of identification of this so-called "quasilinear" molecule are shown in reviews [36].

The detection of a new phenomenon in molecular spectra —the clusterization of energy levels in the spectra of molecules of asymmetric-top type —was also the consequence of exact measurement of frequencies in the submm series of lines of the H₂Se molecule where the beginning of the "convergence" of frequencies in that series was found [42]. (This detection is the second "qualitative" nonrigidity effect, and the first such effect was the detection of "forbidden" spectra.)

An example of an "ordered" study, which required high accuracy of measurement, was the obtaining of laboratory data for the interpretation of astrophysical studies of winds on Venus by shifts of mm lines of the CO molecule. The required accuracy of measurement was within several kilohertz for line frequencies and several kilohertz per Torr for shifts by pressure (for separation of effects). Such measurements were performed in [43].

The first microwave observation of the spectra of negative molecular ions (only the ions SH $^-$ and SD $^-$ were observed) [23] was also made possible by the increased accuracy of measurement with PL systems, since the ion lines were identified by comparison of the observed line frequencies for different mutual orientations of the transmitting radiation and discharge polarity. The frequencies of neutral molecules coincide in both cases, while the frequencies of ion lines differ, owing to the Doppler effect for ions drifting in the discharge. Of course, the sign of the frequency difference depends on the sign of the ion charge. The corresponding frequency differences are varied from 50 to 200 kHz at frequencies of order 600 GHz and the measurement accuracy amounts to ~ 5 kHz.

3.1.2. The next large area was the study of spectroscopic manifestations of interactions between colliding molecules.

Essentially, exact measurements of frequencies at the line centers in the submm range led to putting the studies of collisional shifts of molecular spectral lines ("shifts of spectral lines by gas pressure") into the practice of microwave spectroscopy. Earlier, microwave spectroscopy obtained information on molecule interactions only from the broadening of spectral lines due to pressure. By convention, the shift was assumed to be too small for measurement, and cound not exceed 5% of the broadening according to Townes's estimate [11]. Boggs stated in his review of 1972 [44] that there was not a single microwave measurement of line shifts by pressure at that time. In 1977, we detected microwave line shifts [45] by exact measurements; they appeared to be large and amounted to 40% of the broadening. Later on, it was found that the shift in the microwave region increases with frequency and it is exactly the transition from the centimeter region considered by Townes to the submillimeter region considered by us that mainly increased the shift from Townes's estimates $\leq 5\%$ of the broadening to experimental values 40% or greater in our observations. * Besides the accuracy of PL, these studies were facilitated by the fact that the acoustic detection of signals

^{*}One coauthor had access to the Citation Index and found that one paper, by Narahari Rao K. et al. [40], was cited 56 times for the first three years and two other papers were cited 22 and 15 times; it would be interesting to know citations of other papers in that series but they are not accessible to us.

^{*}We also observed the increase of shifts with frequency (see, e. g., [46]).

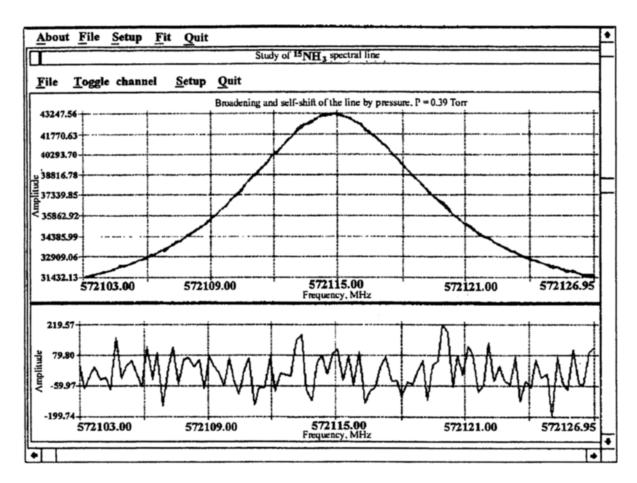


Fig. 3.

from the spectral lines of gas [13] appeared to be more free of the main source of systematic errors in the measurement of collisional shifts of molecular spectral lines —the observation of lines on the slopes of the frequency response, since the volume thermal character of the reception averaged interference in the cell efficiently. Figure 3 shows a typical record by our spectrometer of a collisionally broadened shifted line of ammonia N15H3 in its natural concentration and the results of description of the line profile by a Lorentz curve (the discrepancy of description is given at the bottom) **. The shift is more sensitive to the form of interaction between molecules since its major part is determined by distant, "weak" collisions while the major part of the broadening is completely independent of the model and is the same as in the "collisions of rigid balls" model. This also makes the studies of shifts interesting. A summary of our investigations in this field is given in [46], and more recent results were published in [37]. In particular, microwave studies of shifts by a mixture of gases [47] allowed the error of German researchers in [48] to be removed, and posing the problem of additivity of shifts in molecular transition systems in 1982 [46] ended in 1996 in detection of nonadditivity [49], contrary to what was assumed earlier (see [50]). The microwave data on line shifts attracted theoreticians' attention and began to be included in spectroscopic databases. For example, the paper of Buffa and Tarrini [50] was devoted to the interpretation of only our, more exact measurements of line shifts.

The increased accuracy of measurement also showed the necessity of developing a new theory of broadening and shift in collisions of molecules. The existing theory founded by Anderson [51] in 1949 is a combination of the perturbation theory for distant weak interactions and its artificial "matching"

^{**}The software was developed at the IAP RAS.

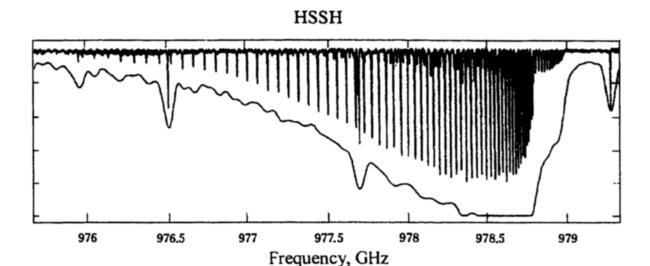


Fig. 4.

with the region of close strong interactions where the probability of transition is assumed to be equal to unity. Anderson stated that the interpolation between these regions is not possible even in principle and the arbitrariness of such a procedure leads to results which can differ within the limits of 20%, which, as Anderson said, is "usually less than the measurement error." The measurement accuracy has recently reached 1–0.5%, and the interpretation of measurements in terms of such a theory is very limited. The development of theory will permit one to determine, for example, the higher moments of molecules and extend applications of measurements. Obviously, the new description will be based on some sort of calculation of the interaction of molecules "from first principles" using supercomputers, as in the modern description of nonrigid molecule spectra [52].

3.1.3. We will also mention the use of accurate frequency methods for the calibration of FIR spectrometers, such as coherent Fourier spectrometers, which until recently were the only wideband spectrometers for this region. For comparison of spectrometer characteristics, we show in Fig. 4 the records of one and the same area in the spectrum of the HSSH molecule at 978 GHz [37]: for a Fourier spectrometer (lower curve) and a microwave spectrometer in the same scale (upper curve). We recall that each "microwave" line can be extended to the scale of Fig. 3.

3.2. Development of other measurements on the basis of frequency methods

The use of high-precision frequency methods permitted accurate "amplitude" measurements in mm and submm-wave bands. We will give several examples.

3.2.1. The use of a frequency synthesizer with exact reproduction of the scanning signal for wideband scanning of the molecular spectrum led to an unexpected useful result, which was demonstrated for the first time in 1993 [53]. Recording first the spectrum of a cell filled with gas (InSb) by a bolometer and then (after several hours) the spectrum of the same cell without the gas (recording mainly the interference pattern), and deducing these spectra stored in the computer one from another, one obtains a record of spectral lines against a suprisingly flat "zero line." This is shown in Fig. 5 for an area of the spectrum of the OCCCS molecule of width 100 MHz taken from a general scan of width 40 GHz in the PL mode [53, 37]. Later on, this result was used in a variety of papers and is essentially the first indication that our high-precision "frequency" methods can also be employed for high-precision "amplitude" measurements.

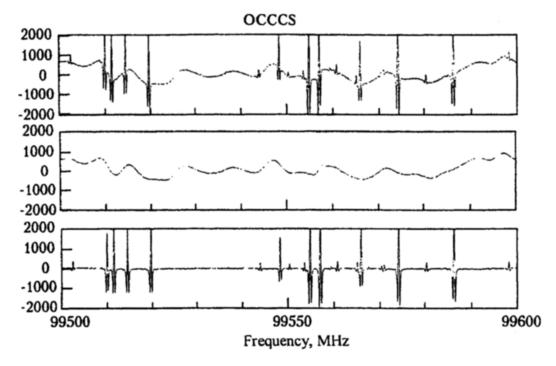
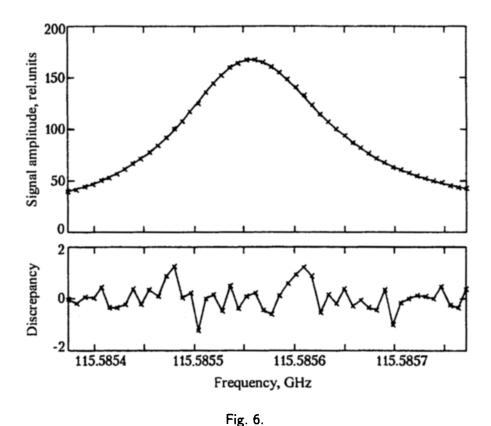


Fig. 5.

3.2.2. In papers dealing with frequency multiplication in BWOs [28, 54], the high-precision frequency control of the radiation source, combined with acoustic detection of signals from spectral lines, made it possible not only to differentiate (by known spectral lines) between harmonic numbers but also to measure the power of each harmonic separately *. These measurements were based on the nondependence of the sensitivity of acoustic reception on the frequency and possibility of calculating absorption coefficients of microwave lines. The coefficients of conversion of power into each harmonic separately can be easily measured over a wide range. The obtaining of frequency characteristics of the multipliers from the fundamental to the highest harmonic (1.5 GHz [28]) gives one new possibilities for understanding and improving of these devices.

3.2.3. The next example is the measurement of ultrasmall losses in dielectrics and metals [55]. The new methods exceed the previous ones in sensitivity by two orders of magnitude. The increase in sensitivity was reached by development of high-quality ($\geq 600\,000$) measuring resonators and use of high-precision mm-wave frequency synthesizers (and software for spectroscopic purposes). Figure 6 presents a record of the resonance curve of a Farby-Perot resonator with Q-factor 637000 and shows the result of description of its Lorentz curve. In these tests, the accuracy of measurement of the width of the resonance curve reached 500 Hz at frequencies near 100 GHz. This permitted high-precision measurement of ultrasmall ($\sim 10^{-6}-10^{-7}$) values of the tangent of the loss angle even in thin (~ 0.5 mm) samples of dielectrics, making it possible to meet higher requirements in future, for example, in the measurement of absorption in the windows of high-power gyrotrons. When the resonator is completely filled up with a sample (e.g., a gas), the sensitivity increases to the loss tangent $\sim 10^{-8}$. Since the losses determining the Q-factor in Fabry-Perot resonators are the reflection losses in mirrors, these methods are also useful for the measurement of small reflection losses (according to measurements, the reflection coefficient of spray-coated silver is 0.9990 at frequency near 100 GHz).

^{*}Using microwave methods, one can easily exclude low-frequency components but it is difficult to separate the required harmonic from those of higher frequencies; moreover [28], the power of the higher harmonic can be greater than the power of the lower harmonic.



3.2.4. A new prospect resulting from exact measurements of line shifts by gas pressure can be the possibility of "integrated" molecular analysis of a gas mixture by the shift of one "test" line of the molecule placed into that mixture (or residing in it). The shift depends on the type and polarity of the molecules, and the shift by the mixture, calculated as a "weighted mean," can serve as an integrated characteristic of the mixture, which can be interpreted in each particular case at a later time. This possibility is similar to the refractometry of condensed media; it was mentioned for the first time in [56] (see also [37]) and is being examined in greater detail at present. Such a technique can also be used for measurement of the dipole

4. EXTENSION OF THE RANGE OF HIGH-PRECISION FREQUENCY METHODS BEYOND THE BWO BAND

moment of large molecules in the gas phase, which has always been a problem for other methods.

The frequency range of the BWOs described back in the sixties [14] remained the same for the last three decades. In [14], Golant et al. mentioned a range of up to 1.5 THz, but the particular spectroscopic studies at such high frequencies are not known to us. The applicability limits of the BWOs known in the literature (see, e.g., [39]) slightly exceed 1.2 THz. At present, this range is completely assimilated by BWO PL systems. The will to extend further the range of accurate "microwave" methods led, on the one hand, to a frequency multiplication of up to 1.5 THz in BWOs (see the text above and [28]) and, on the other hand, resulted in combination of tunable PL systems for BWOs with a "frequency support" in the form of a FIR laser [31]. To avoid losses in accuracy (the frequency of an unstabilized laser drifts inside the spectral line by about one megahertz), the frequency of a FIR laser must also be stabilized by the reference signal [30]. The initiation of such studies has already led to frequency locking at frequencies of up to 2.5 THz in a FIR laser. The phase locking of a FIR laser will be next. Experience in stabilization will be also useful with the advent of long-awaited solid-state terahertz oscillators.

5. CONCLUSIONS

The above studies solved for the first time the problem of extending all the possibilities of high-precision coherent radio methods to the entire frequency range of modern electron oscillators over one terahertz. Commercial high-precision frequency synthesizers are very close to the submm-wave band. There are grounds for further extension of the continuous region of frequencies accessible for high-precision frequency radio methods. A number of high-precision procedures have been developed for frequency and amplitude measurements in the above frequency ranges. Considerable scientific and applied results have already been reached by such procedures. Obviously, the constant desire to extend the frequency range employed in radio engineering will increase still further the role of high-precision coherent radiophysical methods in the high-frequency part of the range for the maximum use of all the possibilities of the frequency bands being assimilated.

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REFERENCES

- 1. H. De Bellescize, Onde Electromagnetique, 11, 230 (1932).
- 2. Peter and M. W. P. Strandberg, Proc. IRE, 43, 869 (1955).
- V. V. Shakhgil'dyan and A. A. Lyakhovkin, Phase-Lock Systems [in Russian], Svyaz', Moscow (1972);
 V. A. Levin, V. N. Malinovsky, and S. K. Romanov, Frequency Synthesizers with a Pulse-and-Phase-Lock System [in Russian], Radio i Svyaz', Moscow (1989).
- 4. Applied Microwave and Wireless, 9, 11 (1997).
- 5. I. L. Bershtein and V. L. Sibiryakov, Radiotekh. Élektron., 3, 290 (1958).
- 6. I. L. Bershtein, Yu. A. Dryagin, and V. L. Sibiryakov, Izv. Vyssh. Uchebn. Zaved., Radiofiz., 2, 130 (1959).
- 7. A. F. Krupnov and V. A. Skvortsov, Prib. Tekh. Éksp., No. 1, 212 (1964).
- 8. A. F. Krupnov and V. A. Skvortsov, Izv. Vyssh. Uchebn. Zaved., Radiofiz., No. 9, 824 (1966).
- 9. A. F. Krupnov, V. A. Skvortsov, and L. A. Sinegubko, Izv. Vyssh. Uchebn. Zaved., Radiofiz., No. 10, 142 (1967).
- 10. D. C. Laine, Rep. Progr. Phys., 33, 1001 (1970).
- 11. C. H. Townes and A. Shavlov, *Radio Spectroscopy* [Russian translation], Inostrannaya Literatura, Moscow (1959).
- 12. W. Gordy and R. L. Cook, Microwave Molecular Spectra, Wiley, New York (1984).
- 13. A. F. Krupnov, Vestnik Akad. Nauk SSSR, No. 7, 19 (1978).
- 14. M. B. Golant, P. L. Vilenkin, E. A. Zyulina, Z. F. Kaplun, A. A. Negirev, V. A. Parilov, E. B. Rebrova, and V. S. Savel'yev, *Prib. Tekh. Éksp.*, No. 4, 136 (1965);
 - M. B. Golant, Z. T. Alekseenko, Z. S. Korotkova, L. A. Lunkina, A. A. Negirev, O. P. Petrova, T. B. Rebrova, and V. S. Savel'yev, *Prib. Tekh. Éksp.*, No. 3, 231 (1969).
- 15. A. F. Krupnov and L. I. Gershtein, Prib. Tekh. Éksp., No. 6, 143 (1970).
- 16. A. F. Krupnov and A. V. Burenin, in: K. N. Rao, ed., Molecular Spectroscopy: Modern Research, Academic Press, New York (1976), p. 93.
- 17. A. F. Krupnov, in: G. W. Chantry, ed., Modern Aspects of Microwave Spectroscopy, Academic Press, New York (1979), p. 217.

- 18. L. I. Gershtein, V. L. Vaks, and A. V. Maslovsky, Prib. Tekh. Eksp., No. 6, 201 (1984).
- 19. M. Bogey, C. Demuynck, M. Denis, J. L. Destombes, and B. Lemoine, Astron. Astrophys., 137, L15 (1984);
 - M. Bogey, C. Demuynck, and J. L. Destombes, Astron. Astrophys., 138, L11 (1984);
 - M. Bogey, C. Demuynck, and J. L. Destombes, J. Phys. Chem., 84, 10 (1986).
- G. Winnewisser, A. F. Krupnov, M. Yu. Tret'yakov, M. Liedtke, F. Lewen, A. H. Saleck, R. Shieder, A. P. Shkaev, and S. A. Volokhov, J. Mol. Spectrosc., 165, 294 (1994).
- S. P. Belov, M. Liedtke, Th. Klaus, R. Schieder, A. H. Saleck, J. Behrend, K. M. T. Yamada, G. Winnewisser, and A. F. Krupnov, J. Mol. Spectrosc., 166, 489 (1994).
- M. Bogey, S. Civis, B. Delcroix, C. Demuynck, A. F. Krupnov, M. Yu. Tret'yakov, and A. Walters, J. Mol. Spectrosc., 182, 85 (1997).
- 23. S. Civis, M. Yu. Tret'yakov, A. Walters, S. Bailleux, and M. Bogey, J. Phys. Chem., 108, 8369 (1998).
- A. F. Krupnov, M. Yu. Tret'yakov, M. Bogey, S. Bailleux, A. Walters, B. Delcroix, and S. Civis, J. Mol. Spectrosc., 176, 442 (1996).
- 25. S. Bailleux, M. Bogey, H. Bolvin, S. Civis, M. Cordonnier, A. F. Krupnov, M. Yu. Tret'yakov, A. Walters, and L. Coudert, J. Mol. Spectrosc., 190, 130 (1998).
- 26. I. Morino, M. Fabian, H. Takeo, and K. M. T. Yamada, J. Mol. Spectrosc., 185, 142 (1997).
- 27. A. F. Krupnov and O. P. Pavlovsky, Int. J. IR & MM Waves, 15, 1611 (1994).
- A. F. Krupnov, M. Yu. Tret'yakov, Yu. A. Dryagin, and S. A. Volokhov, J. Mol. Spectrosc., 170, 279 (1995);
 M. Yu. Tret'yakov, A. F. Krupnov, and S. A. Volokhov, Pis'ma Zh. Éksp. Teor. Fiz., 61, 75 (1995).
- 29. F. Lewen, S. P. Belov, F. Maiwald, Th. Klaus, and G. Winnewisser, Z. Naturforschung, 50a, 1182 (1995).
- R. Bocquet, M. Yu. Tret'yakov, A. F. Krupnov, L. Poteau, and O. Boulogne, Int. J. IR & MM Waves, 17, 1031 (1996);
 R. Bocquet, M. Yu. Tret'yakov, A. F. Krupnov, S. A. Volokhov, and L. Poteau, Int. J. IR & MM Waves, 17, 1181 (1996).
- F. Lewen, E. Michael, R. Gendriesch, J. Stutzki, and G. Winnewisser, J. Mol. Spectrosc., 183, 207 (1997).
- 32. Yu. I. Alekhin, G. M. Al'tshuller, N. F. Zobov, E. N. Karyakin, M. I. Kirillov, and A. F. Krupnov, *Izv. Vyssh. Uchebn. Zaved.*, Radiofiz., 28, 1382 (1985).
- 33. Yu. I. Alekhin, G. M. Al'tshuller, O. P. Pavlovsky, E. N. Karyakin, and A. F. Krupnov, D. G. Pavel'yev, and A. F. Shkaev, Int. J. IR & MM Waves, 11, 961 (1990).
- A. F. Krupnov, Izv. Vyssh. Uchebn. Zaved., Radiofiz., 13, 961 (1970);
 A. F. Krupnov, Izv. Akad. Nauk SSSR, Ser. Fiz., 48, 732 (1984).
- 35. W. Gordy, J. Mol. Structure, No. 97, 17 (1983);
 - E. B. Wilson, Ann. Rev. Phys. Chem., 30, 1 (1979);
 - J. Sheridan, J. Mol. Struct., No. 97, 33 (1983);
 - D. R. Johnson and R. Pearson, in: *Methods of Experimental Physics*, Academic Press, New York (1976), v. 13B, p. 102;
 - G. Baldacchini, G. Buffa, and O. Tarrini, Nuovo Cimento 13D, 719 (1991);
 - D. Papousek and M. R. Aliev, Molecular Vibrational-Rotational Spectra, Academia, Prague (1982).

- M. Winnewisser, J. Mol. Structure, No. 80, 505 (1982);
 B. P. Winnewisser, in: Molecular Spectroscopy: Modern Research, Academic Press, New York (1985),
 Vol. 3, p. 321.
- 37. A. F. Krupnov, Spectrochimica Acta A, 52, 967 (1996).
- 38. A. F. Krupnov, Microwave Spectroscopy, in: Encyclopaedia of Physics, Comprehensive Russian Encyclopaedia [in Russian], Moscow (1992), v. 3, p. 133.
- 39. A. F. Krupnov, V. A. Skvortsov, and L. A. Sinegubko, Izv. Vyssh. Uchebn. Zaved., Radiofiz., 11, 1186 (1968);
 - P. Helminger, F. G. De Lucia, and W. Gordy, J. Mol. Spectrosc., 39, 94 (1971);
 - A. F. Krupnov, M. Yu. Tret'yakov, M. Bogey, S. Bailleux, A. Walters, B. Delcroix, and S. Civis, J. Mol. Spectr., 176, 442 (1996);
 - G. Winnewisser, S. P. Belov, Th. Klaus, and S. Urban, Z. Naturforschung, 51a, 200 (1996).
- Rao K. Narahari, S. Urban, V. Spirko, D. Papousek, R. S. McDowell, N. G. Nereson, S. P. Belov, L. I. Gershtein, A. V. Maslovsky, and A. F. Krupnov, J. Mol. Spectrosc., 79, 455 (1980).
- A. V. Burenin, A. F. Krupnov, E. N. Karyakin, and S. M. Shapin, J. Mol. Spectrosc., 78, 181 (1979);
 E. N. Karyakin, A. F. Krupnov, and S. N. Shapin, J. Mol. Spectrosc., 94, 282 (1982).
- I. M. Kozin, S. P. Belov, O. L. Polyansky, and M. Yu. Tret'yakov, J. Mol. Spectrosc., 152, 13 (1992);
 P. Jensen, G. Ossmann, and I. N. Kozin, in: D. Papousek, ed., Vibrational-Rotational Spectroscopy and Molecular Dynamics, World Scientific, New Jersey (1997), p. 298.
- 43. S. P. Belov, M. Yu. Tret'yakov, and R. D. Suenram, Astrophys. J., 393, 848 (1992).
- 44. J. E. Boggs, in: K. N. Rao and C. W. Mathews, eds., Molecular Spectroscopy: Modern Research, Academic Press, New York (1972), p. 49.
- 45. A. F. Krupnov, E. N. Karyakin, D. Papousek, Yu. M. Shurin, and S. Urban, J. Mol. Spectrosc., 66, 171 (1977).
- S. P. Belov, V. P. Kazakov, A. F. Krupnov, V. N. Markov, A. A. Mel'nikov, V. A. Skvortsov, and M. Yu. Tret'yakov, J. Mol. Spectrosc., 94, 264 (1982);
 S. P. Belov, V. N. Markov, A. A. Mel'nikov, V. A. Skvortsov, and M. Yu. Tret'yakov, J. Mol. Spectrosc., 101, 258 (1983).
- 47. V. N. Markov and A. F. Krupnov, J. Mol. Spectrosc., 172, 211 (1995).
- 48. T. Giesen, R. Schieder, G. Winnewisser, and K. M. T. Yamada, J. Mol. Spectrosc., 153, 406 (1992).
- 49. A. F. Krupnov, J. Mol. Spectrosc., 176, 124 (1996).
- 50. G. Buffa and O. Tarrini, J. Mol. Spectrosc., 101, 271 (1983).
- 51. P. W. Anderson, Phys. Rev., 76, 647 (1949).
- O. L. Polyansky, N. F. Zobov, S. Viti, J. Tennyson, P. F. Bernath, and L. Wallace, Science, 277, 346 (1997).
- V. Wagener, M. Winnewisser, A. A. Uljanov, O. P. Pavlovsky, G. M. Al'tshuller, O. G. Anikin, A. F. Krupnov, E. N. Karyakin, and V. P. Kazakov, in: Proc. of the 48th Ohio State Univ. Int. Symposium on Molecular Spectroscopy, Columbus, Ohio (1993), paper WF05.
- M. Yu. Tret'yakov and A. F. Krupnov, J. Mol. Spectrosc., 172, 205 (1995).
- 55. A. F. Krupnov, V. N. Markov, G. Yu. Golubyatnikov, I. I. Leonov, V. V. Parshin, and Yu. N. Konoplev, *IEEE Trans. MTT* (submitted for publication).
- 56. S. P. Belov, A. F. Krupnov, V. A. Skvortsov, A. A. Mel'nikov, and M. Yu. Tret'yakov, *Izv. Vyssh. Uchebn. Zaved.*, Radiofiz., 28, 1203 (1985).