MICROWAVE GAS SPECTROSCOPY IN THE 200 — 870 GHz RANGE

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We report the first automatic continuous recording of complex submillimeter spectra of gases in the 200 — 870 GHz range, with high resolution and large signal/noise ratio.

Interest in extending the research on microwave gas spectroscopy to the submillimeter band was noted by many workers (see, e.g., [1]). The traditional method for this purpose is the use of harmonics of low-frequency generators and radiospectroscopes with microwave receivers [2]. For a number of reasons, the most important of which is the complexity of the source spectrum, the low harmonic power, and the interference in the microwave systems, this procedure is limited mainly to observations of a narrow spectral region with individual strong lines. The highest frequency attained so far in this manner is 813 GHz [3], at which the OCS line J - 66 → 67 was observed.

The development of broadband tunable primary sources of coherent submillimeter radiation, with traveling wave tubes (TWT), made possible further progress in submillimeter spectroscopy. For example, these sources were used to extend the spectroscopy of solids to a wavelength 0.34 mm (880 GHz) [5]. However, the effective use of TWT in gas spectroscopy, where the spectrum is much more complicated and the lines are narrow and weaker, was made difficult, again

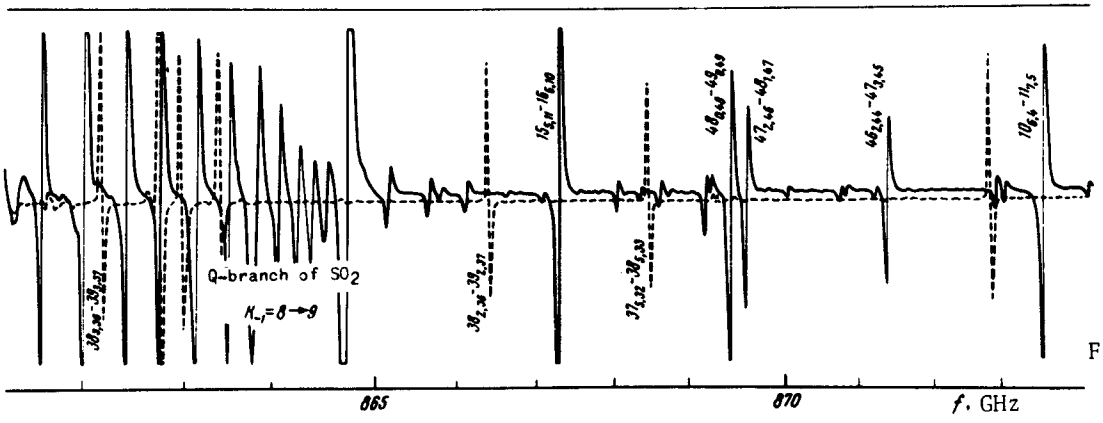

Fig. 1

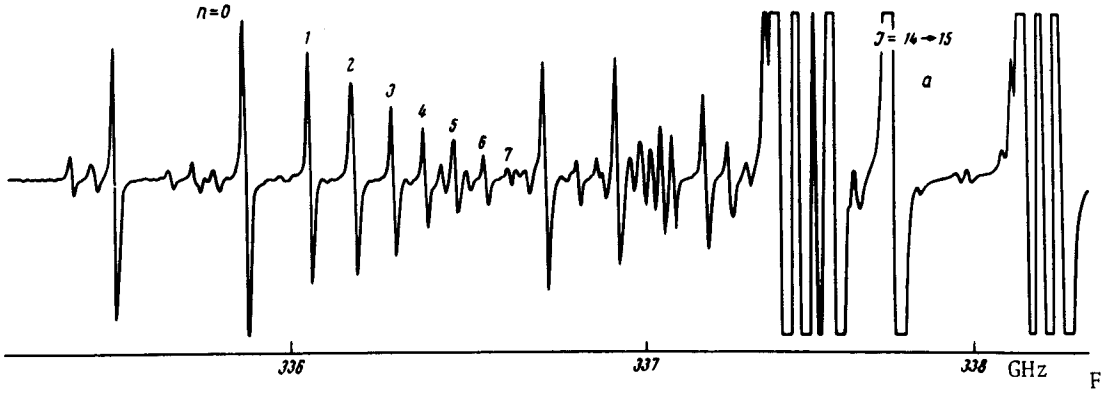

Fig. 2

Fig. 1. Simultaneous recording of the spectra of SO_2 (solid) and HCOOH (dashed) in the 861 - 874 GHz band. The identification of the lines is indicated.

Fig. 2. One of the regular groups of lines (n = 1, ..., 7) of the HCOOH spectrum in the region of 336 GHz. The lines of the "a-component" J = 14 → 15 are identified on the right.

mainly because of the interference in microwave systems, which leads to the appearance of false signals, because of the increased noise in microwave receivers.

The aforementioned limitations were overcome by development of a gas-spectroscopy procedure employing TWT and a radiospectroscope with an acoustic detector (RAD), in which the receivers are acoustic microphones placed directly in the gas cells [6]. We report here the first continuous automatic recording of one or two (simultaneously) submillimeter gas spectra in the range from 200 to 870 GHz (wavelength from 1.5 to 0.345 mm), with high resolution ($10^{-2} - 10^{-6}$) and with large signal/noise ratio (to $10^5 - 10^6$). Figure 1 shows simultaneously obtained spectra of SO_2 and HCOOH in the range 861 – 874 GHz. The signal/noise ratio exceeds that attained in [3] by several orders of magnitude, and the sensitivity attained is not optimal and can be increased by another few orders of magnitude by improving the acoustic receiver and increasing the power of the radiation source. The point is that the noise in the RAD does not depend on the power passing through the cell, whereas the signal is proportional to this power; the limitation on the employed power is imposed only by line saturation. The power obtained from this condition greatly exceeds the values obtained for ordinary microwave spectroscopy with microwave reception [7].

The possibility of obtaining well-resolved gas spectra with a large signal/noise ratio in a bandwidth on the order of hundreds of GHz uncovers new research capabilities. Thus, study of the HCOOH spectrum has revealed, besides the bulk of the lines in the 260 – 360 band, which were identified within the framework of the asymmetric-top model, also regular line groups that did not fit the model. The positions of these is distinctly connected with the positions of the regular groups of the identified lines of the "a-component" of HCOOH. One of these groups

is shown in Fig. 2. Within the limits of the measurement accuracy[1)] (on the order of 3×10^{-5}), the positions of these lines are described by the formulas for the transmission frequencies of a linear molecule in different vibrational states of a certain low-frequency vibration, although the dependence of the effective rotational constant on the proposed vibrational quantum number n is rather complicated. We note that the large value of the effective rotational constant (on the order of 11.2 GHz) is in contrast with the obtained low vibrational frequency (on the order of 57 cm^{-1}). It was difficult to observe these ordered groups in the spectrum either by methods of ordinary microwave spectroscopy (only one group falls in the centimeter band, and large sections of the complex spectra were not observed in the millimeter and submillimeter bands), or by infrared-spectroscopy methods (in view of the low sensitivity and resolution, since the lines in the groups are weaker by an approximate factor of 25 than the typical HCOOH lines, and lie close to the latter).

The development of the described procedure for gas spectroscopy in the submillimeter band, the capabilities of which are far from exhausted, makes it possible, in our opinion, to increase appreciably the importance of submillimeter spectroscopy in the research on molecular spectra.

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[1)]The measurements were performed with the aid of the known SO_2 spectrum. The authors thank Dr. J. Bellet and G. Steenbeckeliers for suggesting this spectrum as a reference and for supplying the tables.

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