

At present radiospectroscopy has become a classical field of physics. The basic principles and many results of radiospectroscopy have been expounded in a number of books [1-5]; its methods are being applied in the most varied fields of research, such as the study of nuclear properties, the structure and properties of molecules and substances, in radioastronomy, quantum frequency standards, masers, fundamental physics research (the Lamb experiment, measurement of the velocity of light, etc.), in chemical and isotopic analysis, etc. At present the basic trend of development in radiospectroscopy is the advance into ranges having ever shorter wavelengths, and the use of maser principles and nonlinear phenomena.

The spectral lines of gases are especially abundant and intense in the millimeter and submillimeter wavelength ranges, which makes these ranges very promising both for the study of the spectra of substances and for the creation of practical devices which use spectral lines. However, this range is the most inaccessible engineering-wise. Its mastery was begun by Lebedev ($\lambda = 6$ mm, 1895 [6]) and by Glagoleva-Arkad'eva ($\lambda = 0.082$ -50 mm, 1922 [7]). Specifically radiospectroscopic investigations in the indicated range began to develop beginning in 1946-1947 with the transition from the continuum to a monochromatic radiation spectrum (harmonics of centimeter-range oscillators were used). Gordy, who advanced to $\lambda = 0.5$ mm by 1959, played a large role in this research. This stage is reflected in [1, 3, 5], and likewise in the review [8].

At present, in our opinion, one can speak of a new stage in the mastery of the millimeter and submillimeter ranges, which is basically characterized by the appearance of primary sources of monochromatic radiation having adequate power. The development of the principle of a maser, which was created by Basov, Prokhorov, and Townes [9], led in 1964 to the creation of the first submillimeter-range lasers [10, 125]. In 1965 a communication on the creation of electronic oscillators having a wavelength down to $\lambda \approx 0.5$ mm appeared, while in 1969 the wavelength reached $\lambda \approx 0.2$ mm [11, 12]. Typical power ratings of these sources range from fractions of a milliwatt to hundreds of milliwatts. Power ratings several orders higher are accessible to the electronic oscillators of a new type created in 1965 - CRM (see review [13]). In those years the engineering of reception in those ranges was perfected. In 1963-1968 a series of low-temperature receivers of high sensitivity was created [14-16] (see likewise the review [17]); in 1968 the range of a point-contact detector was extended down to a wavelength of 10 microns [18]. Microwave elements [19] are being perfected, the most important of which is the Fabry-Perot resonator advanced in [20]. All of this served as a powerful impetus to further research in the millimeter and submillimeter ranges.

The books available in Russian on radiospectroscopy were published fairly long ago (the latest [3] was published in 1954 and was translated into Russian in 1959) and naturally do not reflect the modern state of such a rapidly developing field of research as millimeter and submillimeter radiospectroscopy. This is one of the causes which in our opinion make it useful to write the present review. Another factor lies in the fact that radiospectroscopy has fulfilled (and is fulfilling) an important role in the mastery of these ranges. A number of procedures and devices developed in this field may find more than a purely radiospectroscopic application. Examples can be found in recent successes in the stabilization and multiplication of frequency which has allowed the practical posing of the problem of linking the optical and radio ranges [21-23, 200-203, 245, 246].

The present review is devoted to a development of the millimeter and submillimeter radiospectroscopy of gases during the past ten years; more recent data are presented in [8], and likewise in [1, 3]. A

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considerable bibliography, including papers written up to 1965, is contained in [5] (see likewise [243]). As is assumed in the majority of papers, we shall consider wavelengths of from approximately 10 to 0.1 mm to be in the millimeter and submillimeter ranges. We shall not touch on such fairly independent branches of radiospectroscopy as the investigation of absorption in the atmosphere (see, for example, the review [24]) or radioastronomical investigations of discrete lines (for example, [238]).

1. Radiospectroscopic Features of the Millimeter and Submillimeter Ranges

The millimeter and submillimeter ranges have features which are associated both with the gas spectra proper and with the construction of the experimental installations; these features in many ways determine the trends of radiospectroscopic research in this range. Let us consider the most important of them.

The large width of the range also leads to its high "informativeness" in the radiospectroscopic respect (if it is assumed a priori that the number of spectral lines is proportional to the width of the frequency interval). Combined with broad limits of oscillator tuning [11, 12], this provides the possibility of investigating a large portion of the rotational spectrum of molecules at one stroke, thus increasing the accuracy and reliability of the results.

The rotational spectra of light (having small moments of inertia) polar molecules are located in this range. Let us briefly recall the characteristic features of the spectrum. The rotational spectrum of a linear molecule (whose nuclei lie on one straight line) consists of a series of equidistant (if we neglect centrifugal effects) lines beginning at the frequency $2B$; the frequency distance between lines is likewise equal to $2B$. Such a spectrum is obtained due to quantization of the magnitude of the angular momentum $\omega I = J\hbar$ of the molecule, where ω is the rotation frequency, I is the moment of inertia, J is an integer, \hbar is Planck's constant. The rotation energy under these conditions is equal to $W = \hbar B J(J+1)$, where $B = \hbar/8\pi^2 I$ is the rotational constant of the molecule and is usually expressed in megacycles. The frequency corresponding to allowed electro-dipole transitions $J \leftrightarrow J+1$ is found to equal

$$\nu = 2B(J+1). \quad (1)$$

A molecule of the symmetrical-top type (which already has three moments of inertia, two of which are equal to one another) yields a spectrum differing from the spectrum of a linear molecule in that the single lines are now split into groups of closely spaced lines, each of which belongs to a transition having the same value of J but different projections K of the angular momentum J onto the symmetry axis of the molecule. These lines do not coincide due to centrifugal effects. Levels having $K \neq 0$ are degenerate with respect to the sign of K . The principal difference resides in the appearance of nonresonance absorption for $\nu = 0$, which is associated with transitions between levels which are degenerate with respect to K .

For a transition to a molecule of the asymmetrical-top type (in which all three moments of inertia are different) further modifications occur in the spectrum. In the case of weak asymmetry, when it is still possible to use the quantum number K approximately, degeneracy of the lines with respect to the sign of K is removed; each of the lines (with the exception of $K = 0$) splits into two lines. The splitting is large for small K and decreases abruptly for a transition to large K ; it increases with increasing J . The lines of the spectrum are still grouped in accordance with the number J but occupy a large interval of the spectrum. Each group of lines is framed by lines having $|K| = 1$. Low-frequency lines corresponding to transitions between K -doublets are "split off" from the region of nonresonance absorption at $\nu = 0$. Then, finally, in the case of a strongly asymmetrical top the lines belonging to groups having different J mix. The picture of the spectrum is greatly complicated (also for the reason that new selection rules appear). The procedure for calculating the spectra is well known [1-5].

Thus, in order to investigate the rotational spectrum and structure of light molecules of the linear or symmetrical-top type it is necessary to penetrate into the millimeter and submillimeter region of the spectrum. This applies almost to the same degree to light asymmetrical tops, since the investigation of the low-frequency spectrum of the latter did not provide complete information on the molecular constants (for example, on centrifugal perturbations, etc.). The class of light molecules is very important because of its practical applications, since it is specifically to these molecules that the most intense spectral lines belong. The increased intensity of the lines of the light molecules is caused by the fact that the energy range $\epsilon \leq kT$ which is associated with thermal motion accommodates a comparatively small number of levels of these molecules, and the fraction of molecules at each of the populated levels is considerable.

Let us enumerate several characteristic representatives of the class of light molecules along with the most important fields of their practical application: H_2O (absorption in the atmosphere [24]; detected in space [25]; submillimeter lasers [10]); NH_3 (beam masers [9, 26]; detected in space [27]; infrared lasers [28]); HCN (beam masers [29]; submillimeter lasers [10]; parametric amplifiers [30]); H_2CO (beam masers [31]; detected in space [32]); H_2S (beam frequency-standard radiospectroscope [33]; submillimeter laser [34]), etc. An important variety of light molecules are "fragments" of molecules — radicals of the type OH , NO , etc., which are obtained in a low-temperature plasma (flame, discharge), in chemical reactions, etc. The presence of an electron angular momentum in the radicals makes their spectrum partially similar to the spectrum of an asymmetrical top. The cosmic radio emission from the OH radical reveals maser properties, the inversion mechanisms being unclear for the time being [35].

The investigation of higher-frequency transitions and higher energy levels of the molecules revealed in the cosmos may yield valuable information on the physical conditions in the cosmos. In the case of formaldehyde, for example, which has ortho- and para-modifications like hydrogen, a lower transition of the ortho-modification $1_{10}-1_{11}$ was observed [32]. It is of interest to observe the corresponding lower transition $0_{00}-1_{01}$ of the para-modification at the wavelength $\lambda = 4.12$ mm in connection with the possible influence of ortho-para-conversion processes at low temperatures. Note that for the rotational spectrum (as distinct, for example, from the vibrational spectrum) the intensities of the lines may be rigorously and unambiguously associated with the population of the levels and the dipole moment of a molecule.

The range considered is characterized by a high intensity of the spectral lines. Frequently the lines are so intense that a large part of the power of the signal passing through the gas may be absorbed at wavelengths of the order of centimeters. Besides a dependence of the intensity of the lines on the class of molecules, which was noted previously, the dependence of the intensity of the rotational lines in each individual molecule on frequency is likewise important here. The power absorbed by the gas is equal to the energy of a quantum at the given frequency multiplied by the number of molecules capable of participating in the absorption and by the probability of the given transition of the molecule. The probability of the transition may be assumed in the first approximation not to depend on frequency. The number of molecules participating in the absorption increases in proportion to the square of the frequency for linear molecules for $h\nu \ll kT$, since the growth of the statistical weight of the level associated with degeneration with respect to orientation increases as $2J + 1$, and the difference between level populations, which causes the absorption, increases as $h\nu/kT$. For symmetrical and asymmetrical tops the growth of orientational degeneration is compensated by splitting of the level having the given J into $J + 1$ (or $2J + 1$) sublevels having different K .

Thus, the resultant action of the indicated causes leads to a growth of the intensity of rotational lines with frequency ν in proportion to ν^3 for a linear molecule and in proportion to ν^2 for symmetrical and asymmetrical tops. Such a growth of the intensity is, of course, not limitless; the population of the levels is cut off by the Boltzmann multiplier $\exp(-W/kT)$. However, for the majority of molecules the growth of the intensity takes place in the majority of the range considered. The high intensity of the lines facilitates investigation; moreover, it becomes possible to use the lines and devices of the filter, attenuator, modulator, amplifier type (see the review [30]).

Let us also mention the considerable change in the dielectric constant of the gas in the range of spectral-line dispersion. The maximum change of the dielectric constant is equal to $\Delta\epsilon = \epsilon_{\max} - \epsilon_{\min} = \lambda \gamma_{\max}$, where γ_{\max} is the maximal absorption coefficient of the given line in cm^{-1} ; λ is the wavelength in centimeters. For the most intense lines in the region $\lambda \approx 1$ mm, $\Delta\epsilon$ may reach a value $\sim 5 \cdot 10^{-2}$ in the pressure interval from fractions of a millimeter to centimeters of mercury.

The millimeter and submillimeter ranges are very convenient for investigating effects associated with nonrigidity of molecules, such as centrifugal perturbation and vibrational-rotational interactions, since the frequency of the lines of the rotational spectrum increases in proportion to J , while the corrections to the frequency due to nonrigidity increase as J^3 or even as J^5 . The calculation of the effects of nonrigidity for linear and symmetrical molecules is available in [1-3]; convenient formulas for the complex case of an asymmetrical top are presented in [5]. Measurements in the millimeter and submillimeter ranges showed the insufficiency of the first approximation of perturbation theory for describing the effects of nonrigidity in light asymmetrical tops (see, for example, [36, 37, 124]). Thus, further investigations of the effects of nonrigidity are necessary for a correct description of the spectra, and they likewise allow a quantitative study of valence forces which bind the atoms in the molecule.

Besides rotational spectra, certain other forms of atomic and molecular spectra may be observed in the millimeter and submillimeter ranges. The radiospectroscopy of discrete lines in a low-temperature plasma of the flame or gas-discharge type provides the possibility of a precision investigation of transitions between excited states of atoms and molecules, processes of excitation and relaxation of the corresponding energy levels, resonant coupling of levels, and likewise equilibrium states of a gas. A powerful impetus to these investigations was given by the creation of gas lasers for the submillimeter range which operate on the indicated transitions. Molecular submillimeter lasers operate on vibrational-rotational transitions between the higher vibrational states of molecules; atomic submillimeter lasers operate on transitions between the higher electronic levels which are characterized by the same principal quantum number n and different orbital quantum numbers l .

The problems of measurement and identification of laser lines, which are of greatest interest in radiospectroscopic problems, and likewise the closely related problems of obtaining an inverse population in lasers will be considered below (section 2); here we shall dwell merely on certain examples. The non-equilibrium radiation on the Λ -doubling transitions of the OH radical in a low-pressure flame in the $\lambda = 8$ mm region was revealed in [38]. Using a water laser the frequencies of the transitions $5_{23}-5_{50}$ (the 100-020 vibrational transition, $\lambda = 220 \mu$) and $6_{42}-6_{61}$ (the vibrational transition 001-020, $\lambda = 118 \mu$) were measured with an accuracy of $\sim 10^{-7}$ which exceeds the accuracy of infrared measurements [22, 39] by several orders. Precision measurement of the transitions $3^1P \rightarrow 3^1D$ ($\lambda = 95.8 \mu$) and $4^1P \rightarrow 4^1D$ ($\lambda = 216.3 \mu$) in a helium laser would be of great interest in connection with the fact that these results for helium may be compared with the exact solution of the corresponding quantum-mechanical problem [40]. A review of laser spectroscopy is available in [41]; a number of problems of investigating plasma radiations was considered in [42]. In radio astronomy transitions between very high ($n \sim 100$) states of the hydrogen atom [43] and the spectra of dielectronic recombination (the review [44]) are likewise of interest.

In the centimeter-decimeter wavelength ranges magnetic transitions caused by the interaction of two magnetic moments, one of which has an order of magnitude equal to the Bohr magneton (the moment of an electron), while the other has an order of magnitude equal to the nuclear magneton ($\sim 10^{-3}$ Bohr magnetons) are widely known. Transitions between levels of the hyperfine structure of the hydrogen atom ($\lambda = 21$ cm) or of several metals (Cs, Rb, Tl, . . .), many of which are used in frequency standards [4, 45], can serve as examples. Analogous spectra caused by the interaction of moments, each of which is of the order of the Bohr magneton, already lie in the millimeter-submillimeter ranges. The analog of hydrogen - the positronium atom - in which the transition between levels of the hyperfine structure lies in the $\lambda \approx 1.5$ mm region [46], can serve as an example. Positronium is unstable; however ortho-positronium, due to prohibition of two-quantum annihilation, has a lifetime $\sim 10^3$ longer than does para-positronium. The stimulation of ortho-para-transitions alters the intensity of the annihilation, which is what can serve as an indicator of resonance.

At present the magnitude of the hyperfine splitting of positronium, which is of substantial interest in theoretical physics, is measured indirectly - by stimulating transitions between sublevels of the upper level of the hyperfine structure in powerful magnetic fields (at a frequency ~ 2 GHz [46]). Direct measurements at frequencies ~ 200 GHz evidently allow refinement of the magnitude of the splitting.

Another example is the well-known spectrum of oxygen O_2 [1-3]. Recently the oxygen spectrum caused by transitions within one rotational state (60 and 120 GHz) [47, 48] was refined, and a transition with a change in rotational state at the frequency 424 GHz [49] was observed for the first time. Such types of spectra have been investigated comparatively little; however, they are of great interest if we take into account the fact that their low-frequency analogs have provided the possibility of creating the best frequency standard.

For molecules in the range considered one can observe the spectra of low-frequency (torsional-flexural) oscillations which are retarded by small potential barriers. The problem of investigating potential barriers in molecules can be reduced in broader terms to a study of forces between atoms which do not have a direct chemical bond. These forces determine the features of the configuration of large molecules of the protein, etc., type. Radiospectroscopy has made a fundamental contribution to the investigation of inhibited movements of molecules [5, 50]; with the broadening of the range the possibility will develop of also performing a more detailed study of those spectra which currently are being investigated by methods of infrared spectroscopy.

It is of interest to investigate the spectrum of water dimers $(H_2O)_2$ [24] which increase the absorption of millimeter and submillimeter waves in the atmosphere. Essentially, this is a conventional spectrum of

a weakly asymmetrical top with internal rotation; only the conditions governing its appearance are special. Concentration of dimers is proportional to the square of the concentration of monomers; this leads to a situation where for small pressures the concentration of dimers is extremely low, while at high pressures the lines broaden and by merging make it impossible to observe the individual lines. Therefore, up to the present no direct observations are available of dimer lines.

Let us now consider the principal features of radiospectroscopes for the millimeter and submillimeter ranges, due to which this range is optimal for a number of radiospectroscopic investigations and likewise for certain applications of radiospectroscopy.

In the millimeter and submillimeter ranges it is possible to obtain the lines having the highest figures of merit which are accessible to radio methods; this is of great significance for radiospectroscopy and for the creation of frequency standards. The point is that in the majority of types of frequency standards the magnitude of the absolute width of the spectral line is not directly related to frequency (in view of the fact that the Doppler effect is excluded in them). The width of the line is determined by the time T of interaction of the molecules with the microwave field via the relation $\Delta\nu \sim 1/T$. For example, in using the Ramsey method of diversity fields [4] there are no fundamental constraints on the quantity T . However, the figure of merit of the line, which determines the properties of the line and the frequency standard, increases with frequency ($Q = \nu/\Delta\nu$). In other words, in existing frequency standards it is more advantageous to use transitions having higher and higher frequencies in the same molecules or atoms as those for which the technology of long beams, indicators, etc., have already been worked out.

For example, in beam masers based on H_2CO the absolute width of the lines changed only by a factor of 1.5 for a ratio of working frequencies equal to $\sim 10^5$ [31, 51]. In the recent paper [33] a Q of the line equal to $\sim 10^9$ was obtained in a beam device based on the $1_{10}-1_{01}$ transition of H_2S ($\lambda = 1.78$ mm); this is comparable with the highest currently achieved $Q = 6 \cdot 10^8$ for a hydrogen maser. In [52] a similar device based on ammonia was considered. A further increase in frequency may lead to lines having a still higher Q (according to our estimate 10^{11}), however one should note that this requires a considerable development of the technology of the submillimeter range.

The considered frequency range is most convenient for precision determination of the velocity of light as the product

$$c = \lambda\nu,$$

since in this range one can measure both the frequency (by comparison with the appropriate standard) and the wavelength (by methods of infrared spectroscopy in terms of distance and angles). The first papers in this direction are [8, 53] where the frequency and wavelength of the same transitions of the CO molecules were measured. Under these conditions $c = 299,792.8 \pm 0.4$ km \cdot sec $^{-1}$ was obtained, which is in agreement (and has a comparable accuracy) with the best direct measurements of the velocity of light, although in these papers comparatively broad lines were used in gases. Here the use of a frequency-stabilized submillimeter laser is very promising. The power and appearance of existing unstabilized submillimeter lasers are already adequate for obtaining interference at path lengths of the order of a half-kilometer [54]. In [23] phase-shift automatic frequency control of the frequency of a laser based on HCN ($\lambda = 337$ μ) was achieved relative to the multiplied frequency of a 5 MHz standard, a frequency stability of $\sim 10^{-8}$ being obtained. Note that the measurement of shorter (in comparison with the radio range) wavelengths can in principle be achieved more accurately due both to the higher rate of change of the phase with distance and because with shortening wavelength it is easier to create propagation conditions close to those of free space ($v_{ph} = c$). The development of research in this direction may lead to the creation of a unified time-length standard.

In the millimeter and submillimeter ranges one can increase the accuracy of the measurements of the electrical dipole moments of molecules. The radiospectroscopic method of measuring the dipole moments is based on measuring the frequency shift of the components of the line when a uniform electric field is superimposed (the Stark effect) and is the most exact method. For example, one can radiospectroscopically discriminate the magnitudes of the dipole moments in different vibrational states or for different isotopic substitutions in a molecule. The factor which restricts the accuracy of the measurements is the non-uniformity of the superimposed electric field in various portions of the installation, which leads to a broadening of the components of the line and an uncertainty of their centers. In the range considered it is easy to create a structure having adequate dimensions which are almost ideal from the point of view of field uniformity. Such devices include a Stark cell consisting of two parallel plates to which a voltage is applied and

between which a wave is propagated that has been formed by horns [55],* and Fabry-Perot resonators [20]. At longer wavelengths such structures must be very cumbersome and correspondingly less accurate. The combination of a Fabry-Perot resonator with a molecular beam (i.e., narrow lines) is especially promising. The construction of such a device has been presented, for example, in [56, 79]. Stark cells can serve to create an electric-voltage standard; both the reduction of a voltage measurement to frequency measurements and the fairly large magnitude of the standardized voltages (hundreds and thousands of volts), as compared with voltages of several volts for normal cells, are attractive under these conditions.

Finally, due to the high intensity of the lines in the range considered one can use absorptive gas cells having very small dimensions (typical dimensions: length 5 to 50 cm; cross section $\sim 1 \text{ cm}^2$). This facilitates, for example, investigations of unstable molecules [57-59, 241] (radicals, intermediate products of reactions) which would produce serious difficulties if they filled large cavities (the typical length of a cell in the centimeter range is from several meters to tens of meters). In small cells it is easy to create large magnetic fields for investigation of the Zeeman effect [58]; they may be built unsealed for standardizing the frequency of oscillators or wavemeters according to known spectra [60, 37], etc.

2. Methods of Millimeter and Submillimeter Radiospectroscopy

As in any spectroscopy, the basic problems of procedure in the range considered (besides broadening the range) are obtaining a higher resolving power of the instrument and a higher intensity of the observed spectra. In the investigated range, which is on the boundary between the radiospectroscopic and optical ranges, both "classical" radiospectroscopy methods and explicitly "optical" methods are used (for example, gas lasers, spectroscopy based on "Lamb dip," etc.). In microwave structures for this range quasioptical engineering is extensively used along with the conventional waveguide technology. We shall principally consider the features of this range which are most sharply manifested in its shortwave portion.

a) Gas Radiospectroscopy

Gas radiospectroscopy is the most "classical" type and is dealt with in the largest number of papers. Because of the simplicity and universality of such an installation, which usually allows easy changing of the investigated object and tuning of the frequency over wide limits, this procedure is most convenient for primary investigation of spectra, determination of the class of molecules, for obtaining the values of the rotational and centrifugal constants with a fair degree of accuracy, and likewise for obtaining data on the intensity and width of the lines of the molecule. The frequencies of the lines are usually determined with an accuracy $\sim 5 \cdot 10^{-6}$ – $5 \cdot 10^{-7}$. Gas radiospectroscopy has made the main contribution to the investigation of a thousand molecules which have been more or less studied [61]. The accuracy with which the internuclear distances are determined may reach $\pm 0.00002 \text{ \AA}$ [62]. The block diagram of a gas radiospectroscope is displayed in Fig. 1, while the external view of a radiospectroscope operating at $\lambda = 1.2$ – 0.5 mm is displayed in Fig. 2.

Either harmonics of a comparatively low-frequency klystron which are obtained using a crystal multiplier [8], or electronic oscillators operating in the millimeter and submillimeter ranges [11, 12], or, finally, submillimeter lasers [10] are used as the radiation source which transilluminates the sample. In the latter case it follows that in view of the narrow (several megacycles) limits of the frequency tuning it is difficult to expect coincidence of laser frequencies with the lines of the investigated substance (even if the working substance of the laser is used, since the transitions in the laser occur between excited states). For noncoincidence of the lines one can determine the dependence of the absorption on the wing of the spectral line on various parameters by obtaining information, for example, on the presence of dimers [63] or on the processes of line broadening [64]. In [65] the lines of the investigated substance were tuned until they coincided with the laser frequency using the Stark effect within the limits of $\sim 17 \text{ GHz}$. One of the most important problems of spectroscopy using a laser source is precisely the search for coincidences of the

* In [55] an accuracy of $\pm 0.005 \text{ D}$ was obtained at $\lambda = 3.4 \text{ mm}$; in [138] a value of $\pm 0.0002 \text{ D}$ ($1 \text{ D} = 10^{-18} \text{ CGSE}$) was obtained at $\lambda = 12 \text{ mm}$.

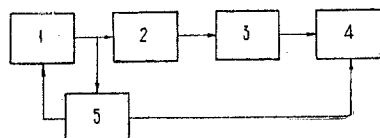


Fig. 1. Block diagram of a gas radiospectroscope: 1) radiation source; 2) absorption gas cell; 3) receiver; 4) indicator; 5) device for monitoring and measuring the frequency.

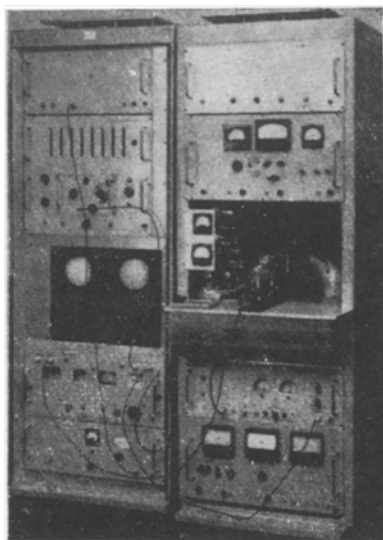


Fig. 2

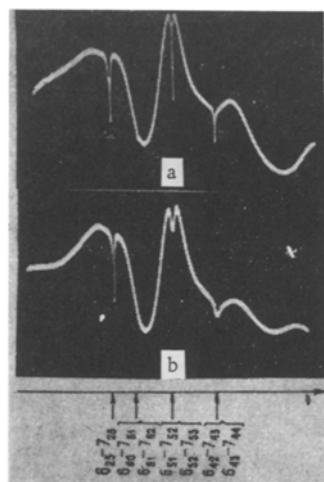


Fig. 3

Fig. 2. Overall view of a radiospectroscope operating at $\lambda = 1.2\text{--}0.5$ mm with quartz frequency reading. The system for measuring the frequency and the indicators are at the left; the radiation source (a backward wave tube), the cell, the receiver, and the system for frequency multiplication and comparison are shown at the right.

Fig. 3. Group of lines for formaldehyde H_2CO and $\lambda = 0.6$ mm. The notation for the lines is given in the figure. Figure 6 shows the result when a nonuniform field $E \approx 1 \text{ kV} \cdot \text{cm}^{-1}$ is applied to the cell. The strong action of the field on the lines which correspond to transitions between pairs of close levels is evident (K-splittings of a weakly asymmetrical top).

absorption lines of the gases with the laser lines (for example, for frequency stabilization of lasers by analogy with [66]). Let us return to the most extensively used spectroscopes having electronic radiation sources. In [8] the principal merits of a source with frequency multiplication are indicated: a broad band when radiation is used at several harmonic numbers, and likewise convenience in measuring and stabilizing a comparatively low frequency of the primary source. The shortcomings of it, however, are the great difficulty of achieving sufficiently efficient multiplication and consequently a very low radiation power at the harmonic frequencies. This impedes the use, for example, of long cells for the detection of weak lines. When the frequency is changed it is necessary to repeat the laborious procedure of tuning the multiplier. In analyzing complex spectra one should remember the simultaneous presence of radiation at a number of harmonics. The construction and operation of such a source (it was one of the earlier ones) have been described in [1, 3, 8] (see likewise the review [67]). Plasma frequency multipliers have also been used [68].

The use of a primary electronic source of radiation in the required range, which assures a power margin, provides the possibility of increasing the signal-to-noise ratio considerably (for example, as in [155]) and greatly simplifies work with the installation. An increase in power allows the investigation of weak lines and an increase in the resolving power of a gas radiospectroscope via spectroscopy within the Doppler lines according to narrow saturation dips; this will be considered below. However, the limits of electronic tuning of modern backward wave tubes, which reach octaves [11, 12], are quite sufficient for the majority of problems. A shortcoming of a radiospectroscope having a primary radiation source in the sub-millimeter range is the necessity of creating a separate circuit for the multiplication of the stable frequency up to this range for measurement or stabilization of the backward-wave-tube frequency. However, the requirements governing the power of the output signal of such a circuit can be reduced due to the possibility of superheterodyne reception of the frequency marker. The first radiospectroscopic investigations of gases using such a source were reported in [69–71, 37]; a typical photograph of lines at $\lambda \approx 0.6$ mm, which was taken using the installation shown in Fig. 2, is displayed in Fig. 3.

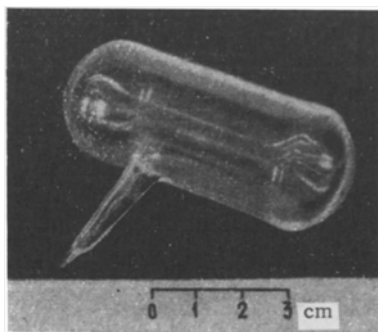


Fig. 4. Quartz sealed cells filled with formaldehyde vapor at a pressure ~ 0.1 mm Hg. The thickness of the quartz is reduced down to fractions of a millimeter at the end faces in order to reduce losses.

The next important component of a gas radiospectroscope is the absorptive gas cell. In order to achieve the least (Dopplerian) width of the line the transverse dimensions of the cell must be fairly large in order to avoid broadening of the line either due to collisions with the walls or due to saturation. Simple formulas for estimating these effects are given in [2]. The optimal length of the cell is determined by the absorption in it; for intense lines in the investigated ranges the optimal length will be of the order of the reciprocal of the gas absorption coefficient. For example, for ammonia at a wavelength $\lambda = 0.52$ mm the optimal length of the cell is ~ 15 cm.

The construction of waveguide cells is generally known [1-3, 8]. In the range considered the resonant properties of such cells are very sharply manifested. The elimination of interfering resonances is achieved by using a Stark spectroscopy or by making the cells smaller. Our experience has shown that certain resonance properties of the microwave channel may be used, for example, to tune the backward wave tube to its power dips. When acoustic indication is used the cell is connected to a microphone [155].

In a Stark cell consisting of two parallel plates it is most convenient to use glass silvered plates and quartz separating inserts which are fairly rigid and can be machined with an accuracy of up to fractions of a lightwave. The microwave radiation is guided through the cell by horns and lenses. In order to avoid fringing effects the width of the plates must be larger than the microwave-field region. By choosing the polarization of the radiation one can achieve the possibility of observing transitions having both $\Delta M = 0$ (the electric fields E of the cell and the radiation are parallel) and $\Delta M = \pm 1$ (the E -fields are perpendicular).

One can use Fabry-Perot resonators as a compact cell. In [58] the Zeeman effect of an unstable CS radical was investigated at $\lambda = 3$ mm using a semiconfocal Fabry-Perot resonator with mirrors having a diameter of 3.8 cm and a distance between them equal to 6 cm, which was enclosed in a glass envelope. In order to retard the reactions the surface of the mirrors was coated with quartz. For a Q equal to 2700 the effective path length $l_{\text{eff}} = Q\lambda/2\pi$ in the resonator was approximately 1.3 m. The resonator was placed between the poles of a magnet. The small resonator dimensions facilitated its filling with the unstable radical which was obtained in a discharge in front of the resonator, and likewise facilitated the creation of fields up to 15,000 G in it.

For a number of practical applications, such as stabilization of the frequency of oscillators from gas lines [70], measurement of the frequency of lines by comparison with known lines of other substances [71], calibration and backward wave tubes and wavemeters, sealed gas cells are very convenient [37, 60]. Figure 4 shows a view of the quartz sealed cell which we used; it was filled with formaldehyde H_2CO vapors, of which the abundance and intensity of the lines, along with a knowledge of their frequencies with an accuracy of $2 \cdot 10^{-6}$ right down to $\lambda = 0.5$ mm [37], make the use of the spectrum of this cell as a reference spectrum convenient. In order to work with such a cell it is placed in the microwave channel between two horns. Figure 3 was obtained using this cell. It is necessary to adopt measures against the accumulation of electrostatic charge on the quartz walls (for example, by irradiating the cell with a quartz lamp and then shielding it). In order to increase the intensity of the lines the cells are frequently cooled.

In [49] a low oxygen-condensation temperature was used very successfully at low pressures in observing the weak magnetic transition $N = 1 \rightarrow 3$, $J = 2 \rightarrow 2$ of oxygen O_2 ($\lambda = 0.71$ mm). In operation the cell was cooled to 77°K (liquid nitrogen), which increased the intensity and reduced the width of the lines considerably. As a result, it was possible for the first time to observe the rotational transition of a molecule having no electrodipole moment and to determine the rotational constant of oxygen by direct experiments.

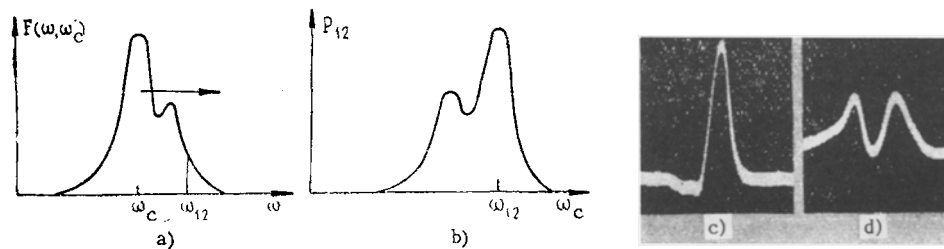


Fig. 5. Shape of the spectral line for transit of a molecule through the region of the microwave field. a) Spectrum of a microwave pulse acting on the molecule, $F(\omega, \omega_c)$. The response of the molecule is proportional to the spectrum component at $\omega = \omega_{12}$. b) Response of a molecule as a function of the signal frequency ω_c (shape of the line); $P_{12} \sim F(\omega_{12}, \omega_c)$. c) Experimentally obtained shape of the line in a beam of molecules which transits through a Fabry-Perot resonator having one field maximum along the trajectory of the molecules (the fundamental oscillation mode). d) Splitting of the line for the higher oscillation mode with two field maxima along the trajectory of the molecules [56].

The radio equipment of gas spectrometers will be considered below. Besides those mentioned in the text, the work described in [162-197] was carried out by gas-spectroscopy methods; the investigated substances at the frequency range are indicated in the references.

b) Radiospectroscopy Having an Increased Resolving Power

The increase in the resolving power of radiospectrometers has led on the one hand to the discovery of very fine interactions of molecules, such as nuclear quadrupole interaction and magnetic interaction of the structure of the spectra, as well as retarded internal motion in molecules, and on the other hand to the development of universally used quantum frequency standards [26, 45]. Since in a gas radiospectrometer the width of the lines is determined in the final analysis by the Doppler effect, the methods considered below for increasing the resolving power are aimed essentially at combatting Doppler broadening of the line. Experimentally an increase of the resolving power has been obtained by two-three orders in comparison with the resolving power of a gas radiospectrometer; methods have been proposed for a further increase in resolving power [33, 52, 72].

In the beginning let us resort to the expression for the shape of the spectral line of a separate free molecule without saturation. The shape of the line is determined by the dependence of the probability of the transition of the molecule from level 1 to level 2 (P_{12}) on the frequency of the signal which transilluminates the sample (ω_c) [4]. The probability of the transition is equal to [73]

$$P_{12} = \frac{1}{\hbar^2} \left| \int_{-\infty}^{\infty} V_{21} \exp(-i\omega_{12}t) dt \right|^2 = \frac{\mu_{21}^2}{\hbar^2} \left| \int_0^{\tau} E(t) \exp(-i\omega_{12}t) dt \right|^2, \quad (2)$$

where ω_{12} is the transition frequency of the molecule; $V_{21} = \mu_{21}E(t)$ is the matrix element of the perturbations; τ is the time for which the microwave field acts (the time of flight of the molecule through the field region, the time between collisions, etc.). Equation (2) is none other than the spectral density of the power of the field $E(t)$ acting on the molecule multiplied by μ^2/\hbar^2 at the frequency ω_{12} (i.e., the shape of the spectral line is determined simply by the spectrum of the microwave field acting on the molecule [74]). The molecule behaves as a "spectrum analyzer" whose response is proportional to the component of the signal-power spectrum at the resonant frequency of the signal (see Figs. 5a and 5b).

For a molecule moving in the field of a plane wave propagating along the z axis, $E(t) = E_0 \cos(\omega_c t - Kz)$, $z = v_z t$ and

$$P_{12} = \frac{\mu_{12}^2 E_0^2 \pi \tau}{4\hbar^2} \frac{\sin^2[\omega_c(1 - v_z/c) - \omega_{12}]\tau/2}{\pi[\omega_c(1 - v_z/c) - \omega_{12}]^2 \tau/2}, \quad (3)$$

where τ is the duration of the interaction with the wave. The second multiplier in (3) determines the line having its center at $\omega_c = \omega_{12}/(1 - v_z/c)$ and a width $\sim 1/\tau$ (for $\tau \rightarrow \infty$ it tends to $\delta[\omega_c(1 - v_z/c) - \omega_{12}]$). The

resultant response of an ensemble of noninteracting molecules is obtained by simple summation of the responses of the individual molecules with the corresponding $E(t)$. In the case of a gas, for example, the averaging of (3) with respect to the Maxwellian distribution $\exp(-mv_z^2/2kT)$ yields the conventional Doppler shape of the line for $1/\tau \ll K\alpha$ (K is the wave vector; $\alpha = (2kT/m)^{1/2}$ is the most probable velocity in the gas).

From (3) it is evident, however, that for each ω_c the field interacts only with one group of molecules for which $v_z/c \simeq \omega_c - \omega_{12}$ (i.e., the Doppler line in essence consists of a set of lines having a width $\sim 1/\tau$). In order to increase the resolving power it is necessary first to isolate one of these lines, and second to increase the time τ for which a molecule interacts with the field. For beam methods of narrowing of the line leave only one group of molecules while truncating the distribution of molecules with respect to v_z ; in the "Lamb dip" method, on the contrary, one of the groups of molecules is eliminated by saturation and the narrow line is observed as a dip in the broad Doppler line. Below we shall consider both methods in greater detail.

The spectral line of one molecule (or of a well collimated beam) is not split in the resonator if the molecule does not depart from one maximum of the microwave field during its motion (i.e., if it practically travels along the front of a plane wave; see Figs. 5c and 5d).† In order to obtain a small line width the front of the plane wave must be sufficiently long. It can be created from "pieces," as in the method of Ramsey diversity fields [4]; in this case the shape of the line can be determined from (2) as the spectrum of a sequence of two microwave pulses having a length τ , which have a time diversity T , where τ and T are the times of flight of a molecule through the resonators and the spaces between them, respectively.

Problems of the shape and width of lines in beam devices were considered in [4]; we shall emphasize only the possibility of monitoring the type of oscillations in Fabry-Perot resonators for the effective narrowing of the line (see likewise [56]). Another method for increasing the resolving power is based on a narrow saturation dip in the Doppler line (the "Lamb dip" [75]) revealed in gas lasers under specified conditions. An exact calculation of the phenomenon is complicated [75]; we shall provide a qualitative picture. In order to obtain the "Lamb dip" interaction with a plane standing wave is required (in a Fabry-Perot resonator).‡

As was noted earlier the Doppler line consists of a set of lines having a width $1/\tau$. In the case of a standing wave (equivalent to two oppositely traveling waves) the signal having the frequency ω_c will already be interacting with two narrow groups of molecules having the velocities $|v_z/c| \simeq |\omega_c - \omega_{12}|$. The increase in radiation intensity (according to the pattern expounded above) leads to saturation of the groups of molecules which interact with the field without involving the remaining ones ("hole burning"). Here, the decisive factor is the existence of a chosen frequency ω_{12} at which both traveling waves interact with the same group of molecules having $v_z = 0$, thus doubling the degree of saturation. The shape of the line as a function of ω_c has a dip with a width $\sim 1/\tau$ at the central frequency of the line for low saturation. If the Doppler line consists of several unresolved components, then such dips will be observed at the center frequencies of each component, which is what provides the possibility of performing "spectroscopy within the Doppler lines" [76]. A planar front of sufficient length (in order to increase τ) may in this case likewise be created from "pieces" [77].**

As has already been noted, the beam method and the "Lamb dip" method are very close. In essence the selection of molecules according to their velocities occurs in each of them, however from the engineering point of view the "Lamb dip" method is more attractive. The use of a gas instead of a beam greatly simplifies the installation and, what is most important, allows operation with large volumes of substance (i.e., it allows the signal-to-noise ratio to be increased). The point is that the optimal power density of the signal in both methods decreases with decreasing width of the line (dip), and an increase in the overall signal power of the detector is possible only together with an increase in the volume of the substance which interacts with the field. However, the creation of a beam of corresponding size is extremely difficult engineering-wise.††

* The shape of the line under these conditions is obtained by averaging (3) with respect to the truncated velocity distribution.

† In a hydrogen oscillator such a state is attained by limiting the motion of the particles by special walls which are such that collisions with them do not change the state of the hydrogen atom [26, 45].

‡ In the beam method it is also the practice to operate with traveling waves [33].

** The molecule may sense diffractive curvature of the front [81].

†† The method of obtaining a narrow non-Gaussian line in a gas without saturation has been described in [82]. Here the volume of the working substance is likewise restricted.



Fig. 6. Saturation dip in the Doppler line (the transition 2_2-3_{-2} H_2O , $\lambda = 1.64$ mm) which was observed in a Fabry-Perot resonator. The signal source was a backward wave tube of the type described in [11]: 1) resonance curve of the Fabry-Perot resonator; 2) Doppler absorption line of water; 3) saturation dip ("Lamb dip") [78].

Let us go over to a consideration of specific papers. In view of the novelty of the "Lamb dip" method, and likewise because it requires a fairly powerful radiation source, this method has not yet been used in radiospectroscopy for the resolution of lines. Figure 6 displays the saturation dip in the 2_2-3_{-2} line of water ($\lambda = 1.64$ mm) which was observed for the first time radiospectroscopically in [78].

We point to [79] as one of the best papers dealing with work carried out by the beam method; here as a result of perfecting a beam collimation system a line width of 4.5 kHz was obtained at a frequency of 168 GHz (i.e., a resolving power which is approximately 50 times as great as that of a gas spectroscope). This made it possible to resolve and investigate the magnetic structure of the $1_{10}-1_{01}$ transition in hydrogen sulfide. The collimation of the beam was achieved by using a freezing honeycomb iris beyond the beam source. A plane-parallel Stark cell 40 cm long and fed by a ribbon beam of the same length was used; the radiation was transmitted perpendicular to the beam by means of horns and lenses. The worst beam collimation [80] allowed only an insignificant narrowing of the lines (down to 100 kHz at a frequency of 100 GHz).

Beam radiospectroscopy in its pure form has not become widely used principally because of the low intensity of the lines obtained by its methods. The development of sensitive reception methods must play a large role. Beam methods using sorting of molecules by states are much more promising.

The sorting of molecules in a beam according to energy states, which was advanced by Basov, Prokhorov, and Townes, led to the creation of the first laser oscillators [9]. A submillimeter beam oscillator using a Fabry-Perot resonator was advanced by Prokhorov [20]. Problems of the generation and reception of infrared radiation by quantum systems were considered in [239]. Beam masers based on HCN [29, 148] and H_2CO [31] were created in the millimeter range. The book [26], where the features of millimeter and submillimeter masers were investigated, was devoted to beam molecular generators. We shall dwell on the radiospectroscopic aspects of beam masers, having likewise considered papers that were published later than [26].

The sorting of molecules can increase the intensity of the observable lines considerably [9]. However, not all transitions are suitable for sorting, and of course this narrows the range of application of this method. The expressions for the Stark effect of the levels of various molecules are made available in [1-5]. For a rough estimate of the possibility of sorting it is useful to remember that the application of an electric field leads to repulsion of the levels between which the transition is allowed, the repulsion force being inversely proportional to the distance between levels. The displacement of a level in the field E is found as the algebraic sum of such repulsions; the number of terms in the sum is usually small when the selection rules are taken into account. From this we immediately obtain the fact that, for example, a pair of levels between which the distance is much smaller than the distance to the remaining levels are repelled by a field (i.e., the energy of the upper levels increases in the field E , while that of the lower levels decreases), which is just what is required for sorting. This scheme corresponds to an ammonia oscillator. The energy of the lowest rotational levels only decreases in the field E , and due to the nonequidistant nature of the rotational energy level (1) the levels having the larger J can be sorted relative to the levels having lower J for specified fields. This is used in oscillators based on HCN and H_2CO . It is likewise clear that with increasing frequency of the transition the sorting efficiency drops; methods of circumventing this difficulty are advanced in [20, 83, 84]. All of them are based on level diagrams which are such that effective sorting in them is achieved via closely situated levels (see Fig. 3b), while inversion is obtained for higher-frequency transitions as well. The limiting case of close levels is sorting of degenerate levels of a symmetrical top; however, in this case it is necessary to remove degeneracy in the resonator by means of an impressed field [83].

Using the focusing action of sorting systems, one can create highly directional beams of molecules of fairly high intensity which allow the time of interaction of the molecules of the microwave field to be

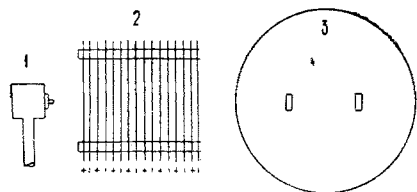


Fig. 7. Diagram of a beam maser operating at $\lambda = 4.12$ mm [56]: 1) source of the molecular beam; 2) flat sorting system; 3) Fabry-Perot resonator. One half of the sorting system and one of the resonator reflectors have been removed; the apertures which provide coupling with the resonator are visible.

increased (i.e., they allow the resolving power of beam spectroscopes to be increased [86, 87]). In [87, 88] a beam length of 2 m was obtained (i.e., a resolving power $\sim 10^8$) using the method of Ramsey diversity fields. A two-cavity molecular generator having a second cavity in which coherent "molecular ringing" is observed may be used as a spectroscope having an increased resolving power even without microwave coupling of the cavities [89]. A further increase of resolving power, which allows the components within a homogeneously broadened line to be isolated, may be achieved by measuring the phase shift of the field created by the "molecular ringing" of the second cavity relative to the field in the first cavity [90, 91]. In essence such a method allows the use of the previously noted dependence of the oscillation frequency in molecular generators on the structure of a line which is not resolvable by conventional methods. The limit of the resolving power in this case is determined solely by the frequency stability of the wave field and according to estimates may reach 10^{10} . This method has not yet been practically implemented.

For radiospectroscopic applications of beam masers the achievement of a masing operating mode is very essential. The methods of tuning the masing frequency to the center of the spectral line allow determination of the frequency of a maser transition with an accuracy of up to 10^{-9} - 10^{-11} [26]. One can study the hyperfine structure according to simultaneous masing on a number of components of the spectral line [240]. The excitation of a two-cavity maser with an amplifier was considered in [247]. The conditions for excitation of millimeter masers were investigated in [92]; the investigation of the frequency responses of a H_2CO maser ($\lambda = 4.1$ mm) was reported in [93] where the frequency of the transition was also measured with an accuracy of $2 \cdot 10^{-9}$. The practical scheme of a beam maser is displayed in Fig. 7 [56]; by the way, the photographs displayed in Figs. 5c and 5d were obtained using this installation. A beam maser operating in the infrared range was considered in [85].

As we have already said, the observation of narrow lines in the millimeter and submillimeter range is made difficult by the necessity of using sensitive receivers in order to operate at low power levels of the transilluminating signal and to avoid saturation of the lines. The reduction of the signal-to-noise ratio, as we know, also degrades the accuracy with which the frequency is replicated in quantum standards [45]. Therefore, the so-called method of electrical resonance in a beam of molecules which was developed in [95, 94, 33] is very interesting. The method likewise allows molecules to be deflected in electrostatic fields, depending on the state of the molecules, just as does the maser method described above; the fundamental difference resides merely in the method of indicating resonance.

Whereas in the maser method the onset of resonance is indicated by a change in the power level of the microwave signal caused by radiation (or absorption) of power by the molecules which perform the transition, in the present method the indication is produced by the molecules themselves after they have made the transition into another state due to the action of the microwave field; for this purpose a "sorting analyzer system" which guides these molecules onto an ionizational or other particle detector is placed beyond the microwave-field region. The method is completely analogous to the magnetic-resonance method [4]. Using this method a Q of $6 \cdot 10^8$ was obtained for the line at the wavelength 1.78 mm and observation of the line in a beam at $\lambda = 0.84$ mm was carried out [33].

Fabry-Perot resonators with flat mirrors irradiated by horns and lenses were used as the diversity microwave-field regions (the Ramsey method); the distance between resonators reached 0.7 mm. A well collimated beam of hydrogen sulfide molecules was passed through the resonators; the parallelness of the mirrors relative to the beam was carefully adjusted. The indication of molecules which have performed the transition was achieved by a detector with electron bombardment which included a mass spectrometer and an electron multiplier. The microwave power required for stimulating the transitions was obtained by multiplying the frequency of a stabilized klystron.

Figure 8 shows the recording obtained for the H_2S line [33]. Let us take note of two factors which must be taken into account in spectroscopy having a high resolution: first, the magnetic field of the earth

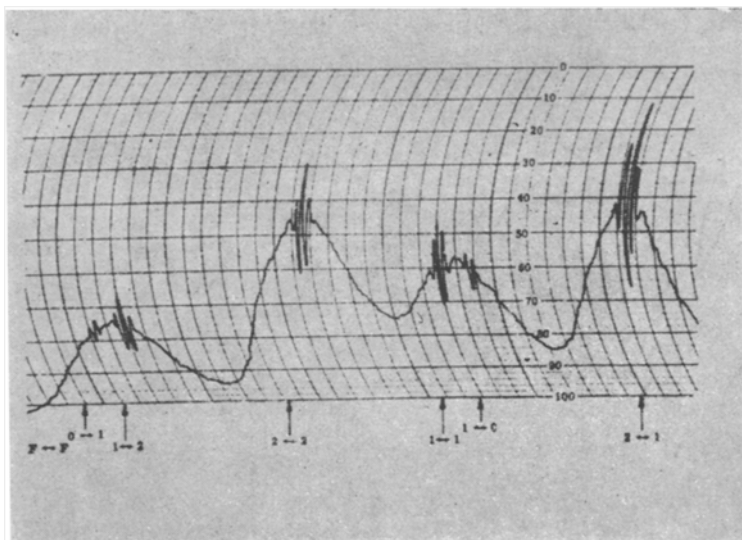


Fig. 8. Magnetic structure of the $1_{10}-1_{01}$ transition of H_2S , as resolved by the method of electrical resonance in a beam of molecules [33]. The width of the Ramsey component is 290 Hz for a transition frequency of ~ 168 GHz.

has a noticeable effect on narrow lines, and this makes it necessary to perform thorough shielding; second, the signal stimulating the transitions, which is obtained via multiplication, must be sufficiently pure in the spectral respect. In [33, 87, 88] stabilization of the signal source relative to a quantum frequency standard was used in order to assure the spectral purity of the signal. A review of the historical development of the method of molecular beams is available in [103].

An interesting group of investigations can be carried out for resonant action of several microwave fields (most often two) having different frequencies on substances. For ammonia it was possible to investigate processes of energy transfer during collisions of molecules by the method of double resonance; under these conditions it was possible to reveal the existence of approximate selection rules for collisional transitions [96, 50]. Thus, in "ammonia-ammonia" collisions allowed electro-dipole transitions are preferable, while in "ammonia-inert gas" collisions there evidently exists a single selection rule $\Delta K = 3n$ [96]. Three-level diagrams are used for maser radiospectroscopy [97]. Various pumping schemes for creating submillimeter masers have been given in [98-100].

The parameters of a radiospectroscope having double resonance was discussed in [101]. In spectroscopy by the method of double resonance, phenomena analogous to the "Lamb dip" can be observed for Doppler spectral lines coupled via a common level; these phenomena may be used to increase the resolving power of the method [102]. The method of double resonance may be used to indicate transitions in the submillimeter range via a change in the intensity of more-accessible low-frequency transitions [20, 26]. Here the most interesting object is again ammonia with which it is possible to create submillimeter lasers [20] and likewise a frequency standard according to the Ramsey scheme with stimulated submillimeter transitions [88].

c) Laser Radiospectroscopy

Such a specific form of radiospectroscopy as laser radiospectroscopy, which uses radio methods to investigate the spectra of a number of substances according to their intrinsic radiation in gas lasers, is also used in the submillimeter range. Table 1 gives a list of the wavelengths and operating substances of submillimeter lasers. This method is used to investigate transitions between excited states of atoms and molecules, the accuracy of the measurements exceeding the accuracy of infrared methods previously used in this range by several orders. The principal difficulty of the procedure indicated resides in the correct identification of the observed transitions. It is enough to say that although the first submillimeter lasers appeared in 1964, a sufficiently reliable identification of a number of transitions of HCN, DCN, and H_2O lasers was obtained only in 1968 [104, 105]. For a number of lasers (based on SO_2 [106-108], ICN [227], H_2S , and OCS [108]) identification is still lacking.

TABLE 1. Table of Submillimeter Laser Lines

λ (μ)	f (MHz)	Substance	Comment
774		ICN	pulsed
538,5		ICN	pul.
537,5		ICN	pul.
372,80		HCN	pul.
337	890759,5	HCN	continuous wave
311	964312,3	HCN	c. w.
309,94		HCN	pul.
225,3		H ₂ S	pul.
223,25		HCN	pul.
220,23	1361282,6	H ₂ O	c. w.
218,5		D ₂ O	pul.
216,3		He	c. w.
215,27		SO ₂	pul.
211,14		HCN	pul.
204	1466787	DCN	c. w.
201,19		HCN	pul.
194,76	1539257	DCN	c. w.
194,70	1539745	DCN	c. w.
192,9		H ₂ S	pul.
192,67		SO ₂	c. w.
190,0	1577789	DCN	c. w.
189,95	1578279	DCN	c. w.
181,90		HCN	pul.
171,67		D ₂ O	c. w.
170,08		D ₂ O	pul.
162,4		H ₂ S	pul.
151,16		SO ₂	pul.
140,85		SO ₂	c. w.
140,6		H ₂ S	pul.
135,5		H ₂ S	pul.
135,03		HCN	pul.
133		Ne	pul.
132		OCS	pul.
130,95		HCN	pul.
130,8		H ₂ S	pul.
129,1		H ₂ S	pul.
128,75		HCN	pul.
126,24		HCN	pul.
126,2		H ₂ S	pul.
126,1		Ne	c. w.
124,4		Ne	c. w.
123		OCS	pul.
120,08		H ₂ O	pul.
118,59	2527952,8	H ₂ O	c. w.
116,8		H ₂ S	pul.
115,32		H ₂ O	pul.
111,74		D ₂ O	pul.
110,49		D ₂ O	pul.
108,88		D ₂ O	pul.
108,8		H ₂ S	pul.
107,91		D ₂ O	pul.
107,73		D ₂ O	c. w.
106,02		Ne	pul.
103,33		D ₂ O	pul.
103,3		H ₂ S	pul.
99		D ₂ O	pul.

Identification is complicated principally by two factors. First, the strong electrochemical action of the discharge on molecular gases leads to the appearance of substances in the laser which differ very greatly from the original ones. Thus, in the most powerful laser at 337 microns the working substance turned out to be prussic acid HCN which is absent in the majority of the original mixtures. Second, there is a great variety of possible combinations of vibrational-rotational transitions, it being true that far from all of the rotational lines of a given vibrational transition are usually generated, and this makes any kind of systematization difficult.* This is evidently due to the fact that the corresponding matrix element of the dipole moment of the transition is large only for so-called perturbed pairs of levels [124,198]. It would be useful to know the regularities governing the excitation of the particular levels, which would allow a narrowing of the scope of possible versions.

* In general it should be noted that the "threshold" character of such spectroscopy complicates investigations. In our opinion it would be of great interest to investigate a gas discharge by conventional radiospectroscopic methods (with a transilluminating signal); this would allow unexcited lines to be seen, and also the establishment of the systematic configuration of these lines and the choice of the conditions for their maximal intensity.

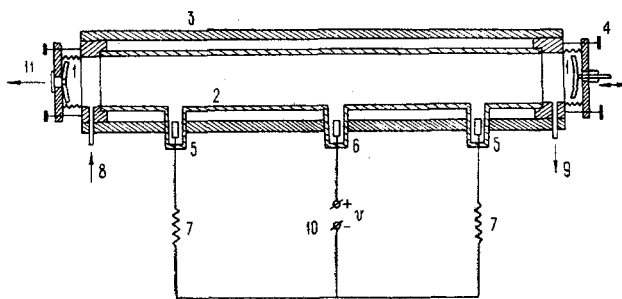


Fig. 9. Diagram of a submillimeter gas laser: 1) mirrors of the Fabry-Perot resonator; 2) glass vacuum tube; 3) housing of the laser; 4) adjusting screws; 5) water-cooled cathode; 6) anode; 7) ballast resistors; 8) admission of the working substance; 9) evacuation; 10) high-voltage source; 11) laser-radiation output.

In view of the fact that this new form of radiospectroscopy is of considerable interest, and likewise taking account of the fact that at present there is no systematic exposition of this problem, we shall dwell on submillimeter gas lasers in greater detail and present the bibliography which is accessible to us.

A submillimeter laser is a Fabry-Perot resonator confined in a vacuum tube in which a glow discharge is occurring in the appropriate gas (Fig. 9). The diameter of the laser tube is usually 5 to 10 cm, and its length is 2-6 m. The usual pressure range of the gas is 0.1 to 0.5 mm Hg; the discharge currents in the continuous-wave mode are 0.4 to 1.2 A (up to 10 A in the case of helium [40]). The pulsed operating modes which are used are quite varied. In view of the absence of sufficiently transparent materials for the windows, submillimeter lasers usually use internal mirrors; there are also constructions with external mirrors in which the vacuum tubes of the laser are implemented using thin (of the lavsan type) films [109]. Spherical concave mirrors coated with a layer of gold or silver are usually spaced somewhat closer to one another than they are in the confocal case. The output of the radiation is most often accomplished through an aperture in the mirrors; sometimes partially reflecting films placed at 45° with respect to the laser axis are used. For selective excitation of lines one of the mirrors is replaced by an echelette [110], which yields still another form of coupling to the cavity resonator.

In this range the distance between adjacent longitudinal laser-cavity modes is larger than the width of the line, and the primary determination of the wavelength of the radiation from a submillimeter laser may be carried out using the fact that for tuning of the laser cavity the radiation maxima appear approximately every $\lambda/2$. A typical recording for two generated lines is displayed in Fig. 10. The analysis of such interferograms is carried out by the usual method of Fourier transforms (see, for example, [111]). A substantial increase in accuracy is obtained when the transition is made to radiospectroscopic methods - measurement of the frequency of the transitions according to beats with the multiplied frequency of a quartz oscillator ([21, 22, 39, 123, 145, 135] and Table 1). In order to increase the accuracy conventional methods of tuning the lasing frequency to the center of the line are used; in the case of a laser based on water the accuracy is increased due to the possibility of tuning according to the "Lamb dip" (Fig. 11).

The excitation mechanism is known sufficiently well only for atomic submillimeter lasers based on He and Ne [40, 112]. Here inversion is obtained for excitation by electron impact. The probability of excitation by electron impact is in the first approximation proportional to the probability of the corresponding dipole transition, and if the ground level 1S is the original level, then the excitation process corresponds to the allowed transition $1S \rightarrow nP$, where $n = 3-9$, while inversion is obtained on the transitions $nP \rightarrow nD$. The population of the level likewise depends on the processes of radiation "capture" [40].

For molecular submillimeter lasers the excitation mechanism is still unclear at present. The interpreted spectra of lasers based on HCN, DCN, H₂O, and D₂O and consideration of analogous infrared lasers (based on CO₂, N₂O, etc.), allow the conclusion to be drawn that inversion is obtained between vibrational levels belonging to different vibrational modes of the molecules. In a gas discharge the population of each vibrational mode may be described in the first approximation by its vibrational temperature [121].

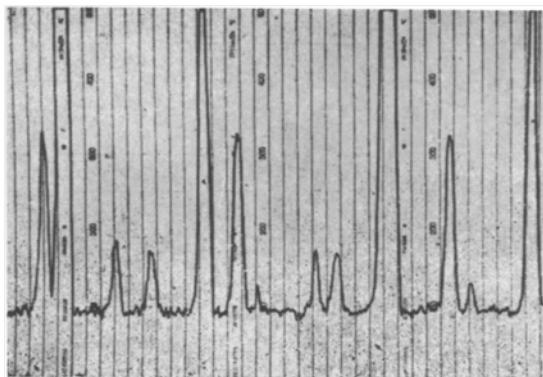


Fig. 10. Recording of the radiation from a submillimeter laser based on $D_2O + D_2$ for tuning of the laser cavity. The large peaks represent lasing at the wavelength $\lambda = 171.6 \mu$ via TEM_{00} and TEM_{01} oscillations alternately; the intermediate peaks represent lasing at $\lambda = 107.7 \mu$, and the small peaks correspond to lasing in the higher cavity modes. In order to excite the 107.7μ line one of the mirrors is a matte copper mirror (it attenuates the competing high-frequency line) [132].

Note the fundamental importance of this fact, which allows the use of inversion between levels differing in energy by a fraction of an electron-volt (in the submillimeter range) for the excitation, for example, of electrons having a continuous spectrum in an interval of several electron-volts, as long as these levels belong to different vibrational modes of the molecule. However, the mechanism of predominant population is unclear. This may be excitation by electron impact, excitation as a result of mechanical processes, or, finally, resonant energy transfer ($CO^* \rightarrow CO_2$, $N_2^* \rightarrow CO_2$, and perhaps $OH^* \rightarrow H_2O$). In triatomic molecules inversion is usually obtained between valency (upper level) and deformational (lower level) vibrational modes. The deformational vibration is of low frequency and relaxes more rapidly.

In considering Table 1 it is evident that laser action in the millimeter range is obtained using fairly light triatomic molecules. Let us attempt to provide a certain explanation of this fact. In order for the frequencies of the rotational-vibrational transitions to fall within the submillimeter range (for conventional selection rules $|\Delta J| = 0; 1$) it is necessary for the upper and lower vibrational laser levels to be closely spaced (i.e., the levels must belong to different vibrational modes of the molecule).[†] The presence of more than one vibrational mode is likewise essential for obtaining inversion. The existence of several vibrational modes of a molecule is possible only when at least three atoms are present in the molecule. A pronounced increase in the number of atoms is also disadvantageous, since under these conditions the intensity of an individual line (see above) decreases and the role played by the relaxation mechanisms increases. For the same reasons it is disadvantageous for the molecules to become heavier. A molecule must be sufficiently stable (or selfreproducing) in the discharge.

In order to obtain a sealed operating mode of H_2O (D_2O) lasers an admixture of H_2 (or D_2) was used which shifted the equilibrium of the water dissociation-recombination reaction and yielded an increment of power (for $D_2O + D_2$ almost by two orders) [129, 131, 132, 216]. The "soft" excitation of unstable substances — for example, soft excitation by nitrogen, as in the first papers on CO_2 [113], is very interesting.

An investigation of a CO_2 laser led to the detection of a very general method of obtaining inversion via vibrational-rotational transitions of molecules (see, for example, the review [113]). It turns out that in order to obtain maser action via a series of vibrational-rotational transitions of the P-branch it is sufficient for the condition $T_k \gg T_{bp}$ to be fulfilled, where T_k , T_{bp} are the vibrational and rotational temperatures which describe the populations of the corresponding levels. Such a laser is very similar to a heat machine with T_k corresponding to the heater temperature and T_{bp} corresponding to the refrigerator temperature. Due to the fast rotational relaxation (usually one or a few collisions are sufficient for this) T_{bp}

[†] The transitions between levels of the same vibrational modes yield a spectrum in the infrared region.

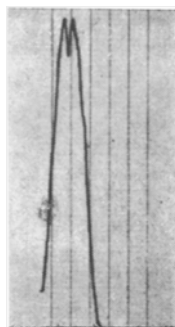


Fig. 11. Radiation from a sub-millimeter H_2O laser ($\lambda = 118.6 \mu$) for tuning of the laser cavity. A "Lamb dip" is visible on the top of the line.

is maintained close to the temperature of the walls of the vessel (laser tubes). A high temperature of T_k can be obtained by the methods already mentioned above – if the discharge T_k is close to the electron temperature ($\sim 10^4\text{K}$); the energy of the chemical reactions is frequently released in the form of vibrational energy [115]. Finally, due to the fact that vibrational relaxation is approximately 10^3 times slower than rotational relaxation, the condition $T_k \gg T_{bp}$ may be fulfilled for rapid cooling of the heated gas [116]. The excitation processes in nonequilibrium gases have been considered in the review [235].

Let us now consider the procedure for identifying the laser transitions. The primary search for the substance responsible for laser action is characterized by varying the composition of the gases which enter the laser. Thus, the starting point for identification of the HCN laser was the proof of the necessity of the presence of C, N, and H (or D for DCN) in the discharge [117]. The investigation of the Zeeman effect of a laser operating at 118.59 with water vapor, which yielded a value of the order of the nuclear magneton for the magnetic moment, allowed the version with OH to be eliminated [118]. An indication of the fact that laser transitions correspond to transitions between higher vibrational–rotational states lies in the results of [119, 110] which showed on the one hand the weak absorption of laser radiation in an unexcited medium (i.e., the energy of the levels $\epsilon \gg kT$), while on the other hand an increase in power occurs for almost all laser lines for a one-frequency laser operating mode (since fast thermalization of the rotational sublevels leads to a certain competition between all rotational–vibrational transitions between given vibrational states).

However, all of these data still left considerable arbitrariness in the choice of possible versions of laser transitions, since the accuracy with which the rotational and vibrational constants of the excited states are known is usually not adequate for an unambiguous identification of the transitions. Finding correlations between laser lines which are evidence of the fact that these lines have common energy levels [120] is decisive for the identification of laser lines in water vapor. If two laser transitions have a common upper or lower level, an increase in lasing power at one transition leads to the suppression of lasing at the other. Such transitions are called competing transitions.

However, if the lower level of one laser transition is the upper level of another, then an increase in lasing power at one transition increases the power (or creates conditions for lasing in the first place) at the

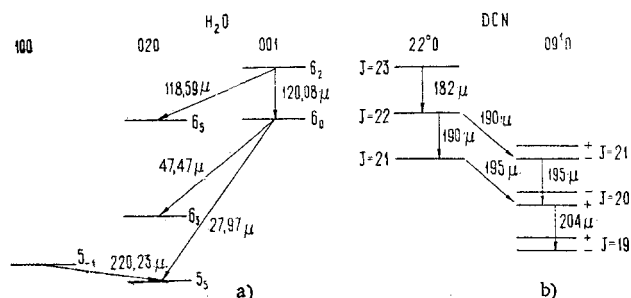


Fig. 12. Level diagram for submillimeter lasers based on H_2O (a) and DCN (b). The vibrational levels are identified above the lines, while the rotational levels are identified next to the lines. The arrows denote the laser transitions.

other. These are cascade transitions. The ideal cavity for investigating such correlations is a twin Fabry-Perot resonator with echelettes replacing one of the mirrors [122]. In submillimeter lasers a large number of correlations was revealed between lines, which allowed a reliable check to be carried out of the identification of the transitions. The identification of lasers based on H_2O and D_2O is given in [105, 124, 244]; for lasers based on HCN and DCN it is given in [104], for He lasers in [40] and for Ne lasers in [125]. Under these conditions the data on the fact that for $\lambda = 118.6 \mu$ (H_2O) J is an integer and is larger than or equal to 2, $\Delta J = 0$ [118], which were obtained in investigating the Zeeman effect, were substantiated. A convincing check was the detection of new laser lines which fit within the scheme advanced previously [123]. Figures 12a and 12b show the level diagrams for several typical laser transitions.

The other branch of laser radiospectroscopy in the millimeter and submillimeter ranges is measurement of the difference frequencies of lasers having shorter wavelengths [18, 126, 127]. Such measurements allowed, for example, a considerable refinement of the rotational and centrifugal constants of the CO_2 molecule [126]. The linear CO_2 molecule is nonpolar due to symmetry and cannot have a purely rotational spectrum. Oscillations of a CO_2 laser ($\lambda = 10.6 \mu$) were heterodyned by another laser of the same kind; the lasers were stabilized on adjacent rotational transitions of one and the same vibrational transition. Under these conditions their difference frequency, which was determined directly by the rotational and centrifugal constants, lay in the millimeter range and was measured by conventional radiospectroscopic methods.

Besides the papers mentioned in the text, H_2O lasers were investigated in [208-216, 224], D_2O lasers in [224-226, 214, 212], HCN lasers in [214-223, 231, 237], ICN lasers in [227-229], and He lasers in [230]. Mixing of laser harmonics was investigated in [128], and field submillimeter lasers were investigated in [129-132]. A review of submillimeter lasers was given in [133, 242], and the use of lasers in this range for radiospectroscopy was covered in the review [134]. A very full review of water lasers was given in [124]. The role of laser radiospectroscopy must increase with the perfection of lasers and the expansion of the variety of substances used in them.

3. Radio Equipment for Millimeter and Submillimeter Radiospectroscopy

The use of the radiospectroscopic procedures mentioned above has become possible due to the development of the radio engineering portion of the equipment used in the ranges considered. In considering the corresponding equipment we should like to emphasize the accessibility of the millimeter and submillimeter ranges at the present time, along with the difficulties involved; of course, this accessibility has been achieved at the cost of a great deal of work by a number of investigators. Thus, frequency multiplication in this range turned out to be effective enough to observe laser beats of harmonics as far away as the 23-rd of klystrons which have been stabilized according to a standard frequency [135], and to multiply the oscillations of a laser at 28μ to 9.3μ [246]; submillimeter lasers have also turned out to be fairly powerful (up to 0.6 watts in the continuous-wave operating mode [136]); notwithstanding unfavorable predictions, it has been possible to use electronic oscillators to cover the range down to $\lambda = 0.2 \text{ mm}$ [11, 12], while point-contact detectors have been used as far down as $\lambda = 10 \mu$ [18]. We shall devote our basic attention to the short millimeter and submillimeter ranges in which there is no choice of standard equipment.

The sources of radiation in the range considered are the lasers considered above, semiconductor frequency multipliers (see [1-3, 8] and the reviews [67]), intrinsically semiconductor oscillators [137], and traveling-wave tubes [11, 12]. Semiconductor oscillators using various bulk effects in the solid state are very promising. By now values of power of the order of hundreds of milliwatts at wavelengths down to $\lambda = 4 \text{ mm}$ [137] have already been attained using them; however, these investigations have not yet progressed beyond the laboratory stage. Spectral characteristics of the radiation from these sources are also unavailable.

At present backward-wave tubes are the most convenient devices for radiospectroscopic application. Their parameters are given in [11, 12], while the ways of developing electronic devices for this range have been considered in the review [139]. We shall consider problems of stabilization and measurement of the frequency of backward-wave tubes, since it is precisely on the solution of this problem that a further development of millimeter and submillimeter radiospectroscopy depends, both in terms of the expansion of the range and in the realization of the potential possibilities for increasing the resolving power and sensitivity of radiospectroscopes. This problem also has great significance for a number of practical problems which extend beyond the scope of radiospectroscopy.

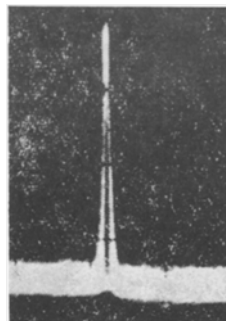


Fig. 13. Beats of a submillimeter HCN laser ($\lambda = 337 \mu$) with the eighth harmonic of a backward-wave tube [145].

In order to measure frequencies in the millimeter and submillimeter ranges the multiplied frequency of oscillators operating in the conventional band is frequently used; this frequency is monitored in the conventional manner, while its harmonics are compared with the measured frequency. The original oscillator is a fairly stable quartz oscillator whose frequency is brought up to ~ 300 – 500 MHz by a chain of vacuum-tube multipliers; after that the multiplication is accomplished using crystal detectors and usually extends to the $\lambda = 3$ – 1.5 cm range. In this range phase-shift automatic frequency control (afc) of a fairly powerful oscillator is performed relative to a stable harmonic for purposes of subsequent multiplication, and beyond that the stages of multiplication and stabilization are repeated the required number of times.

The clarification of the problem of choosing the stages and frequency-multiplication coefficients is essential. Practice shows that in order to obtain quartz markers down to the 0.3 to 0.5 mm range it is sufficient to stabilize a 4 -millimeter klystron having one intermediate phase-shift afc system incorporating a 3 -centimeter klystron; in order to obtain markers down to $\lambda = 0.1$ mm it is sufficient to stabilize a 2 -millimeter klystron with an intermediate stage at $\lambda = 1.5$ cm [21, 140, 37, 141]. Frequency tuning is achieved by changing the harmonic number by stages in any multiplication stage and smooth tuning of the auxiliary oscillator [33], or by using a tunable master oscillator [37]. In [142–144] a frequency-measurement system is described in which the last stage (a backward wave tube at $\lambda = 2$ or 4 mm) is not stabilized with respect to the harmonics of the previous stage; its frequency is stabilized using a Fabry–Perot resonator and is simultaneously compared with both the measured frequency (at the harmonic) and the standard frequency (at the fundamental frequency of the backward wave tube). The output of the klystron (or of the backward wave tube) of the last stabilization stage is applied to a crystal mixer-multiplier to which the radiation from the laser or the backward-wave tube whose frequency needs to be measured is applied.

The multiplier-mixer is the most specific component. It is usually implemented using crossed waveguides which are penetrated by a tungsten electrolytically sharpened needle whose contact with the silicon crystal is achieved in the narrow waveguide.* In [37, 69, 71] standard crystal diodes operating at longer wavelengths were also used successfully for this purpose down to wavelengths of $\lambda = 0.5$ mm. The beats obtained in the mixer are amplified by an intermediate-frequency amplifier, detected, and applied to an oscilloscope. Usually the frequency of the measured backward wave tube is modulated for observation of the spectral line. In this case a pulse appears at the detector output any time the beat frequency coincides with the intermediate frequency. This pulse is treated as a frequency marker and is made to coincide with the measured line, after which the frequency is read. The usual accuracy of such a procedure is 10^{-6} to 10^{-7} ; i.e., it is adequate for a gas radiospectroscope. Measurement of the frequencies of lasers is carried out analogously; Fig. 13 displays the beats of a laser operating at $\lambda = 337 \mu$ with the eighth harmonic of a 3 millimeter backward wave tube [145].

In order to solve a number of problems it is convenient to use a system for stabilizing the frequency according to a tunable Fabry–Perot resonator, or, in just the reverse way, according to a spectral line which is independent of external conditions. An example of the use of the first system can be found in the detailed obtaining of the spectrum in a fairly wide frequency range, while an example of the second is a frequency reference, or the pumping of a maser or parametric amplifier at the given spectral line. In these cases a conventional scheme is used for automatic frequency control with respect to the resonant element whose response slope is used to convert the frequency-modulated signal into an amplitude-modulated signal, the phase of the modulation depending on the sign of the detuning of the oscillator and the resonant element. The envelope after synchronous detection is what constitutes the control signal.

* See comment during editing (p. 782).

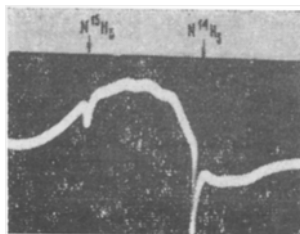


Fig. 14. The lines $J = 0 \rightarrow 1$, $K = 0$ of conventional ($N^{14}H_3$) and isotopic ($N^{15}H_3$) ammonia at $\lambda = 0.525$ mm. The $N^{15}H_3$ content is approximately 12%.

In order to improve the purity of the signal spectrum one should use increased frequencies and low modulation indices. Systems for performing frequency stabilization using a Fabry–Perot resonator for waves down to $\lambda = 0.8$ mm are presented in [142, 143, 70], while systems for frequency stabilization according to a spectral line at $\lambda = 3$ mm are discussed in [147] and at wavelengths down to $\lambda = 0.8$ mm in [70]. The constructions of gas cells have been described above. A further development of a system for stabilization of backward-wave tubes relative to a spectral line can be found in stabilization according to a saturation dip in the Doppler line ([70], and likewise see Fig. 6).

As in ranges corresponding to lower frequencies, systems for frequency stabilization of oscillators according to a stable reference signal (for example, a signal obtained by frequency multiplication, such as the quartz markers described above) must play a principal role. In [146] a system for automatic frequency control of a backward-wave tube relative to a stable harmonic in the $\lambda = 0.57$ –1 mm range is described. The system of phase-shift automatic frequency control of a backward-wave tube in the $\lambda = 0.8$ –4 mm range was described in [199]. A communication on frequency stabilization of a laser at $\lambda = 337 \mu$ is also available [23].

Frequency stabilization of the signal source in investigations having a high resolution acquires special significance, since the "floating" of the signal frequency during the observation time or the impurity of its spectrum may lead to substantial distortion of the line profile. Insufficient stability likewise does not allow the use of time averaging in order to increase the sensitivity of reception. In investigations of lines having $Q \gtrsim 10^8$ the signal source was stabilized relative to quantum frequency standards [33, 87, 88].

Let us also describe the procedure for measuring frequency in comparison with a standard spectrum, and a new version of measuring the frequency by means of a Fabry–Perot resonator. The high intensity of the lines in the indicated ranges and the tuning width of a backward-wave tube facilitate simple primary identification of substances and transitions according to "the spectrum as a whole." For this purpose the oscillation frequency of the source is slowly tuned (for example, by a motor) over a wide range, and first the investigated and then the standard spectrum (or the investigated spectrum with the standard superimposed on it) are recorded on an automatic pen recorder. The standard spectrum is used to plot a calibration graph. Under these conditions a null radiospectroscope with acoustic indication is very convenient [155]. In the case when the measured line is spaced no further than ~ 500 MHz from the standard line, the accuracy of measurement may be increased considerably by using measurement of the distance between lines by the well-known method of double frequency modulation of the source [1–3]. Under these conditions it follows that since small frequency differences are being measured the measurement error will be no more than tenths of a megacycle at a wavelength $\lambda = 0.5$ mm.

Figure 14 shows the lines $J = 0 \rightarrow 1$, $K = 0$ of conventional and isotopic ammonia at $\lambda = 0.525$ mm; the distance between them is equal to 384.8 ± 0.2 MHz [71]. The frequency of the transition for isotopic ammonia ($N^{15}H_3$) was measured according to the known [141] frequency of the transition for conventional ammonia ($N^{14}H_3$). The difficulty in this method consisted in ensuring a sufficiently dense overlap of the range by the reference lines.

In the range considered it is comparatively easy to implement a Fabry–Perot resonator having a Q of 10^5 – 10^6 , which in principle determines the allowable accuracy of the measurements. However, it is fairly complicated to implement it in the operating mode of a conventional resonant wavemeter, both due to the necessity of a precision reading of the length and due to the unmonitorable changes in the resonator parameters. In [78] a different method was proposed and implemented, which basically reduces to frequency measurement. Let us clarify the essence of the method.

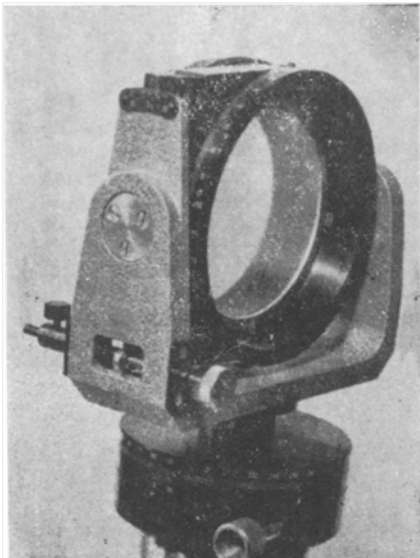


Fig. 15. Reticular element in the adjusting adapter [19].

The resonant frequency of a Fabry–Perot interferometer is equal to

$$\nu = F(q + \delta), \quad (4)$$

where $F = c/2L$ is the intermode distance; L is the resonator length; q is the number of longitudinal modes; δ is a correction which is calculated from the geometry of the resonator. The principal feature of the method is the replacement of measurement of L by measurement of the intermode distance F again using double frequency modulation of the signal source by analogy with measurement of the distance between lines in the previous method. The modulation frequency of the backward-wave tube is measured by an electron-counting frequency meter. In order to determine the quantity q the index q is varied by a certain known number n (measured according to the number of resonances which are passed through to the oscilloscope screen) at the same frequency ν , and the intermode distance F' is measured again; this provides the possibility of calculating q according to (4). Let us focus attention on the fact that since q is an integer, it follows that the accuracy of determining it with an absolute error of several tenths is sufficient. This error does not affect the determination of the frequency ν , and the error of measuring ν will be of the order of the error in measuring F .

In radiospectroscopy of the range considered, problems of constructing the appropriate microwave channel are very essential. Here both waveguide and quasioptical methods are used. Waveguide devices are generally known; we note merely that in order to reduce the losses of the channel in this range it is the usual practice to employ waveguides having larger dimensions. Quasioptical methods in millimeter radiospectroscopy were not considered in [149]. We shall dwell merely on the very essential quasioptical elements, which were not dealt with sufficiently in [149], such as reticular elements and high- Q Fabry–Perot resonators.

Grids consisting of parallel wires were already being used by Hertz and Lebedev as polarizers and analyzers of radiation; recently this method has been developed further [19, 150]. Flat metallic grids made of thin parallel wires whose dimensions satisfy the conditions

$$a \gg \lambda > l > d, \quad (5)$$

where a is the aperture, λ is the wavelength, l is the period of the grid, d is the diameter of the wire, have a reflection coefficient in the range from 0.001 to 0.986–0.997 in the submillimeter range, depending on the angle between the wires and the vector \mathbf{E} of the wave incident on the grid. The reflection is minimal for perpendicular directions of \mathbf{E} to the wires, and it is maximal for parallel directions. Such grids allow the creation of practically all the analogs of waveguide devices, including Fabry–Perot resonators having $Q \approx 10^4$ – 10^5 , attenuators, directional couplers, interferometers, etc. Their merits are low losses, a very large bandwidth (practically the entire millimeter and submillimeter ranges), and easy achievement of the required coupling coefficient and oscillation mode.

From the radiospectroscopic point of view such devices are very convenient for filling with gases, transmitting molecular beams, etc. The grids usually employed were made of gold-coated wires having a diameter $d = 8$ – 15μ which were stretched with a period $l = 30$ – 150μ on a mounting having a diameter $a = 40$ – 90 mm (Fig. 15). A quasioptical channel is combined with waveguide channels (the output of a backward-wave tube, the input of a detector) using horns having a small aperture angle which are equipped with Teflon, polyethylene, etc., lenses. The methods of tuning a complex microwave channel in this range have been expounded in [94].

Another important device used in the range considered is a Fabry–Perot resonator having the maximum possible Q and a monitorable oscillation mode. The description of such resonators has been given, for example, in [70, 78]. The resonator consists of two concave mirrors 110 mm in diameter which are fabricated with optical accuracy and are coated by vacuum deposition of a silver layer $\sim 5 \mu$ thick. The distance between mirrors is 300 mm; the radius of curvature of the mirrors is 1200 mm. A lavsan coupling film 10μ thick is stretched midway between the mirrors at an angle of 40° with respect to the

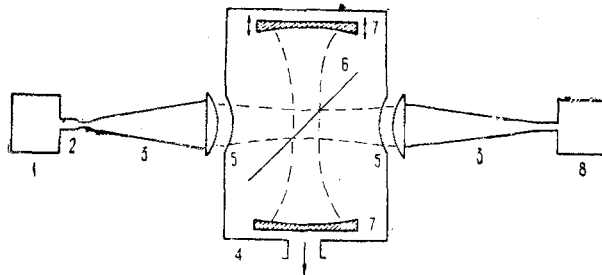


Fig. 16. Diagram of a radiospectroscope using a Fabry-Perot resonator: 1) signal source (backward-wave tube); 2) filter which eliminates the higher oscillation modes; 3) horn with a Teflon lens; 4) vacuum chamber; 5) windows made of lavsan film for transmitting the radiation; 6) film for coupling the Fabry-Perot resonator; 7) mirrors of the Fabry-Perot resonator; 8) receiving detector. The dashed lines indicate the region of the microwave field.

resonator axis. The mirrors and the film are equipped with devices for alignment; one mirror can be moved along the axis for tuning purposes. The housing of the resonator is made of invar. The coupling film is irradiated by horns having an aperture 40×55 mm and a length 230 mm. Such a coupling construction does not introduce inhomogeneities, is easily controlled, and ensures excitation of only the fundamental oscillation mode when it is properly adjusted. The resonator ensures $Q = 5 \cdot 10^5$ and $\lambda = 1$ mm.

Figure 16 displays a typical diagram of a radiospectroscope with a Fabry-Perot resonator by means of which the photographs shown in Figs. 8 and 18 were obtained. The use of Fabry-Perot resonators in radiospectroscopy is likewise described in [232-234].

The traditional and most widely used receiver in radiospectroscopy is a semiconductor detector having a point contact. Its constructions for the millimeter and submillimeter ranges have been described in [1-3, 8]; later data (including detectors, mixers, and frequency multipliers) are given in the reviews [67].* The silicon-tungsten pair is most widely used; however, successes in detecting radiation at a wavelength of 10μ by means of a tungsten-silver or tungsten-steel point contact [18] may stimulate the search for new (as is evident, quite unexpectedly) detector pairs. The tendency here is to increase the mobility of the carriers in the semiconductor and likewise to use thin semiconductor films to reduce the spreading resistance. The construction of the coupling element is of great significance. A new and well-proven construction of a detector having loop coupling is given in [151]. Figures 8 and 18 were obtained using this detector. The use of superheterodyne receivers in the range of shorter wavelengths is for the time being limited in connection with the fact that their successful operation requires the heterodyne frequency be stabilized, and likewise in view of the difficulties of tuning over a wide range.

The use of optico-acoustic receivers (Golay cells) in this range is generally known. In view of their long time constant a high stability of the signal frequency and its smooth tuning are required during the observation of narrow lines. The development of the Veingerov [152] acoustic infrared receiver may turn out to be very promising for radiospectroscopy; in this device the radiation is absorbed directly in the gas filling the cell, so that the absorptive cell and the receiver are combined. In radiospectroscopy such a method was realized in [155] in the range of wavelengths 2.4-0.5 mm using a monochromatic signal with a tunable frequency, a high sensitivity being obtained.† The null character of the method is essential, in which the receiver does not respond to any radiation outside of the absorption lines of the gas. This allows, for example, the sensitivity to be increased by increasing the power of the radiation transilluminating the cell. However, the allowable (not leading to saturation) power density increases as the square of the line width [2].

* See comment during editing (p. 782).

† For example, a signal-to-noise ratio up to 10^4 .

TABLE 2. The Most Accurately Measured Frequencies of Lines in the Millimeter and Submillimeter Ranges

No.	Wavelength (mm)	Substance	Method	Transition			Measured frequency (kHz)	Accuracy
				vibrational	rotational	hyperfine structure		
1	2	3	4	5	6	7	8	9
1	4,14	DCN	Beam maser, emission line [148]	0	$J = 1 \rightarrow 0$	$F_N = 1 \rightarrow 1, F_D = 1 \rightarrow 0, 1, 2$ $F_N = 1 \rightarrow 1, F_D = 2 \rightarrow 1, 2$ $F_N = 1 \rightarrow 1, F_D = 0 \rightarrow 0, 1$ $F_N = 2 \rightarrow 1, F_D = 1 \rightarrow 0, 1, 2$ $F_N = 2 \rightarrow 1, F_D = 3 \rightarrow 2$ $F_N = 2 \rightarrow 1, F_D = 2 \rightarrow 1, 2$ $F_N = 0 \rightarrow 1, F_D = 1 \rightarrow 0, 1, 2$	72 413484,3 72 413514,3 72 413558,4 72 414905,4 72 414927,0 72 414973,2 72 417029,7	$\pm 1 \cdot 10^{-8}$
2	4,12	H ₂ CO	Beam maser, masing [93]	0	$1_{01} \rightarrow 0_{00}$		72 838338,860	$\pm 2 \cdot 10^{-9}$
3	3,39	HCN	Beam maser, masing [148]	0	$J = 1 \rightarrow 0$	$F = 1 \rightarrow 1$ $F = 2 \rightarrow 1$ $F = 0 \rightarrow 1$	88 630415,7 88 631847,3 88 633936,0	$\pm 1 \cdot 10^{-8}$
4	2,07	DCN	Beam maser, emission line [148]	0	$J = 2 \rightarrow 1$	$F_N = 1 \rightarrow 0, F_D = 1 \rightarrow 1$ $F_N = 1 \rightarrow 0, F_D = 2 \rightarrow 1$	144 826841,4 144 826809,7	$\pm 1 \cdot 10^{-8}$
5	1,78	H ₂ S	Beam, electri- cal resonance [33]	0	$1_{01} \rightarrow 1_{10}$	$F = 0 \rightarrow 1$ $F = 1 \rightarrow 2$ $F = 2 \rightarrow 2$ $F = 1 \rightarrow 1$ $F = 1 \rightarrow 0$ $F = 2 \rightarrow 1$	168762734,310 168762737,777 168762759,521 168762775,283 168762778,950 168762796,986	$\pm 2 \cdot 10^{-10}$
6	1,7	HCN	Beam maser, masing [148]	0	$J = 2 \rightarrow 1$	$F = 2 \rightarrow 2$ $F = 1 \rightarrow 0$ $F = 2 \rightarrow 1$ $F = 3 \rightarrow 2$ $F = 1 \rightarrow 1$	177259676,7 177259923,3 177261110,4 177261223,2 177263445,0	$\pm 1 \cdot 10^{-8}$
7	0,220	H ₂ O	Laser, lasing, Lamb dip [39]	100-020	$5_{23} \rightarrow 5_{90}$		1361282600	$\pm 1 \cdot 10^{-7}$
8	0,118	H ₂ O	Laser, lasing, Lamb dip [22]	001-020	$6_{42} \rightarrow 6_{01}$		2527952800	$\pm 1 \cdot 10^{-7}$

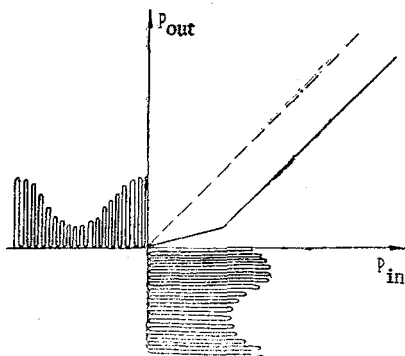


Fig. 17. Idealized graph of the dependence of the power which is passed through the absorptive gas on the incident power with allowance for saturation. The passage of an amplitude-modulated signal through a medium having such a characteristic leads to the attenuation of the carrier and the increase in the power of the sideband components.

In the submillimeter range pyroelectric receivers [161] are used (for example, in investigating lasers). Recently a communication appeared on a new pyroelectric material – SBN (strontium–barium–niobate) [153] – which is superior by one order to previous materials in sensitivity and by several orders in speed of response. This receiver is very convenient to use due to its small dimensions and simplicity of handling.

The low-temperature receivers which have appeared in the last few years have the highest sensitivity; however, they are still rarely used in radiospectroscopy. Let us note a receiver based on indium antimonide [14], a low-temperature bolometer [15], and very interesting receivers based on the Josephson effect [16, 154]. A review of receivers for the range considered has been given in [17].

4. Prospects for the Use of Millimeter and Submillimeter Radiospectroscopy

Historically the development of radiospectroscopy began in the centimeter range in connection with the existence of a technology which has been developed for other purposes. However, in terms of the abundance and intensity of lines, as Gordy put it: "the heart of radiospectroscopy must evidently be found in the millimeter and submillimeter ranges" [8]. Recently an ever greater portion of radiospectroscopic research, judging by the publications, is actually dealing with the ranges indicated. A further development of papers can be expected principally, of course, in the study of spectra and the use of the possibilities which are unavailable in ranges covering longer wavelengths. The high resolving power in investigations using the methods of millimeter and submillimeter radiospectroscopy is associated with the use of a monochromatic signal and allows the accuracy of investigation to be increased by several orders for those spectra which were previously investigated solely by methods of infrared spectroscopy. A comparison of radiospectroscopes for this range with the corresponding infrared spectroscopes has been carried out in [19].

Work in the millimeter and submillimeter ranges allows a considerable broadening of the range of substances whose structure can be studied by the most reliable (radiospectroscopic) methods and also allows an increase in the accuracy with which a number of interactions in molecules are studied, investigation of processes accompanying the formation of light unstable molecular fragments, and likewise the study of atoms and molecules in excited states. There exists a proposition to use frequencies above 450 GHz for analyzing the content of such substances as O_2 , NO , O_3 , N_2O , CO , H_2O , OH , NO^* in the trails of aircraft [234]. Those same components may be responsible for absorption, especially in the upper layers of the atmosphere. A number of other examples has been given in Section 1.

Recently the detection of a number of spectral lines of light molecules in space (OH [35], NH_3 [27], H_2O [25], H_2CO [32]) by radioastronomy methods has provided a new instrument for studying the Universe. The investigation of the higher-frequency lines of these molecules is very pressing, for example, for explaining "cosmic masers." Such "cosmic radiospectroscopy" always precedes the laboratory investigation of the corresponding spectra.

At present it would seem to be very promising to use radiospectroscopy to create and investigate maser devices by searching both for methods of obtaining conversion and for specific substances and transitions which are suitable for use in masers and also for the investigation of the physics of the processes which occur in masers. Radiospectroscopic methods have played a considerable role in the identification of lasing transitions and the explanation of the lasing mechanism in submillimeter gas lasers. The development of

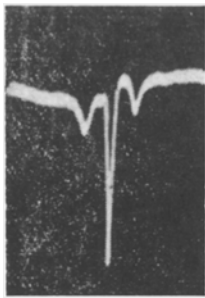


Fig. 18. The effect of dispersion of the spectral line 1_1-1_{-1} of water ($\lambda = 0.538$ mm) on the resonance response of a Fabry-Perot resonator filled with water vapor. The middle dip is the absorption line at the pressure $\sim 10^{-2}$ mm Hg. When the resonator is tuned to the line it resonates at three frequencies. The middle resonance is quenched by absorption, while the side resonances are visible on the photograph. The Q of the resonances which have been frequency-shifted beyond the limits of the absorption line by dispersion is of the order of $(1 \text{ to } 2) \cdot 10^5$.

research in the field of submillimeter gas lasers has to a considerable degree been stimulated by obtaining unexpectedly large values of power and efficiency in molecular lasers in the infrared range. In turn, the development of masers provides new methods for radiospectroscopic investigations (see Section 2). The very principle of maser action is a consequence of the development of radiospectroscopic ideas [9, 156].

Besides the indicated spectroscopic (or close-to-spectroscopic) investigations, the investigation of spectral lines in this range may also have other purposes that are more likely associated with the process of mastering the millimeter and submillimeter ranges by radio methods, and likewise with applications of radiospectroscopy. The first and oldest application of radiospectroscopy is the use of narrow invariant spectral lines for frequency stabilization and calibration. Development in this direction is likewise going on in the range considered. Table 2 presents the currently most accurately measured reference points in the millimeter and submillimeter ranges. Work has begun on the method of electrical resonance at $\lambda = 0.84$ mm [33]. In this range many methods considered in the review of optical frequency standards [66] are applicable; one of its merits is the already existing connection with rf frequency standards. Along with standards of increased accuracy, a necessity exists in having simple standard frequencies of intermediate quality, such as a general-purpose quartz oscillator for the radio range. Such standards have been considered in [60, 37, 70]. Certain other meterological applications have been indicated in Section 1.

In other cases the considerable strength of the lines in the ranges considered is used. Thus, in investigating an apparently generally known saturation effect the possibility of using it for parametric amplification in the submillimeter range [157] was recently clarified (this is in addition to the possibility of using it to increase the resolving power of radiospectroscopes using the "Lamb dip" technique discussed in Section 2). An amplifier constructed on the basis of using the effect of saturation of a spectral line is based on the nonlinear dependence of the absorption on the power.

An idealized graph of the dependence of the power which has passed through the gas on the incident power is displayed in Fig. 17. When an amplitude-modulated signal of sufficient power is applied to a medium having the characteristics shown in Fig. 17 the condition

$$P_{\text{in}}^c P_{\text{in}}^{\text{sb}} = P_{\text{out}}^c P_{\text{out}}^{\text{sb}} \quad (6)$$

where P^c , P^{sb} are the amounts of power in the carrier and sideband components, respectively. Thus, the attenuation of the central component is accompanied by the intensification of the sideband components.* In a practical amplifier the role of the central component is fulfilled by a saturating pumping signal, while the sideband components correspond to the amplified signal, the gain being proportional to the intensity of the original line. Experimentally a gain of 16 to 20 dB at wavelengths down to $\lambda = 1.17$ mm has been obtained. An essential fact is that the parametric medium may be any sufficiently intense lines. In [30] a coupling system at $\lambda \approx 1$ mm was considered which used gas devices for frequency stabilization, used the Stark effect for power modulation, achieved low-noise amplification, and likewise filtered the undesirable spectral components of the signal.

Possibly, the dispersion phenomenon for strong spectral lines (see Section 1) will also find application. While absorption in the wings of the spectral line decreases as $\Delta\omega^{-2}$, where $\Delta\omega$ is the frequency detuning from the center of the line, the real part of ϵ decreases only as $\Delta\omega^{-1}$ (i.e., its magnitude may be

* The "specular" phenomenon will consist of the attenuation of the amplitude modulation during passage of the signal through the intensifying medium under saturation conditions. The effect of the amplitude variation of the sideband components during resonance saturation is used in one version of a balanced radio-spectroscope [159].

fairly large in the region where the absorption is already comparatively small). On the photograph in Fig. 18, which was obtained and kindly provided to us by Dryagin and Farshin, the response of a Fabry-Perot resonator tuned to the 1_1-1_{-1} absorption line of water ($\lambda = 0.538$ mm) is shown. Due to the dispersion of the gas the resonator resonates at three frequencies in one and the same oscillation mode (the middle resonance is quenched by water absorption), the values of Q for the extreme resonances being fairly high $((1-2) \cdot 10^5)$. As has already been stated (Section 1), the maximal change in ε for $\lambda = 1$ mm may reach $\sim 5 \cdot 10^{-2}$ for the strongest lines.

The saturation effect was likewise used for the absolute measurement of power at $\lambda = 1.17$ mm [158]. Such a measurement is in many respects analogous to measurement by means of a thermal receiver. Actually, for incidence of a sufficiently intense resonance radiation on a two-level gas both levels are "heated" in the sense that their populations tend to equalize. Their "temperature" is measured by determining the absorption coefficient which depends on the difference between the level populations. The range of measurable values of power is 10^2-10^{-6} watts for an accuracy $\sim 5\%$. This method may constitute a successful addition to the existing method in the intermediate range where difficulties exist in using either the calorimetric method or the method of comparison with the thermal radiation of a blackbody.

The importance of applying radiospectroscopy in chemistry is generally known; this problem has been considered in detail in the recent review [50] and in [160]. We shall concern ourselves solely with making a few comments. The principal contribution of radiospectroscopy to chemistry lies in obtaining very reliable data on the structures of molecules. The problem of structure is not trivial even for simple molecules. Examples can be found in the S_2O molecule in which the sequence of atoms turned out to be S-S-O (the molecule also turned out to be bent), and the S_2F_2 molecule which exists in two forms - chain and pyramidal. An analysis of quadrupole and magnetic interaction provides data on the electron distribution in molecules. Under these conditions it is easy to establish the form of the chemical bonds (ionic or covalent), their direction, and the mean-square distance of the electron from the center of mass. A study of retarded movements in molecules provides information on the forces acting between atoms which are not directly coupled by chemical bonds; these forces determine the configuration of complex molecules. All of these data are extensively used in theoretical chemistry to check various theories of molecular structure, chemical bonds, etc. [50].

Radiospectroscopic methods are used considerably more rarely for analytical purposes; this is evidently associated with the high complexity of the equipment and with the very procedure for comparison with other methods of research. However, in these cases also the considered ranges are often preferable due to the high intensity of the lines. Radiospectroscopic methods may be used to carry out rapid nondestructive analysis of very small ($10^{-7}-10^{-12}$ moles) quantities of substance with an accuracy of several percent. It is important to note that because of the high resolving power the lines of the isotopes are resolved just as easily as the lines of the different substances, and radiospectroscopic isotopic analysis does not cause any difficulties (see Fig. 14). For the same reason the investigation of complex mixtures is also facilitated; this procedure is very difficult when infrared spectroscopy methods are used. In this connection let us note that the rotational spectrum is the most characteristic of complex molecules, since it is determined by the structure of the entire molecule as a whole.

Recently the interest in the millimeter and submillimeter ranges of radio waves has increased considerably (see, for example, [236]). This is definitely connected with the fact that the width of even a few "transparency windows" of the atmosphere is greater in the indicated ranges than in the entire remaining radio range. However, many applications are also possible (for example, investigations of the structure of matter) which are not associated with propagation in the atmosphere. The history of development of radio shows that the mastery of each new range also brings new applications of radio methods. In all probability the role of quantum methods and devices, to the development of which gas radiospectroscopy is also making its contribution, will necessarily be great in the mastery of the millimeter and submillimeter ranges.

We have attempted to indicate the principal trends of development in millimeter and submillimeter radiospectroscopy and research performed using it. The rapid progress in this field during the last few years permits us to hope that new interesting results and applications will be obtained in the future.

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Comment During Editing. While the review was in press, two useful books appeared: R. A. Valitov, S. F. Dyubko, V. V. Kamyshan, V. M. Kuz'michev, B. I. Makarenko, A. V. Sokolov, and V. P. Sheiko: "Submillimeter-wavelength Engineering," *Izd. Sov. Radio*, Moscow (1969), and "Engineering of Spectroscopy in the Far-Infrared, Submillimeter, and Millimeter Ranges of the Spectrum," D. Martin, Editor [Russian translation], *Izd. Mir*, Moscow (1970).