

Present state of submillimeterwave spectroscopy at the Nizhnii Novgorod Laboratory

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Abstract

A review of recent developments in microwave spectroscopy techniques in the Terahertz range and some examples of molecular spectra achieved at the Nizhnii Novgorod Microwave Spectroscopy Laboratory are presented.

Techniques and methodics developed include: development (jointly with the KVARZ Institute of Electronic Measurements, Nizhnii, Novgorod) of a unique series of commercial frequency synthesizers covering the 53–178 GHz range, which are now used in several Western Laboratories; development of laboratory versions of synthesizers up to frequencies exceeding 500 GHz; development (jointly with the Physical Institute of the University of Cologne, Germany) of precise microwave broadband scanning spectrometers covering a range exceeding 1 THz; development of alternative (non-synthesizer based) techniques of microwave spectroscopy in the submillimeter range; extension of the range of microwave spectroscopy up to 1.5 THz by multiplication of frequency of the submillimeter backward wave oscillators.

New objects of submillimeter microwave spectroscopic studies include: spectra of molecular complexes in equilibrium and in supersonic jets; spectra of some light molecules; studies of effects connected with high excitation of vib–rot states; clustering of energy levels in asymmetric tops; development of new methods for describing the spectra of non-rigid molecules and their applications.

Further studies of molecular interactions (pressure line shifts and broadenings) include: achievement of new measurement accuracy limits; study of the shape of strongly shifted lines; studies of the temperature dependence of shift and broadening and its applications; study of some new effects: experimental demonstration of the existence of non-additivity of pressure lineshifts in the system of molecular transitions; experimental demonstration of the absence of non-additivity of pressure lineshifts in mixtures of gases.

The studies of molecular spectra and molecular interactions were carried out, in part, jointly with the University of Cologne, University of Giessen, Kiel University, Wuppertal University, Molecular Physics Division of the National Institute of Standards and Technology, and London University.

Some perspectives for the development of submillimeter microwave spectroscopy techniques discussed in this paper include: further extension of the range of microwave spectroscopy well beyond 1.5 THz; extension of the range of frequency synthesizers; some non-spectroscopical applications of the techniques and methods developed.

Keywords: Microwave spectroscopy; Molecular spectra

1. Introduction

The previous review paper by the author [1] was published in 1984, i.e. more than ten years ago, and due to the prevailing circumstances it was very brief. At approximately the same time the microwave review papers of Gordy [2], Winnewisser [3] and Sheridan [4] appeared. In their 1984 book "Microwave Molecular Spectra" Gordy and Cook presented the broad scope of the field [5]. Since that time, at least as far as the author knows, no general microwave spectroscopy review papers have been published (a summary was presented in the article "Microwave Spectroscopy" in the Physical Encyclopaedia [7] in 1993). During the last decade, and particularly within the last few years, very significant experimental developments have been achieved in extending the continuous frequency coverage into the terahertz region and beyond, and in performing high precision measurements of line-shifts and broadenings. As the reader may know, changes in Russia also affected the field of spectroscopy; in one positive sense, scientific and technical collaboration can now be performed more easily. The present paper reflects this new situation and is mostly concerned with the developments in the Nizhnii Novgorod Microwave Spectroscopy Laboratory now achieved in close collaboration with colleagues from the Physical Institute of the University of Cologne, Germany, the Institute of Physical Chemistry of Giessen University, Germany, Kiel University, Germany, and Wuppertal University, Germany, the National Institute of Standards and Technology, Molecular Physics Division, Gaithersburg, USA, the Time and Frequency Division, Boulder, USA, and London University, UK. The reader can get acquainted with the previous work of our laboratory in the field of submillimeterwave spectroscopy using an earlier paper published in 1979 in English [6].

2. Some developments in the technique and methods of millimeter/submillimeter microwave spectroscopy

Almost always, the development of techniques and experimental methods is of primary impor-

tance for the progress of the field. We shall consider here some of the new developments made over the last decade by the Nizhnii Novgorod Microwave Spectroscopy Laboratory.

2.1. Appearance of commercial millimeterwave frequency synthesizers from 53 GHz up to 178 GHz and some experiences of their spectroscopic use

The KVARZ Institute for Electronic Measurements, in close collaboration with the Laboratory of Microwave Spectroscopy of the Institute of Applied Physics, was the first to develop a family of commercial millimeterwave frequency synthesizers based on Russian-made backward wave oscillators (BWOs). (All millimeter and submillimeter BWOs mentioned in this paper have been developed and produced by the ISTOK Research and Production Company, Fryazino, Moscow region [11].) At the present time several microwave spectroscopic laboratories throughout the world (Cologne and Giessen Universities in Germany, the National Institute of Standards and Technology, Gaithersburg and the University of California in the USA, Bologna University in Italy, etc.) have already implemented these synthesizers which cover steps in three the frequency region 53 to 178 GHz in three steps (53–78, 78–118 and 118–178 GHz). A further extension of the frequency range is under consideration. The frequency output of these sources is phase-locked to an internal quartz oscillator, which can be stabilized to a standard radio signal of an external atomic clock. Synthesizers can be fully PC-controlled through a standard IEEE-488 interface (all settings – frequency, frequency increments, number of frequency steps per second, attenuation, modulations, etc.). From the front panel keyboard, through an internal microprocessor, many functions can be carried out without a PC. The smallest frequency step is 100 Hz at millimeterwave frequencies.

The power of the synthesizers' output varies depending on the band covered and the function selected, e.g. power leveling, amplitude modulation, etc., from a few to several tens of milliwatts. A general front view of a millimeterwave synthesizer is shown in Fig. 1. A description of the

KVARZ synthesizer which at the moment has the highest frequency range of the commercial synthesizers (118–178 GHz) is presented in Ref. [12].

A first example of the use of the new millimeterwave synthesizer for spectroscopic purposes is the OCCCS molecular spectrum recorded by Wagener et al. [8], which was carried out jointly at the Justus Liebig Universitaet, Giessen. In addition to the synthesizer, a free space absorption cell equipped with a liquid He-cooled InSb bolometer was employed. Synthesizer control and data acquisition were computer controlled. The part of the spectrum recording covering 100 MHz from the entire 40 GHz studied, is shown in Fig. 2. It is the first time that such a wide and sensitive spectral scan has become possible, resulting in a large number of observed and also assigned lines of many different vibrational states; the measured frequency range covers the rotational spectrum of OCCCS from $J = 28$ – 27 up to $J = 41$ – 40 .

The stability and reproducibility of the synthesizer output signal over a period of several hours led to an unexpected but highly welcomed result: the recording of the OCCCS spectrum lasted several hours, after which the gas cell was evacuated

and a new recording was performed. Subtraction of the two spectra after digital smoothing gave a surprisingly flat baseline which can be seen in Fig. 2. (see also Ref. [9]).

Over 5000 lines of OCCCS were recorded permitting the assignment of many low-lying excited vibrational states, including the ν_7 bending mode at 78 cm^{-1} . In this study a sensitivity level around 10^{-8} cm^{-1} for a 120 ms time constant was reached. Part of the OCS “calibration” spectrum is shown in Fig. 3.

The same type of synthesizer was used jointly at the Molecular Physics Division (NIST Gaithersburg) in the electric resonance optothermal spectrometer (EROS), to investigate the broad band spectrum of the heavy water dimer D_2O – D_2O in a cooled beam with a resolution better than 100 kHz, as determined by the time of flight broadening [10].

A good indication of the high spectral purity of the KVARZ millimeterwave frequency synthesizer’s output radiation is observation at the University of Cologne of the Lamb dip on the $1_{0,1}$ – $1_{1,0}$ line of H_2S at 168 GHz with some tens of kilohertz HWHM in the microbar pressure range [12].

2.2. Laboratory submillimeterwave frequency synthesizer from 180 GHz to 500 GHz

As prototypes of higher-frequency synthesizers, laboratory devices ranging from 180 GHz up to 500 GHz were constructed at the Applied Physics Institute; they are powered by BWOs packeted in compact “laboratory made” small permanent magnets; the harmonics of the output frequencies of microwave synthesizers (also developed and produced by the KVARZ Institute) were obtained in a balanced multiplier–mixer, using a pair of planar Schottky diodes, which served as a source of the reference signal. The first stage of these studies, up to 370 GHz, was reported in Ref. [13].

2.3. Precise microwave broadband scanning spectroscopy in THz region

Precise microwave broadband scanning spectroscopy in the terahertz region [14] is accomplished by adding some new components to the

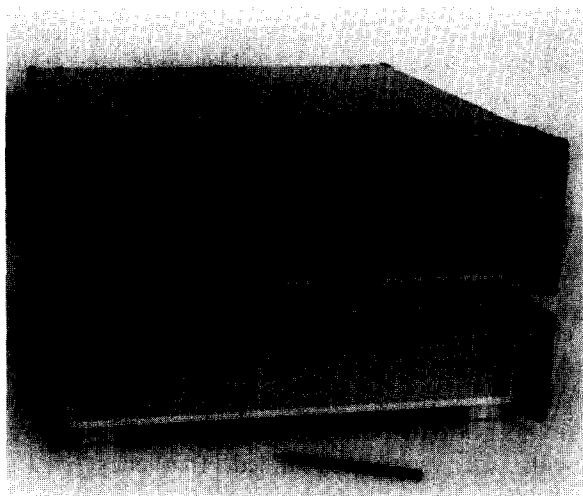


Fig. 1. General view of 118–178 GHz frequency synthesizer: output CW power, milliwatts; minimal frequency step 100 Hz; fullt microprocessor (or PC) controlled through standard IEEE-488 interface. Waveguide output is seen to the left of the center of the lower unit.

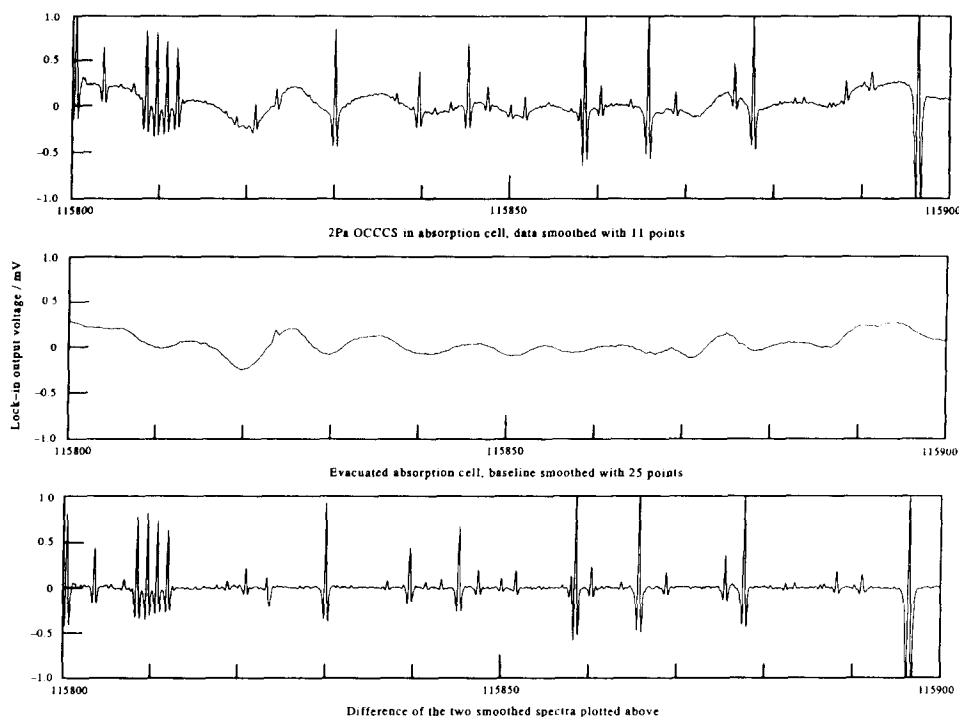


Fig. 2. Portion of the OCCCS spectrum in the 115.8–115.9 GHz region obtained using a PC-controlled 78–118 GHz frequency synthesizer as radiation source and liquid He bolometer as detector. Frequency modulation and second harmonic detection were used. (Top) Record of the filled cell; (middle) record of empty cell several hours later; (bottom) result of subtraction of first two spectra (note flat baseline obtained [6]). A 3 m long free space cell was employed.

Cologne submillimeter spectrometer. They are as follows: the KVARZ millimeterwave synthesizer as reference oscillator whose output is fed into a broadband millimeter/submillimeter multiplier–mixer based on a planar Schottky diode which was developed for this purpose; its intermediate frequency output is further amplified by a high electron mobility transistor intermediate frequency pre-amplifier and fed into a digital lock loop phase controlling the high frequency of the backward wave oscillator; the main portion of its output radiation is focused through the absorption cell and detected by a hot electron InSb bolometer.

A general block diagram of the spectrometer that was constructed jointly by the Nizhnii Novgorod Laboratory and the Physical Institute of the University of Cologne is presented in Fig. 4 [14].

As far as the author knows, it is the first time that such a broadband performance has

been achieved; the stabilization signal (beat note) using the fifth harmonic of the synthesizer output frequency was not lost over the entire scan of the 78–118 GHz synthesizer, i.e. over 200 GHz on BWO submillimeter frequency. A schematic picture of the beam lead planar Schottky diode-based multiplier–mixer developed at the Nizhnii Novgorod Laboratory is shown in Fig. 5.

Using this spectrometer several light and often chemically unstable molecules were investigated. An example of its performance (somewhat restricted by the scanning software with a limited number of data points) is presented in Fig. 6 (a–c) with successively expanded frequency scales, showing the $'Q_3$ branch of DSSD near 489 GHz [14]; analogous records of the $'Q_4$ branch near 629 GHz are presented in Ref. [9]; a record of the $9_{8,1}–9_{7,2}$ line of H_2S near 1 THz is presented in Fig. 7.

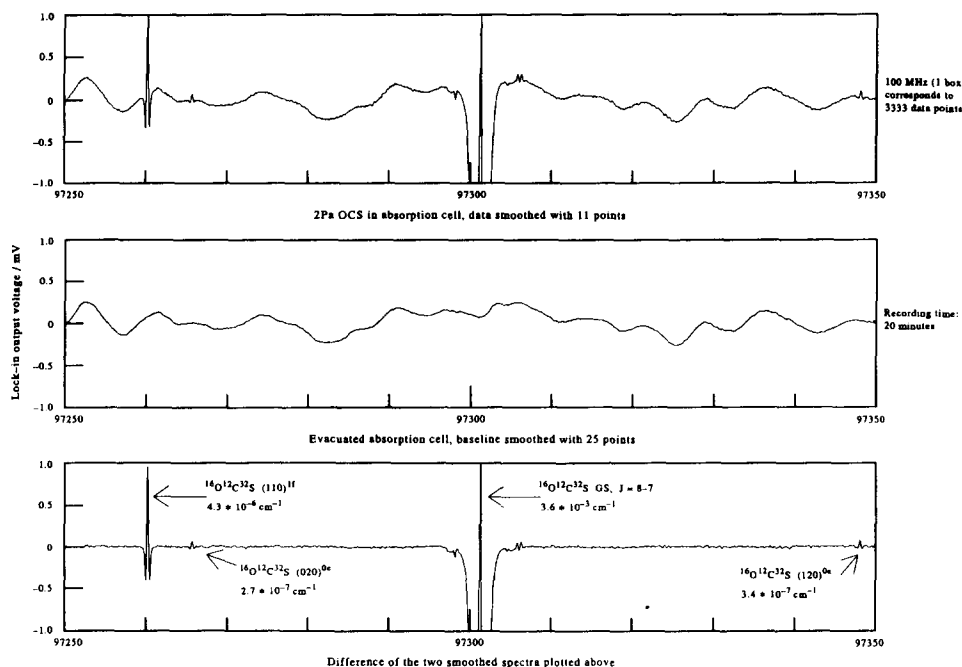


Fig. 3. Record of portion of OCS spectrum illustrating the sensitivity of the spectrometer operated with a synthesizer and liquid He bolometer: time constant 120 ms; intensities of the lines are shown in the figure.

2.4. Alternative (not synthesizer-based) broadband scanning technique with the automatic use of a reference spectrum

In some cases the synthesizer technique de-

scribed here can be difficult to realize, for laboratories not having the funds or the experience in this field. The alternative technology which is not synthesizer-based, developed at the Nizhnii Novgorod Laboratory, combines relative simplicity

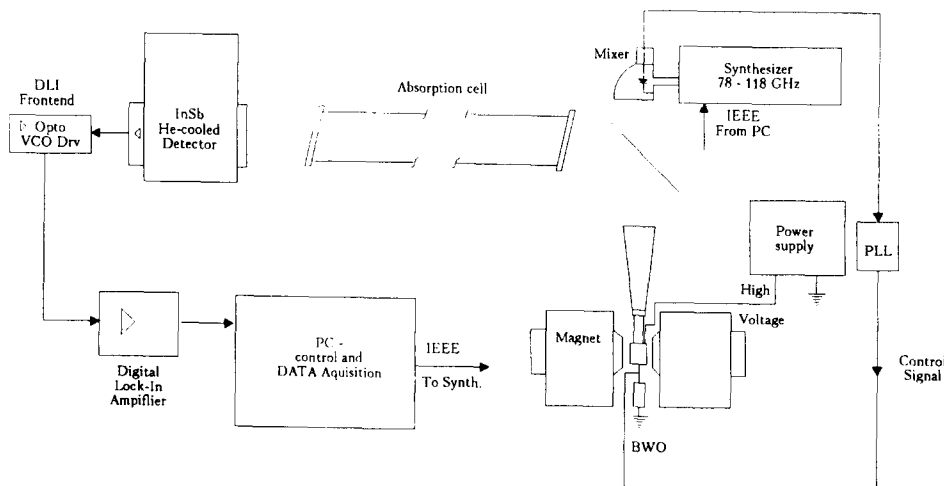


Fig. 4. Block-diagram of Cologne terahertz spectrometer. BWO from 150 GHz up to 1 THz as used with the same multiplier-mixer system.

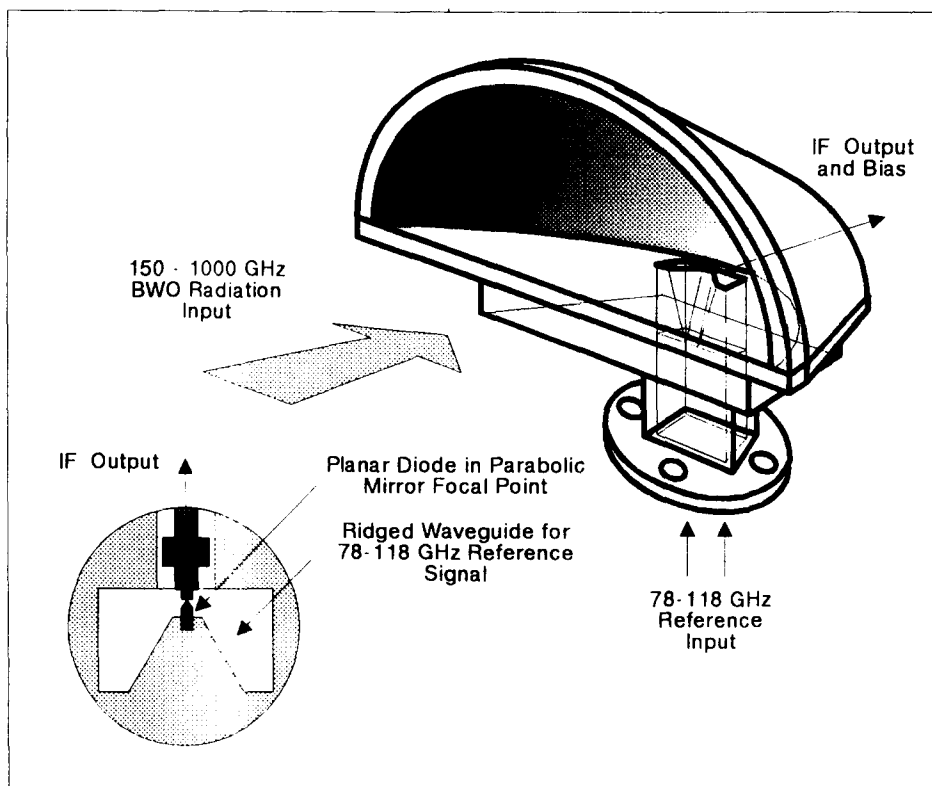


Fig. 5. Schematic view of the broadband submillimeter multiplier-mixer.

with automation and operates with a frequency accuracy somewhat lower than can be achieved by synthesizers [15]. It has been designed for making routine broadband scans in the whole submillimeter-wave region before the advent of synthesizers. Perhaps it will find its application for chemical and/or isotopic molecular gas analyzers (experiments showed good (up to $10^{-6}\%$ sensitivity, good selectivity and self-calibration properties of RAD spectrometers used for practical molecular chemical analysis [82,83]). A block diagram of this type of spectrometer is presented in Fig. 8. The spectrometer resembles the one with BWO and two absorption cells with acoustic detectors through which the radiation is passed; in one cell (etalon) a reference spectrum is recorded which serves to calibrate the newly investigated spectrum [16]. The difference between the two spectrometer

types described here (sometimes called RAD-3, assuming that RAD-1 is the simplest version without stabilization of frequency and the RAD-2 spectrometer is the version with the frequency synthesizer) is that the frequency of the BWO is stabilized via the resonance profile of a high-Q Fabry-Perot cavity. Tuning is achieved by scanning one of the mirrors. Automatic frequency control (AFC) of the submillimeter BWO against the Fabry-Perot resonator is analogous to that described earlier [18] (see also Ref. [19]); some technical details will be described later. The displacement of the Fabry-Perot mirror is measured by an optical Michelson interferometer, fed by a frequency-stabilized He-Ne $0.63\ \mu\text{m}$ laser. One of the acoustic cells is again used for an etalon gas with a well-known reference spectrum (e.g. measured earlier by the synthesizer); SO_2 is commonly

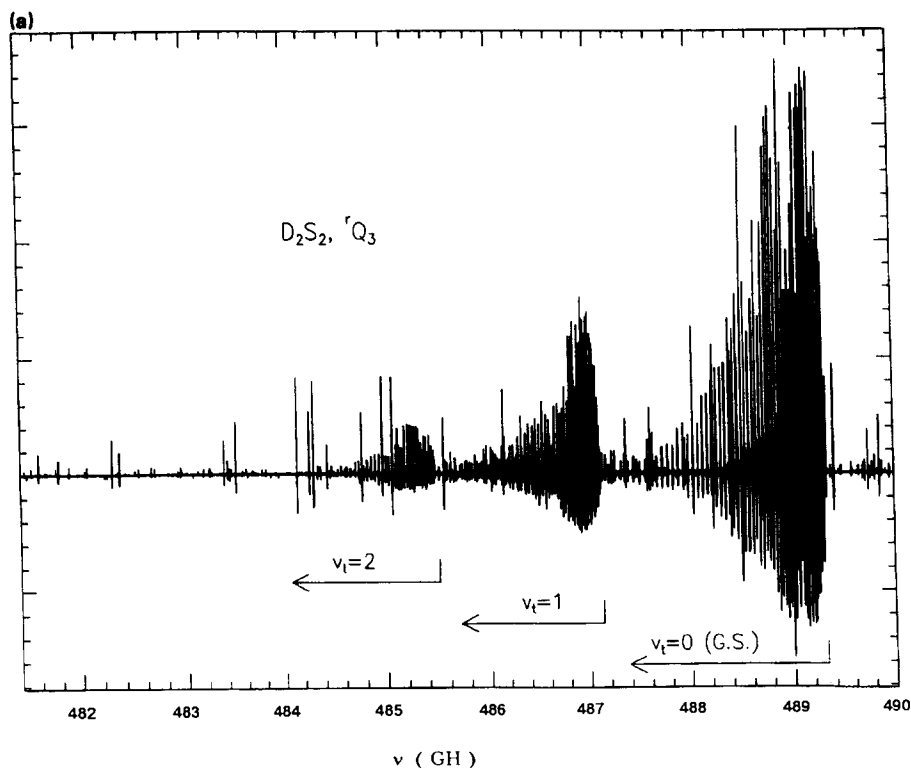


Fig. 6. (a) A portion of the DSSD submillimeterwave spectrum: broad scan showing $'Q_3$ branches of ground and first and second excited torsional states of the molecule. (b) Part of scan showing band head of the ground state $'Q_3$ branch with increased spectral resolution. (c) Part of scan (b) showing band head of ground state $'Q_3$ branch with further increased resolution up to $J = 20$. J values are marked in the figure.

used [17]. The other acoustic cell is filled by the gas to be investigated. Frequency modulation of the BWO is used both for cavity AFC and the recording of the gas spectra.

The spectrometer operates as follows. The BWO's frequency follows the resonant frequency of the Fabry–Perot cavity, and three signals are registered by computer: the spectrum to be investigated, the reference spectrum, and the optical interferogram, which serves for a precise interpolation between reference lines; one period corresponds to several hundreds of kilohertz at submillimeterwave frequencies. The scheme is analogous to the one used commonly for diode lasers but here is used for the first time for microwave spectroscopy. One important difference between a diode laser and a BWO is that the frequency of the latter is always known unam-

biguously from the setting of the power supply voltage to an accuracy of the order of 10^{-4} . This permits one to make the last step in automation of the spectrometer: i.e. automatic assignment of the reference spectrum lines [20]. The details of the RAD-3 spectrometer are described in Ref. [21]; two more important details are AFC detector (a planar Schottky diode placed inside the Fabry–Perot cavity) which removes most of unwanted interference pattern, i.e. improves the accuracy, and astatic element of the AFC system, controlling the high voltage power supply. It expands the single scan frequency tuning range to the entire range made possible by the BWO. The spectrometer also has Doppler-limited resolution; the average accuracy of line frequency measurements is about 300 kHz; automation also includes lineshape processing; the frequency range deter-

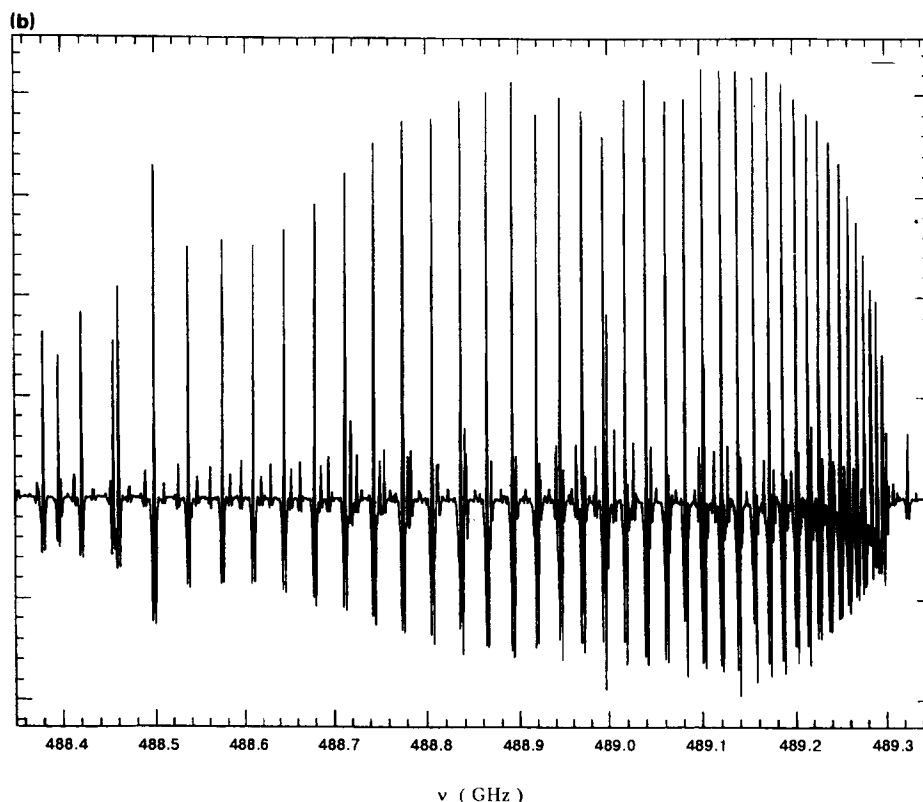


Fig. 6 (b) (continued).

mined by available BWOs covers the frequency range up to 1250 GHz; it enables one also to record and process spectra with hundreds and thousands of spectral lines during a short period of time.

Practical applications of this type of spectrometer were demonstrated in several publications [24–28].

2.5. Extension of the range of microwave spectroscopy to 1.5 THz

It is well known that the upper frequency limits of both methods of submillimeter microwave spectroscopy (using frequency multiplication from powerful microwave/millimeterwave radiation sources or primary submillimeterwave radiation sources) stayed around 1 THz for at least a decade (see, e.g. Refs. [5,6,14]). The natural next step would be an attempt to multiply the frequency of the submillimeter BWO.

Very recently an extension of the range of microwave spectroscopy to 1.5 THz has been achieved at the Nizhnii Novgorod Laboratory by frequency multiplication of a submillimeter BWO working in the 300 GHz range up to the fifth harmonic on the developed multiplier using a beam leak planar Schottky diode [22,23].

As a receiver our common spectroscopic cell with acoustic detector was used [6]; harmonics were registered by observation of proper spectral lines of gases; therefore the acoustic cell also served for harmonic selection. SO_2 lines in the 541–1524 GHz range were observed in the second, third, fourth and fifth harmonics of the fundamental frequency of the BWO.

Radiation of the submillimeter BWO, the frequency of which was stabilized by a phase lock loop, was directed by a waveguide to the multiplier developed by us on the basis of construction of a multiplier–mixer described above. A beam

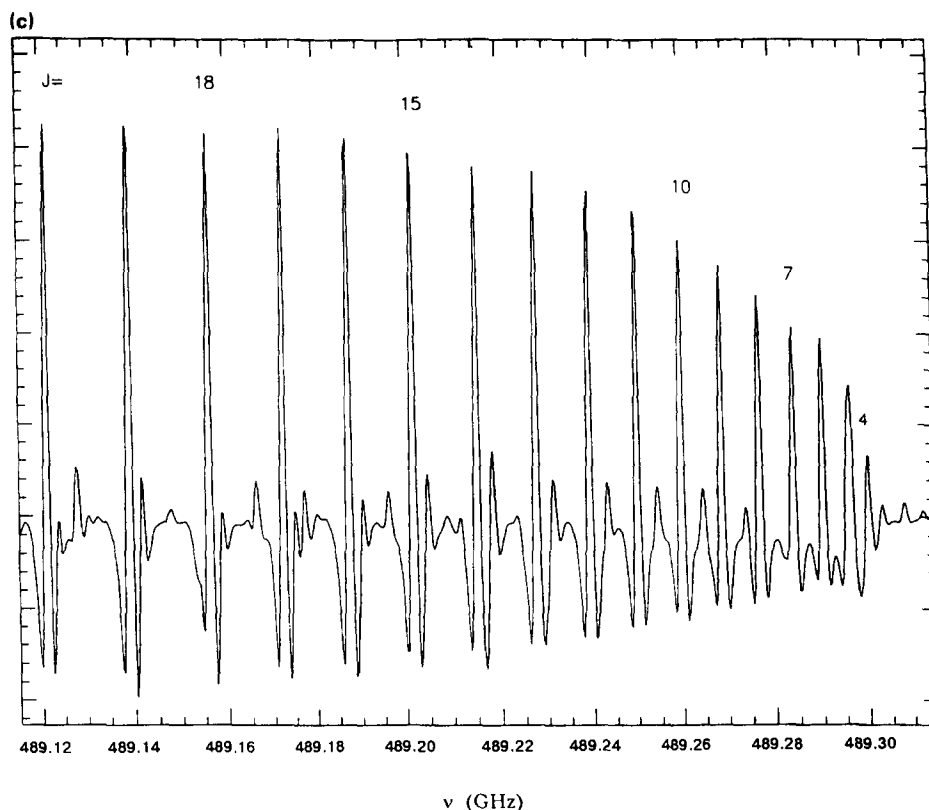


Fig. 6(c) (continued).

lead planar Schottky diode with 0.007 pF capacitance and 10 Ω resistance was used. Regulated bias voltage was applied to the diode.

The output radiation of the multiplier containing unselected fundamental and harmonic spectral components was directed by a semi-parabolic mirror (or the horn) to the spectroscopic cell with an acoustic detector usually used for our type of experiments [6].

The well known SO_2 rotational spectrum was chosen for harmonics observation. Pressure broadened lines observed in the harmonics looked narrower on the records than pressure broadened lines in the fundamental because of faster change of frequency; the intensity of lines observed in the harmonics depended strongly on the diode bias voltage whereas the intensity of lines observed in fundamental modes does not visibly depend on the diode bias. These features, together with coin-

cidence of observed and calculated frequencies of the lines within 10^{-6} – 10^{-7} (rel. units), served as criteria for assignment of the lines observed. In the second, third, fourth and fifth BWO harmonics around 30 lines were observed altogether; some of them are in Figs. 9–11.

In Figs. 9 and 10 portions of SO_2 records illustrating features mentioned above are shown; the BWO frequency in megahertz is plotted on the scale; bias voltages and line assignments, table (calculated) frequencies of the lines and harmonic numbers in which lines were observed (1 corresponds to the fundamental frequency) are shown in Figs. 9 and 10.

In Fig. 11 the line at the highest presently observed frequency for microwave spectroscopy (1524 GHz) is presented. This extends range of microwave spectroscopic methods by almost one half.

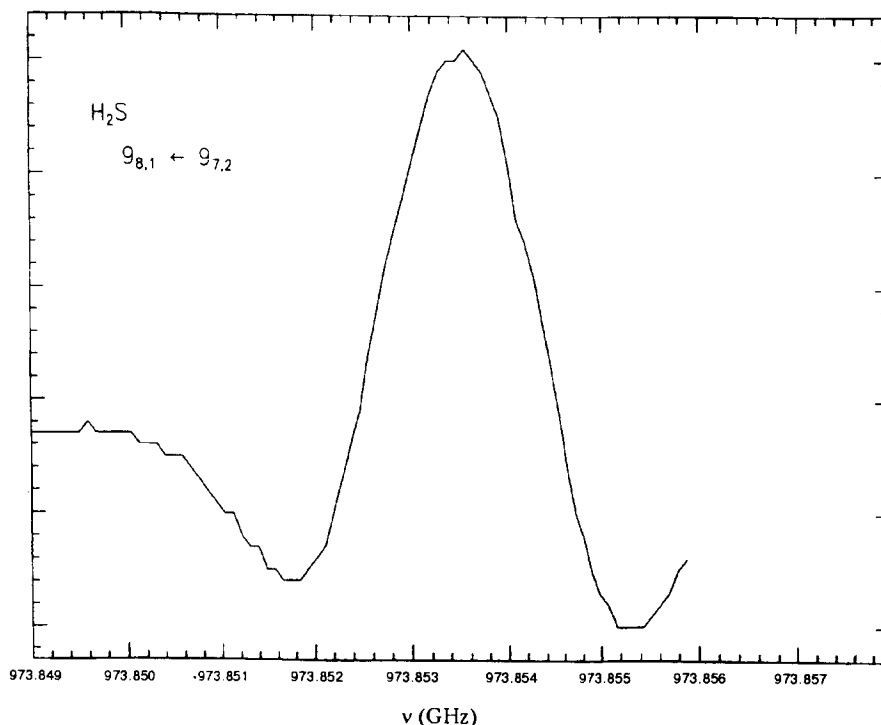


Fig. 7. H_2S $9_{8,1}-9_{7,2}$ line record near 1 THz.

In our opinion a further very significant extension of the microwave spectroscopy range could be achieved simply by the use of a more sensitive receiver than a thermal acoustic detector at room temperature (which was the only one at our disposal) with the same combination of the submillimeter BWO and Schottky diode multiplier used. As such a receiver the InSb bolometer at liquid He temperature as in Ref. [14], or the even more sensitive magnetically tuned or ^3He -cooled InSb bolometers can be used.

We also plan to try and use higher power and frequency submillimeter BWOs as fundamental source for multiplication experiments, and to try and improve conditions of the harmonic radiation of the diode e.g. by providing the diode with antennae which are resonant for harmonics.

Extension of the range of the microwave spectroscopy by one half in the first experiments looks promising for development of this direction of microwave spectroscopy technical progress.

3. New objectives of submillimeter microwave spectroscopy

During the period considered, some new molecular objectives came within the reach of submillimeterwave spectroscopy, which can only be investigated at submillimeter wavelengths and in the terahertz region. We will mention some molecular objectives tackled for the first time at the Nizhnii Novgorod Laboratory, both alone and in collaboration with other spectroscopic laboratories.

3.1. Submillimeter spectra of molecular complexes in equilibrium and in cold beams

At the Nizhnii Novgorod Laboratory broadband submillimeter spectra of molecular complexes in equilibrium (cooled cell) were obtained for the first time, using a spectrometer employing BWOs and acoustic detection [28,62]; some of them were the first microwave spectra of com-

SUBMILLIMETER MICROWAVE RAD-3 SPECTROMETER

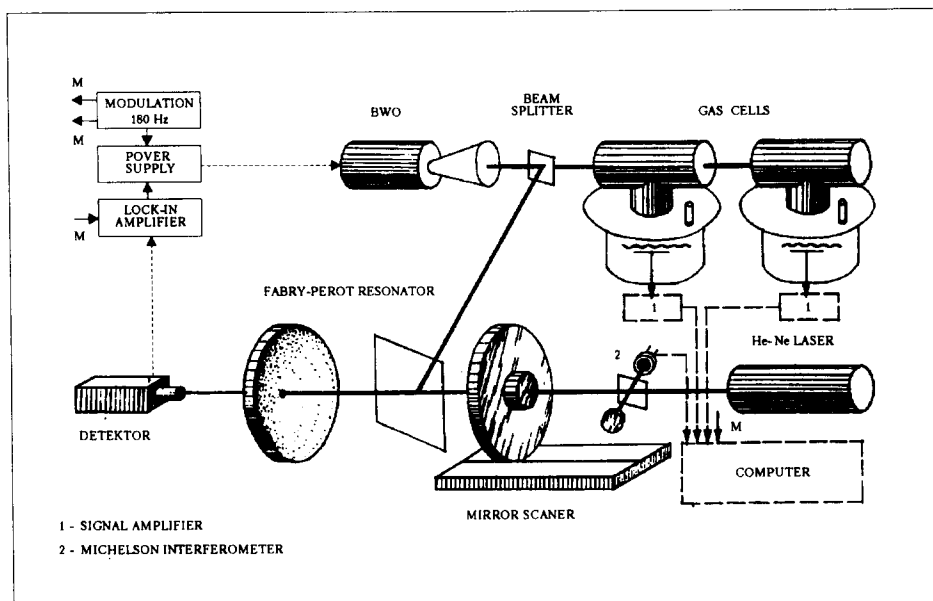


Fig. 8. Block-diagram of RAD-3 spectrometer.

plexes such as HCl-HCl [63]. Advantages are seen in the high sensitivity of the RAD spectrometer in the region where the rotational spectra of many complexes display their intensity maxima, and the relatively high pressure in the cell (from tenths of torr up to several torr) which leads to a concentration increase (quadratically with pressure) of complexes at equilibrium.

The study of the spectra of molecular complexes under equilibrium conditions permits the observation of higher excited states due to higher temperature than in cooled beams; also important is the possibility of line intensity measurements giving information about the bonding energy, line broadening and shift, none of which have yet been studied for molecular complexes: in a broad sense the methods of cold molecular beams and cooled cells are complementary. Study of the HF-HF dimer is reported in Ref. [28], $\text{H}_2\text{O-HF}$ complex in Ref. [64] and $\text{H}_2\text{O-NH}_3$ in Ref. [65]. The working temperature of the cell varied from room

temperature for $\text{H}_2\text{O-HF}$ to approximately 120 K for HCl-HCl .

In Fig. 12 part of the spectrum of the $\text{NH}_3\text{-H}_2\text{O}$ complex around 328 GHz ($J = 27 \leftarrow 26$) is presented; the existence of several internal large amplitude motions leads to the high complexity of the observed spectrum.

Some complexes are very difficult to study under equilibrium conditions; the most known example is water dimer; for deuterated water species, studies were conducted in cold beams in collaboration with NIST, Gaithersburg, USA (e.g. Refs. [10,66]); Nizhnii Novgorod Laboratory supplied the millimeterwave or laboratory submillimeterwave synthesizers described earlier, and NIST provided the cold beam EROS.

Fig. 13 presents an example of the spectrum of the $\text{NH}_3\text{-NH}_3$ molecular complex at around 229 GHz. This spectrum was obtained by the EROS operating with a Nizhnii Novgorod submillimeter synthesizer.

3.2. Spectra of some light molecules

The study of HSSH and its isotopomers was carried out jointly with Winnewisser and co-workers at Cologne University, Germany [29]. An example of the DSSD spectrum was presented earlier in Fig. 6(a–c). In Fig. 14(a) we present a survey scan over the complete ${}^{\prime}Q_3$ region of HSSH near 1 THz and for comparison a Fourier-transform spectrometer recording of the same portion of the spectrum, which was obtained before this work was completed. In Fig. 14(b) a more detailed view of the ${}^{\prime}Q_3$ bandhead is given; in Fig. 14(c) the high J band tail of the same Q-branch shows K -doubling. The intensities of

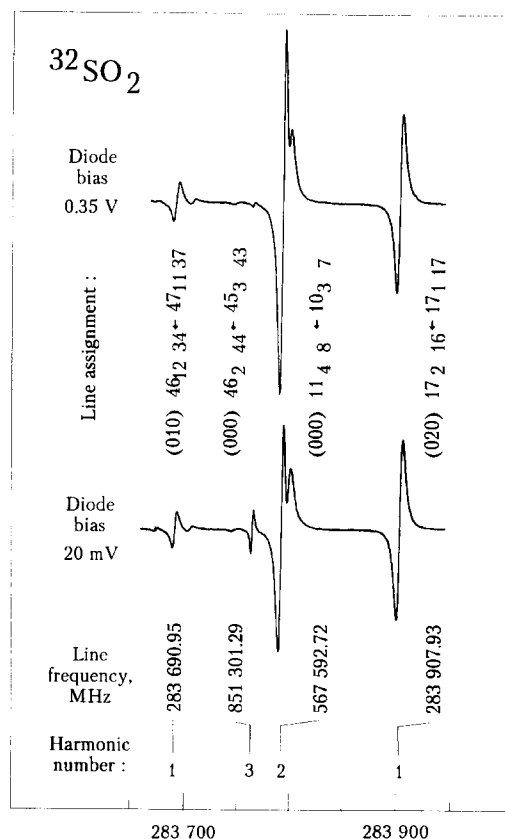


Fig. 9. Record of the portion of SO_2 spectrum observed in fundamental frequency and in harmonics of BWO; different dependences of the intensities on the Schottky diode bias voltage and different width of the lines observed in first, second, and third BWO harmonics are visible.

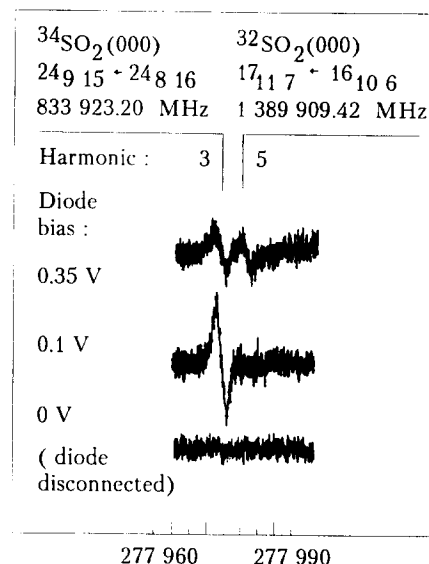


Fig. 10. Record of the portion of SO_2 spectrum containing lines observed in third and fifth harmonics of BWO.

the observed K -doublet lines are as follows: for even J the lower frequency component carries statistical weight unity and the upper component carries weight three, and vice versa for odd J values. This intensity alternation reveals the anomalous K -doubling for the $K_a = 3$ levels and was observed for the first time. (A precise study of HSSH was carried out later and is reported in

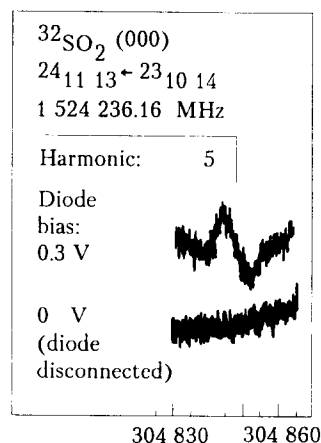


Fig. 11. Record of the SO_2 line observed in the fifth harmonic of BWO at the present highest frequency for microwave spectroscopy, 1 524 236.16 MHz.

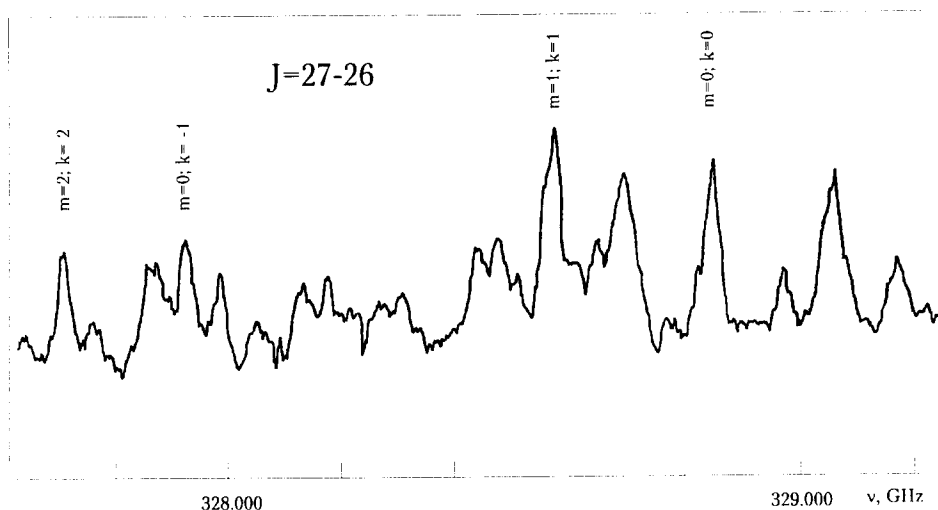


Fig. 12. Part of $\text{NH}_3\text{-H}_2\text{O}$ molecular complex spectrum around $J = 27 \leftarrow 26$ in equilibrium conditions (cooled cell). The existence of a number of large amplitude internal motions greatly complicates the observed spectrum.

Ref. [30].) A further joint project with Cologne University was the study of HOOH [31]. In Fig. 15 the lower $^{\circ}\text{Q}_2$ branch of HOOH at 1.05 THz observed for the first time by microwave spectroscopy methods is presented. H_2O studies included weak lines in terahertz range [26]. Transitions between excited vibrational states of the non-polar DCCD molecule also were detected and studied [35]. The PH_3 , AsH_3 and CH_3F studies continued the symmetric top spectra work which had been started earlier on the ammonia molecule [27,36–38,81]. The SO_2 study was aimed firstly at obtaining a good working reference spectrum for the “alternative” technique mentioned before [17]; also studies on SO_2 , H_2S and many other molecular species of astrophysical interest are carried out jointly with Cologne University, Germany for astrophysical purposes.

The study of the importance of internal rotation in energy relaxation in molecules was initiated on acetaldehyde by J. Hougen at NIST, Gaithersburg, USA and some Nizhnii Novogorod Laboratory members carried out the submillimeterwave measurements [24,25]. H_2Se studies were connected mainly with the first experimental investigation of fourfold level clustering in asymmetric tops.

3.3. Effects connected with high vibrational/rotational excitation in molecules: clustering of energy levels in asymmetric tops

The grouping of energy levels in spherical top molecules, usually referred to as energy level clusters, is well known [40–42,44]. Recently, similar phenomena have been discussed theoretically for asymmetric top molecules [42,43,46]. The main goal of the H_2Se investigation in our laboratory was the experimental observation of the phenomenon also predicted for asymmetric tops, the rotational level clustering in H_2Se with increasing J after some critical value of the rotational quantum number J_{CR} .

As a first step, measurements in the 300–650 GHz region were carried out [47,48] using the RAD spectrometers with BWO and acoustic detection [49]. The accuracy of the measurements was 100 kHz for the spectrometer with the submillimeter frequency synthesizer [16] and 300 kHz for the spectrometer using cavity AFC and reference spectra [21].

There are six isotopic (selenium) species of H_2Se ; the group character of the spectrum was very useful for line assignment. Due to the frequency region, Q-type transitions of H_2Se were

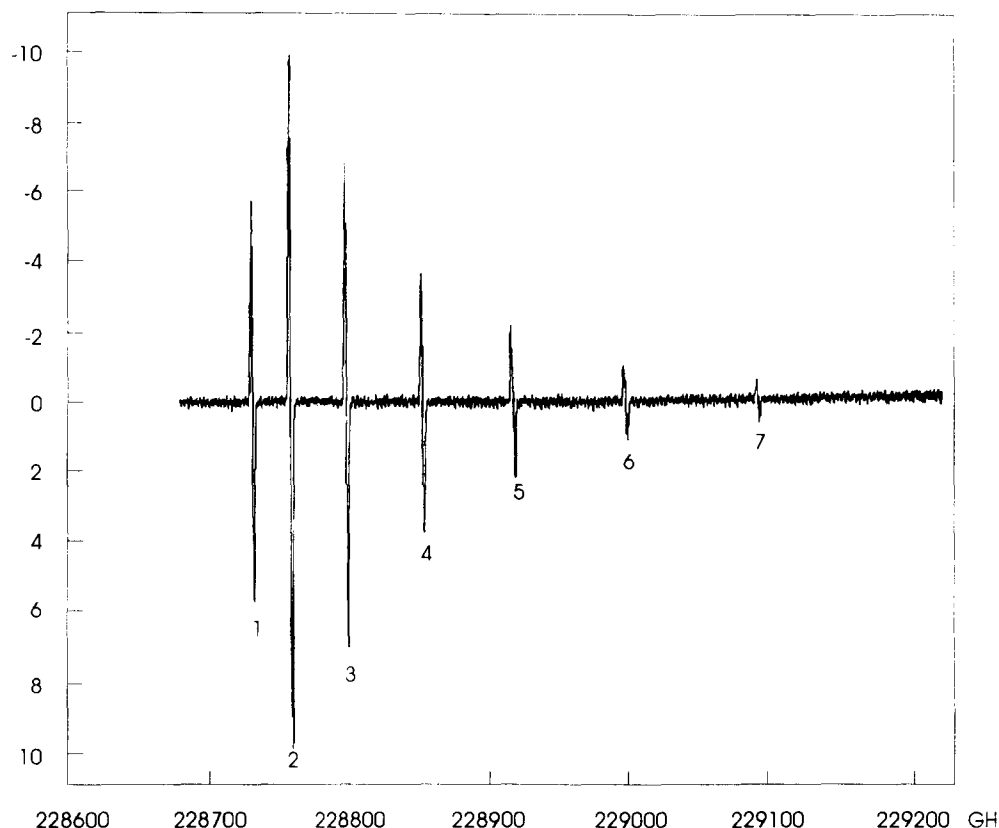


Fig. 13. One of the Q branches of $\text{NH}_3\text{-NH}_3$ molecular complex, observed near 229 GHz in a cold beam with the KVARZ frequency synthesizer and EROS. J values are marked in the figure.

usually measured. The most interesting of them are transitions of the type $J_{J,0} \leftarrow J_{J-1,1}$ and $J_{J,1} \leftarrow J_{J-1,2}$ because the energy levels involved in these transitions are clustered together with the increase of J beginning with $J=13$. These “intracluster” transitions were traced up to $J=20$. The line intensities of the transitions with $J=19,20$ were rather weak due to a small Boltzmann factor. For example, the line intensity of the transition $20_{20,0} \leftarrow 20_{19,1}$ of the most abundant selenium isotopomer is about $2 \times 10^{-8} \text{ cm}^{-1}$. To measure the frequencies, the cell was heated to 50–60°C, a temperature sufficient to increase the line intensity by 3–4 times. The temperature dependence of the line intensity was an additional criterion for the assignment of a transition.

The critical phenomenon expected after $J = J_{\text{CR}}$ should change the rigid rotor rotational level

structure usually observed for asymmetric top molecules and result in the fourfold clustering of the energy levels. This change is illustrated by Fig. 16. The frequency increase with J of the lines of the subbranches $J_{J,0} \leftarrow J_{J-1}$ and $J_{J,1} \leftarrow J_{J-1,2}$ of the Q-branch should be changed into a frequency decrease after the critical J value is surpassed.

When measurements up to 650 GHz were performed, it was found that the frequencies of those “intracluster” subbranches increased with J up to $J=12$ and started to decrease from $J=13$. This is one of the main results of the work and means that the clustering in the H_2Se vibrational ground state spectrum really takes place. Some level positions deduced from observations are shown by circles in Fig. 16(b).

By measuring $J_{J,0} \leftarrow J_{J-1}$ and $J_{J,1} \leftarrow J_{J-1,2}$ transition frequencies, the energy spread of the upper

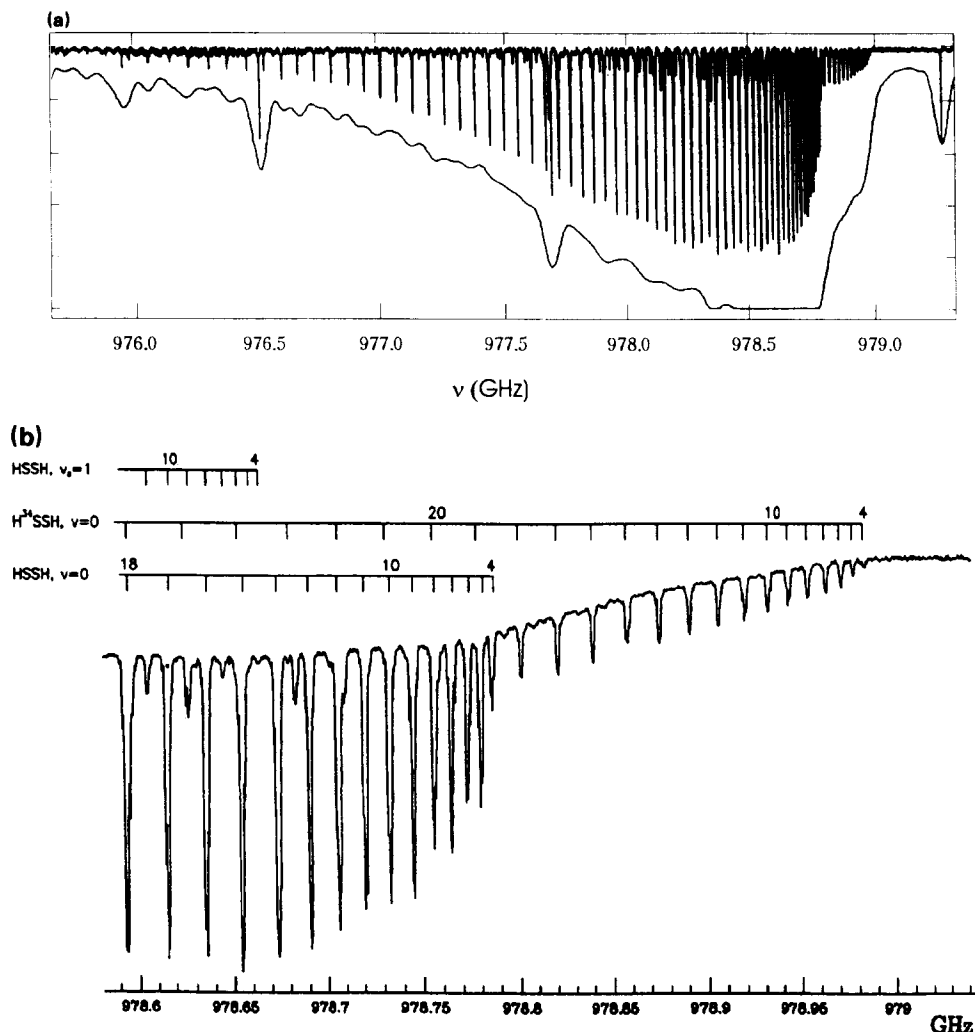


Fig. 14. (a) Records of HSSH Q_3 branch near 1 THz produced by microwave spectrometer with BWO and liquid He bolometer (upper trace) and high resolution Bruker Fourier transform spectrometer (lower trace). The spectral resolution of the FT spectrum is instrument limited, whereas the terahertz spectrum is Doppler limited. (b) Band head of HSSH Q_3 branch microwave record with increased resolution; visible are the ground state of main isotope lines, ground state of S^{34} isotope lines and first excited stretching state of main isotope lines. (c) Band tail of HSSH Q_3 branch microwave record with increased resolution; visible is K doubling at high J (around 60) values; 3:1 intensity alternation.

fourfold cluster was defined for different J values with high accuracy. Fig. 16(b) shows that the cluster spread decreases drastically with increasing J . For $J = 23$ the measured spread of the cluster is 20 times smaller than the distance to the nearest level of the same J multiplet [51].

These results provided the first experimental verification of the existence of the clustering phenomenon in asymmetric top molecules. Further

experimental and theoretical investigations showed some new aspects of this phenomenon [50–54].

3.4. New methods of describing spectra of non-rigid molecules and their applications

Effective Hamiltonians are widely used as means of representing molecular rovibrational

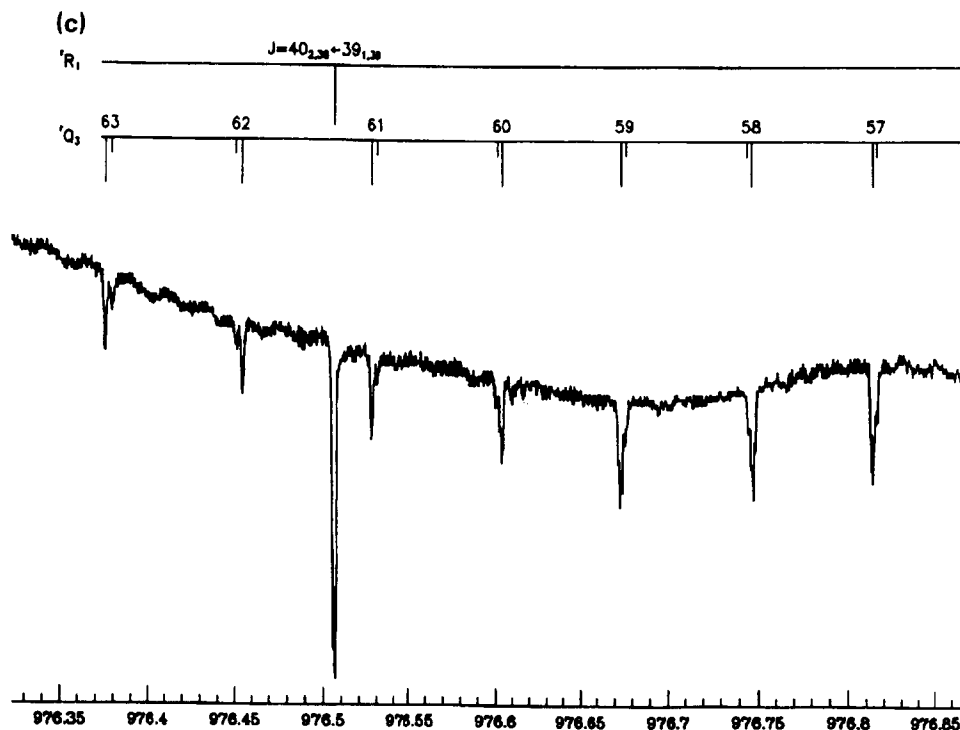


Fig. 14 (a) and (b) (continued).

spectroscopic data. For rotational levels, these effective Hamiltonians are conventionally expressed as power series expansions in terms of the quantum numbers $J(J+1)$ and K^2 . However, power series for light molecules and molecules with large amplitude vibrational motion are often poorly convergent. In some cases, such as water [55], the power series actually diverge.

As a solution to this problem, other effective Hamiltonian expansions have been suggested by the Nizhnii Novgorod Laboratory. They are based on the study of quadratically perturbed harmonic oscillators, and include the use of Padé and Borel approximants, especially in the form of a one-dimensional Padé approximation which was found to be convenient and preserve the same common definition of molecular constants [55]. These new approximations have been found to give greatly improved representations of the spectroscopic data of water [55,56], H_2D^+

[57,58], and C_3O_2 [59] when compared to power series expansions with the same number of parameters.

Recently, the advantages of the Padé and Borel effective Hamiltonian representations of the exact energy eigenvalues of molecular rovibrational Hamiltonians were justified by considering the behavior of the power series expansions in the complex (J,K) plane [60].

Padé approximants were successfully applied in the investigations of the $(\text{HF})_2$ dimer which is known to be very non-rigid. The better reliability of the newly developed methods gave the possibility of also predicting, on the basis of the available data, the new $K=3$ band center, which then was found experimentally [28].

Recently the one-dimensional approach was applied to the advanced assignment of H_2D^+ for ground vibrational state rotational levels up to $J=30$ [61], which were calculated variationally.

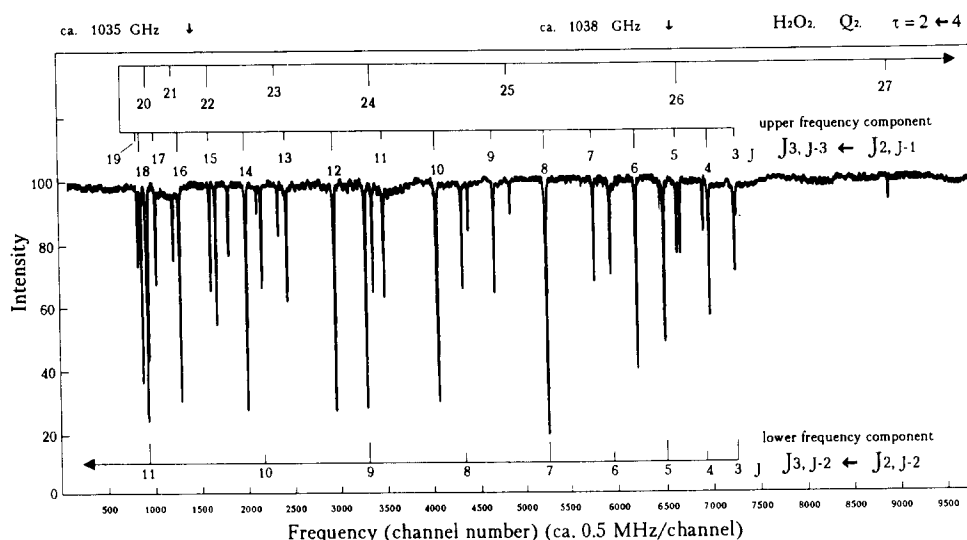


Fig. 15. First microwave record of HOOH 7Q_3 , lower frequency branch $\tau = 2 \leftarrow 4$ above 1 THz.

4. Further pressure lineshift and line broadening studies

4.1. New limits of accuracy in pressure lineshift measurements

Pressure lineshift studies have progressed rapidly over the past decade. As recently as the 1970s Boggs, one of the creators of modern short/broadening theory, stated, “in fact, there is no published observation of a shift in the line center frequency as seen by conventional microwave technique” [67]. During the 1980s not only microwave observations of lineshifts, but also shifts comparable with the broadenings were discovered [68]. Data of pressure shifts began to appear in databases such as, for example, HITRAN [69]. A new source of information about molecular interaction appeared; lineshift also has “one more degree of freedom” compared to line broadening, the sign of the shift. Nevertheless until recently the number of lineshift studies was very limited due to experimental difficulties. Typical experimental accuracies are on average of the order of tenths of megahertz or torr upon looking through, for example, the compilation of data for the most widely studied ammonia molecule [70]. Recently the situation has changed drastically in millimeter/sub-millimeter and infrared spectroscopy [72,94].

Precisions of the order of a few kilohertz or torr are reached in the best studies. This should be very important both for refining the theory and also for practical uses of pressure lineshift measurements, which we are unable to discuss here in detail due to the lack of space. (Examples are precise CO lines studies with 1 kHz and 1 kHz/torr accuracies for frequency and corresponding pressure shifts for interpretation of measurements of winds of Venus [72] or some gas polarity measurements through lineshifts [79,80].) At this new level of precision new effects also seem to occur which will be mentioned briefly.

4.2. Shape of a strongly shifted absorption line

In the book [67] it was expected that the lineshift effect “may be more prominent in distortion of the lineshape than it is in the direct shift in the center frequency”. There seemed to be some grounds for this expectation. Investigation of this effect was of essential interest for further studies and the lineshift study was initiated at the Nizhnii Novgorod Laboratory. In one case, in which the lineshape of the $1_{1,0}-1_{0,1}$ transition of the water molecule broadened by ammonia gas was investigated, the shift constituted 32% of the broadening, and distortion of the lineshape was not observed within experimental accuracy. The line profile is

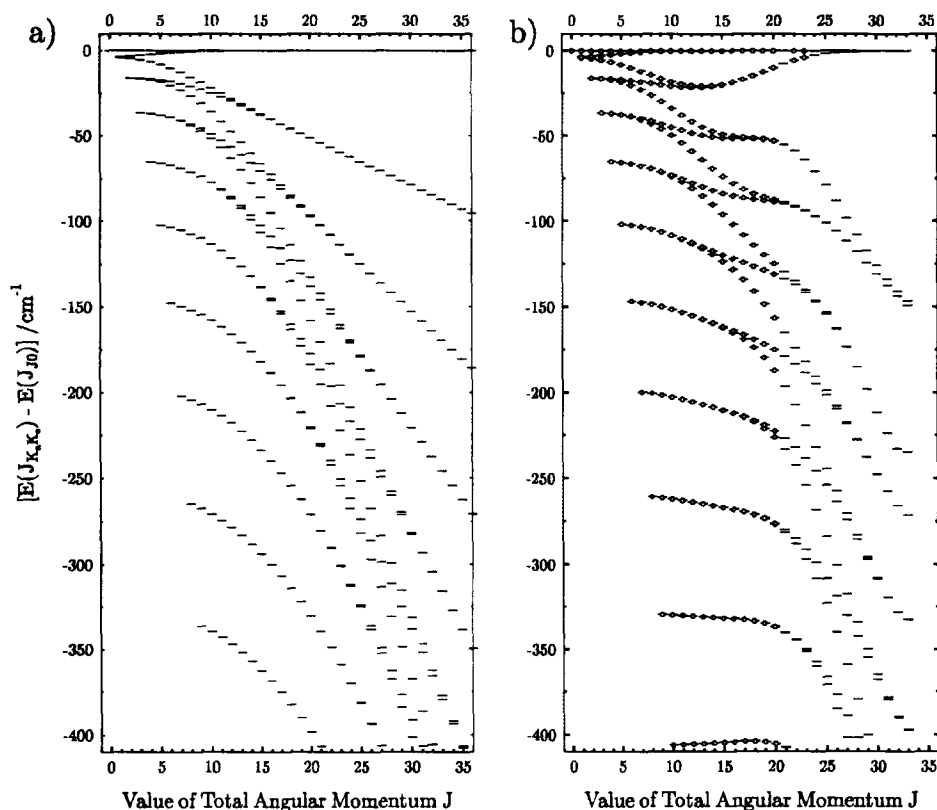


Fig. 16. The rotational energy level structure in the vibrational ground state of $\text{H}_2 \text{ } ^{80}\text{Se}$: (a) rigid rotor approximation; (b) real spectrum. Term values are plotted relative to the highest term value for each J multiplet. The calculated term values are given as horizontal lines, and experimental term values are shown as circles.

shown in Fig. 17 together with the differences between the theoretical (Lorentzian) and experimental lineshape fit. It was found that the shape of the strongly shifted spectral line of about six halfwidths coincides with a Lorentzian one with an accuracy of better than 1% of the maximum of the line [78].

4.3. Temperature dependences of shift and broadening and their possible practical use

Temperature dependences of pressure lineshift and line broadening are of significant interest both for understanding molecular interaction and for practical use, e.g. in the interpretation of atmospheric spectral measurements. However these measurements are not numerous, because of the high accuracy and reproducibility of measurements needed.

At Nizhnii Novogorod some experimental investigations of temperature dependences have been performed [32,74–76]. As an example let us consider the results of the studies of self-shift and self-broadening of the $6_{4,3}-5_{5,0}$ water line in the temperature range 250–390 K. The pressure dependence of the center frequency and the half-width of this line are displayed in Fig. 18 (a,b). The center frequency was found to be equal to $\nu_0 = 439\,150.791(10)$ MHz. This value agrees well with the measurement in Ref. [77] of $\nu_0 = 439\,150.812(50)$ MHz, and the small numerical difference is probably a consequence of the pressure shift not being taken into account in Ref. [77]. The exponents of temperature dependence were found for the shift as $\alpha = 2.59(20)$ and for broadening $\beta = 0.62(9)$, respectively. It is very interesting in our case that the difference between the exponents of self-shift

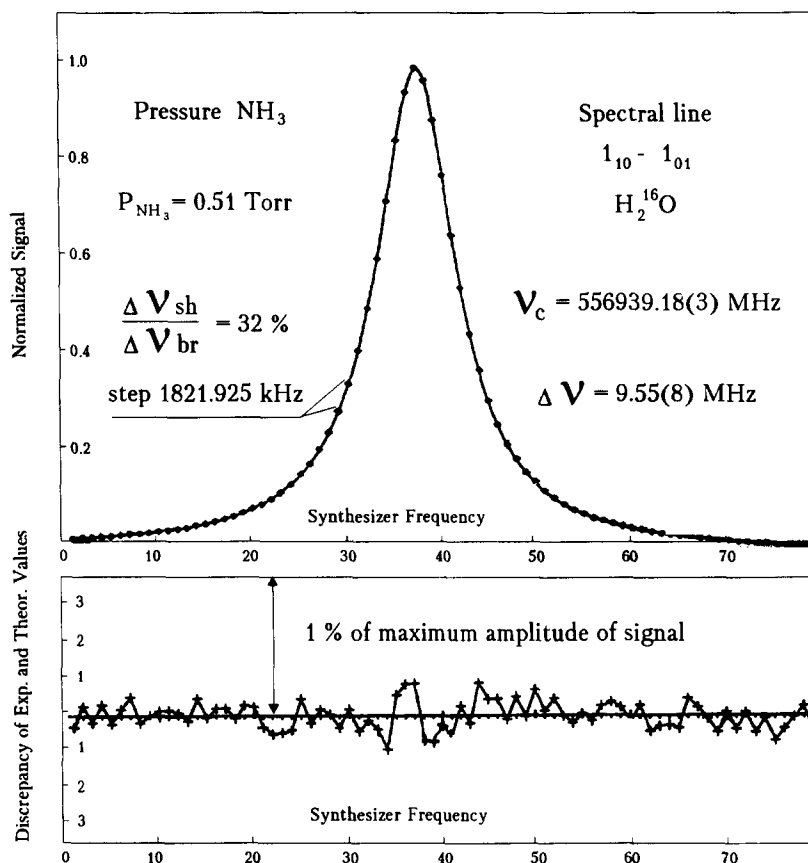


Fig. 17. Experimental lineshape of strongly shifted line (points) and fitting to Lorentzian lineshape (line). Residuals of the fit are plotted below.

and self-broadening for the $6_{4,3}-5_{5,0}$ water line is large, $\alpha - \beta = 1.94$. This behaviour can lead to the possibility of implementing a new method of remote temperature measurements based only on shift and broadening of “probe line” measurements. In Fig. 19 the broadening-to-shift ratio versus temperature for the $6_{4,3}-5_{5,0}$ line of water is presented. It is worth noting that this function is valid over a very wide range of pressures corresponding to binary collisions, i.e. from low pressures up to atmospheric pressure. The function of Fig. 19 depends only on the transition, the temperature, and composition of the gas. In the laboratory one can measure this function for a chosen “probe” spectral line and gas composition and then use it for remote determination of the tempera-

ture of the gas. The method does not require measurements of gas pressure or line strengths, etc.

The choice of a “probe” line is defined by convenience and the large difference of temperature exponents for the shift and broadening to give better sensitivity of the method.

4.4. Some new effects studies

Here the story of two new effects found during the last few years will be told. One of the effects was seemingly experimentally verified and the results of calculations available agree with experiments; the other effect, at least at the existing level of accuracy, was not confirmed and the source of the error was found to be different concentrations

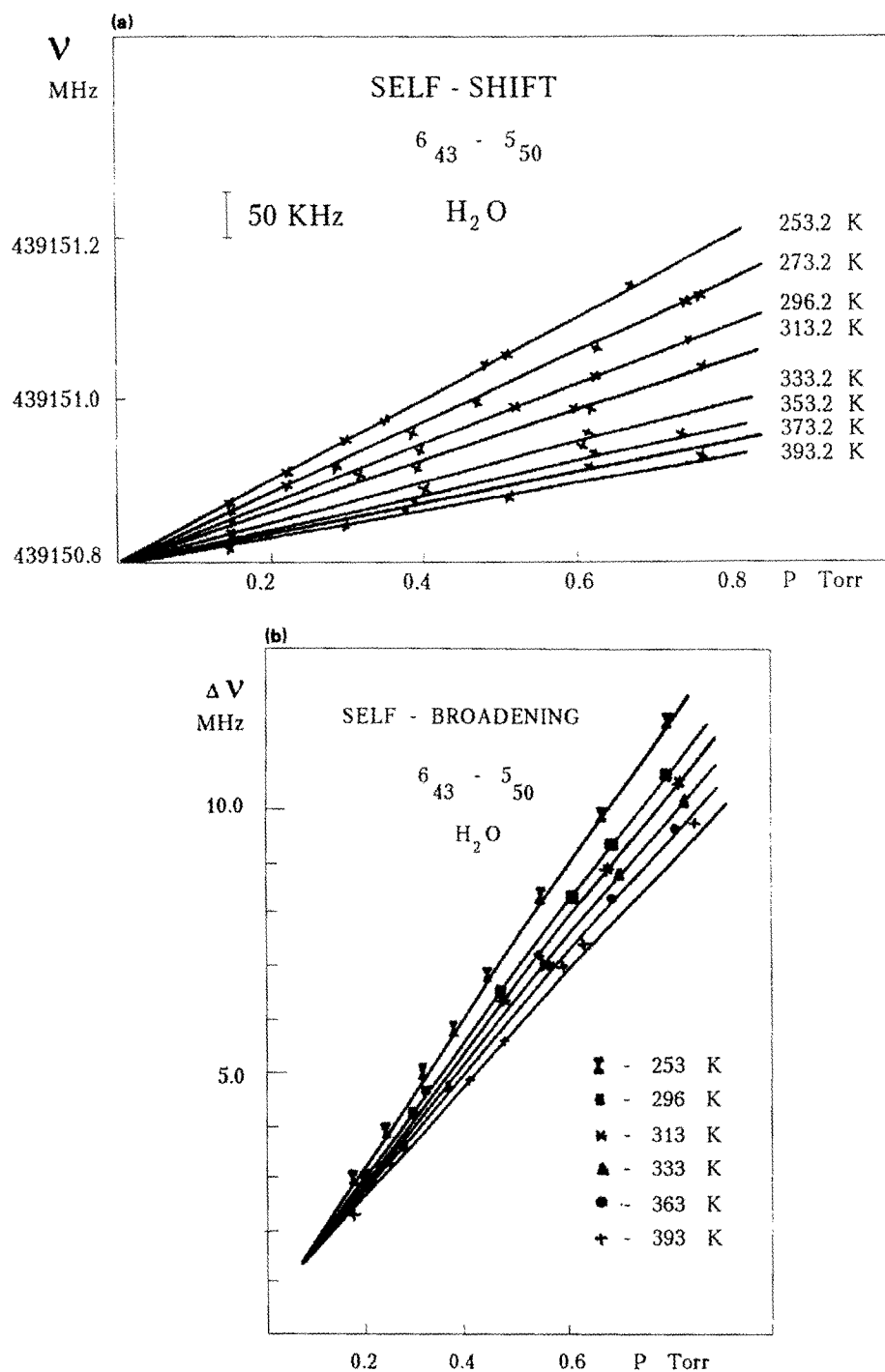


Fig. 18. Example of measured temperature dependence of (a) the self-shift and (b) self broadening of the $6_{4,3}-5_{5,0}$ water line.

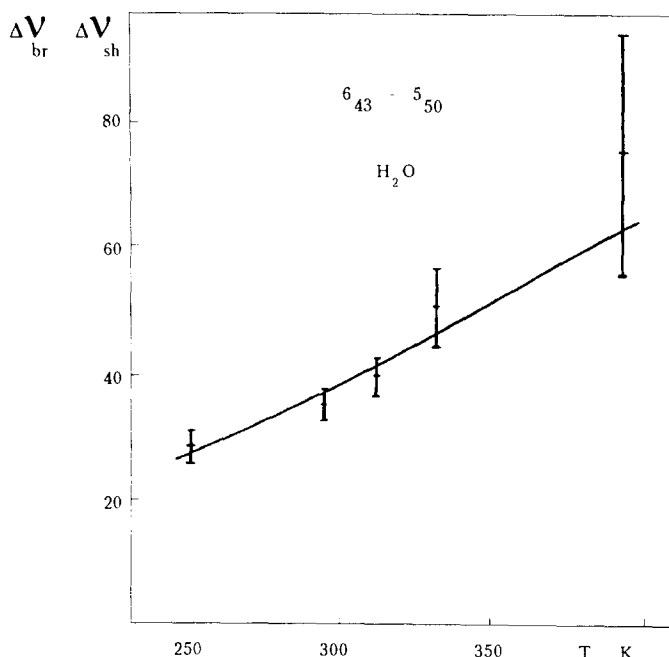


Fig. 19. Method of temperature measurements: broadening to shift parameter ratio vs. temperature for the $6_{4,3}-5_{5,0}$ water line.

of trace gases in the samples used. However, the possible origin of the second effect seems interesting; perhaps it can be found in future by more precise experiments. These studies led to an unexpected and interesting result, so we have decided to recount the stories of both effects.

4.4.1. Nonadditivity of pressure lineshifts in transition systems

Very often initial and final energy levels can be connected via different measurements of experimental lineshift parameters for these transitions forming two paths connecting the same initial and final levels, it is of interest to compare the algebraic sums of the lineshift parameters along different paths. There are few experimental lineshift data available at the moment, especially for the sets of lines mentioned forming a loop of transitions connecting the energy levels involved.

The first example was found in the ammonia spectrum [85] and showed coincidences between the sums of lineshifts within the accuracy limits quoted. As far as the author knows there was no experimental evidence of inequality of sums of lineshifts ("nonadditivity of lineshifts") until re-

cently, when one example was found [9] also in the ammonia spectrum. Combination of our measurements with recent IR ones [86,87] permitted the finding of a second example of nonadditivity [88].

For completeness both schemes in which nonadditivity was found are shown in Fig. 20(a,b) where experimental pressure self-shift parameters and their sums along the different paths are also presented. In Fig. 20(a), the first scheme of transitions involving the ground and v_2 states of the ammonia molecule together with the experimental pressure self-shift parameters is shown [9]. The results of summing the pressure self-shift parameters along two paths showed that the difference between the sums exceeded the sums of error limits quoted by the authors, namely $+0.39 \text{ MHz/Torr} \pm 0.17 \text{ MHz/Torr}$ for the left path and $+1.03 \text{ MHz/Torr} \pm 0.47 \text{ MHz/Torr}$ for the right path [9].

In Fig. 20(b), the second scheme of transitions also involving the ground and v_2 states of ammonia molecule together with experimental pressure self-shift parameters is presented. The results of summing the pressure self-shift parameters along

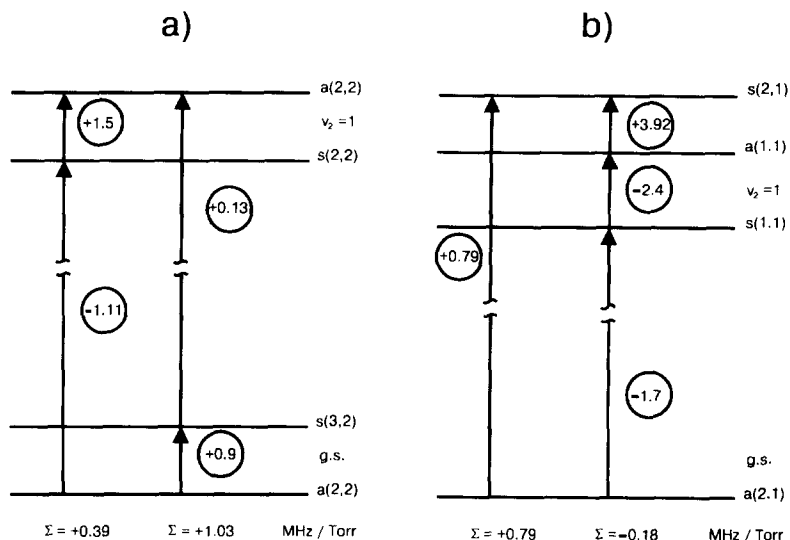


Fig. 20. A part of vib-rot energy levels diagrams of NH₃ where initial and final levels are connected by transitions forming two different paths. Values in circles are measured lineshift parameters in MHz/Torr; note inequality of sums of measured lineshift parameters along different paths.

two paths do not coincide, and the difference between the two sums is 0.97 MHz/Torr. Unfortunately, no error limits are quoted for some of the lineshift parameters included in the chain.

Of course, these two examples cannot solve the problem and further studies are very desirable. One difficulty is that measurements of such sets of transitions necessarily require a broad range of frequencies of the lines to be measured, spanning in the cases mentioned from millimeter up to infrared wavelengths, with accuracies matching each other, and very well-defined experimental conditions.

Physically, the possibility of nonadditivity of the pressure lineshifts arises from the fact that the effective distance of nearest approach of the perturbing molecule b_0 (speaking in terms of Anderson-type theories), i.e. average perturbing on the distance is nonlinear. The effective distance of nearest approach is defined, e.g. for adiabatic collisions, as the distance at which the phase shift produced in the collision approaches π . Clearly it will depend on the "Stark sensitivity" of the transition in the case of Stark perturbation, etc. Collisions closer than this distance ("strong collisions") do not (on average) contribute to the shift. Hence, at the same time in the same gas,

different transitions experience different effective Stark fields (in the case of Stark perturbation), and measurements of transition frequencies along different paths correspond, roughly speaking, to measurements of lines in different Stark fields, which obviously can lead to different results of summing of the line frequencies along different paths.

Fortunately for the second scheme (Fig. 20(b)) values of calculated pressure self-shift parameters are available for all transitions forming the chain [89,90], and they agree with the experimental ones. The sum of calculated lineshift parameters along the left path of Fig. 20(b) is equal to +1.1 MHz/Torr which agrees with the experimental value of +0.79 MHz/Torr; the sum of calculated lineshift parameters along the right path of Fig. 20(b) is equal to zero, which agrees with the experimental value of -0.18 MHz/Torr; the difference between sums of calculated lineshift parameters along two paths equals 1.1 MHz/Torr which is very close to the experimental difference value of 0.97 MHz/Torr shown in Fig. 20(b).

Therefore, from the principal point of view, the phenomenon considered probably has to be rather more common than rare; nevertheless, it was not experimentally verified until recently. Quite possi-

bly lack of experimental evidence simply reflected a scarcity of pressure lineshifts studies, especially at the high accuracy required.

One of the consequences of the nonadditivity of pressure lineshifts in the system of transitions to be kept in mind is that if one measures positions of centers of collisionally broadened lines, their sums (which seem to be the distance between initial and final levels) can be different when obtained from different paths or sets of transitions, and this difference can approach several megahertz at pressures of the order of some torr, being significant at existing accuracies of measurement. Therefore this phenomenon can be not only of theoretical (as some limit of accuracy of reconstruction of energy levels from pressure broadened line measurements), but also of practical interest.

4.4.2. Additivity of pressure lineshifts in mixtures of gases

It was found in the Cologne laboratory [94] that the shift of two measured infrared water lines $13_{2,12}$ – $14_{1,13}$ and $9_{5,5}$ – $10_{6,4}$ caused by pure air does not agree with the weighted mean of the shifts measured by the collision of pure nitrogen and oxygen, in contrast with the broadenings which do. Such result was obtained for both lines for which a full set of measurements (air, nitrogen and oxygen lineshifts and broadening) existed.

Firstly it was interesting to look through the analogous measurements available, even though they had been made by a technique not as sophisticated and accurate as Cologne's highly stabilized diode laser spectrometer. To our surprise only three papers were found, which belonged to another research group using fourier transform infrared spectrometry [92]. They studied isotopically substituted water molecules. Similar behavior was found among these results [92], with some data showing the aforementioned differences between measurements and calculations as weighted mean lineshifts well outside three times the standard deviation listed in Ref. [92]. A statistical analysis of data clearly shows, for all three papers, that the deviation of air-shifts from the weighted average of the nitrogen and oxygen shifts does not follow the normal Gaussian distribution, suggesting that

these deviations do not originate from statistical errors.

Possible explanations of these findings can include firstly, some experimental error of unknown origin common for different types of spectrometers, and secondly, some molecular origin, e.g. "memory about previous partner in collision" which can lead to concentrations cross-term in summary lineshift.

At the Nizhnii Novgorod Laboratory microwave measurements on the $1_{10} \leftarrow 1_{01}$ water line near 556 GHz using also nitrogen and oxygen and their mixture as perturbers were carried out and the results did not show non-linearity due to concentration [91].

One source of experimental error was recently found in Cologne and consisted simply in the effect of different water concentrations on the different air samples [93]; when this effect was controlled, dependences on concentrations measured on a Q(6,3) ammonia line were found to be linear. Then, recently, re-measurements of lineshifts of the same two water lines on which the effect of inequality of lineshift by air to the weighted mean of nitrogen and oxygen was found [94] were made by Cologne group [100] and showed absence of non-linearity within the accuracy of the measurements. Therefore the problem can seemingly be counted as settled.

However, recently a paper [99] appeared with results of measurements of ozone broadening and shifts by air, nitrogen and oxygen, in which the authors note that while the measured broadening coefficients consistently follow the linear relationship mentioned, the measured shifts by air do not always correspond to a linear combination of the N_2 and O_2 shifts. Hence some additional clarifying studies seem to be desirable.

The unexpected practical consequence of the study mentioned above is that registration of differences in concentrations of trace gases through their effects on the lineshift is in fact the experimental demonstration of the feasibility of "integral chemical analysis" through shift of a "probe line" by mixture of gases investigated, proposed earlier at the Nizhnii Novgorod Laboratory [79,80].

5. Some perspectives for development of the technique of submillimeter microwave spectroscopy

5.1. Extension of the range of microwave spectroscopy by frequency multiplication

As was pointed out in one of the previous sections of this review paper, frequency multiplication looks very promising for further development. Starting from the observation of the beat note between the third harmonic of BWO and the sixteenth harmonic of the 78–118 GHz synthesizer at a frequency near 1.7 THz, which was obtained during the development of precise microwave broadband scanning spectroscopy in the terahertz range [14], followed by detection of the harmonics generation by the BWO itself [96], these experiments have already led to the extension of the range of microwave spectroscopy by one half, up to 1.5 THz by BWO frequency multiplication on the planar Schottky diode even using a room-temperature thermal acoustic detector as receiver [22]. The next natural step would be studies with the most sensitive cryogenic receivers; also improvements in the construction of multipliers and diodes can be expected on the basis of experience gained in these first submillimeter BWO frequency multiplication experiments. Therefore we can expect deep penetration of microwave spectroscopic methods into the terahertz region in the near future.

5.2. Extension of the range of commercial frequency synthesizers

A very important step towards a real automatic frequency synthesizer for higher submillimeter wave frequencies was the successful development of a broadband multiplier–mixer and sensitive IF amplifier which permitted, for example, retention of the stabilization of signal-beats over the whole range of the millimeterwave synthesizer (40 GHz) on the fifth harmonic, i.e. over 200 GHz on the submillimeter BWO frequency [14]. The transition from laboratory models to commercial devices operation at higher submillimeter frequencies now determined by the present necessity for the higher frequency BWOs to use large electromagnets (or

very expensive permanent SmCo magnets) and relatively high supply voltages and the water cooling, etc. of BWOs which are all more a question of convenience, price and size of the device, rather than principal problems. It should be noted that such a situation appears for the first time in the long story of development of submillimeter microwave spectroscopy.

Construction of BWOs packeted in permanent magnet devices permits an extension of the frequency range. At the Nizhnii Novgorod Laboratory a 526–714 GHz range BWO OB-80 worked in a SmCo permanent magnet during tests of a precise extremely broadbanded (100–600 GHz without any changes or tunings) Fabry–Perot wavemeter [101]. There exist plans to develop the next generation of synthesizers up to 250 GHz by KVARZ with packeted low-voltage BWOs developed at ISTOK. These developments represent the next steps to the full coverage of the range of BWOs available from precision synthesizer technology; the existence of frequency synthesizers as radiation sources is one of the most important criteria of availability of the frequency region considered for extensive uses and applications.

5.3. Some “external” uses of the millimeter/submillimeter spectroscopic technique developed

Millimeterwave synthesizers can be used for extension of the tuning range of side-band spectroscopic techniques or techniques of triple mixing of two CO₂ lasers and one microwave synthesizer (“TuFIR” spectrometer [97]). At least, there are such plans to use laser and millimeterwave synthesizer combination at CALTECH [98]. Chemical and isotopic molecular analysis by several millimeterwave spectroscopic methods has already been mentioned. Another very important possibility is the use of millimeterwave synthesizers, their harmonics, and locked BWOs and their harmonics as a local oscillator technique for interstellar molecular radioastronomy receivers, especially having in mind the low power levels needed for SIS mixers, etc. Hence there is great scope for implementing precision microwave methods.

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