Journal of Molecular Spectroscopy 331 (2017) 9–16

Contents lists available at ScienceDirect

Journal of Molecular Spectroscopy

journal homepage: www.elsevier.com/locate/jms

Molecular gas spectroscopy using radioacoustic detection and high-power coherent subterahertz radiation sources

M.A. Koshelev *, A.I. Tsvetkov, M.V. Morozkin, M.Yu. Glyavin, M.Yu. Tretyakov

Institute of Applied Physics, Russian Academy of Sciences, 46 Ulyanov Str., Nizhny Novgorod 603950, Russia

ARTICLE INFO

Article history:
Received 17 June 2016
In revised form 21 October 2016
Accepted 21 October 2016
Available online 22 October 2016

Keywords:
Gas molecular spectroscopy
Radio-acoustic detection
Sensitivity
High-power radiation
Gyrotron

ABSTRACT

We study the "power" approach to improve the sensitivity of the radioacoustic detection method by increasing the radiation power. A gyrotron is the source of high-power continuous monochromatic radiation in the spectrometer. As a result of analysis of experimental profiles of known lines of the rotational SO_2 spectrum, it was demonstrated for the first time that an increase of radiation power by about three orders of magnitude leads to a proportional increase of the RAD spectrometer sensitivity. This permitted us, in particular, to observe the weak transitions predicted earlier in the SO_2 molecule.

1. Introduction

Sensitivity is one of the key parameters of any spectrometer, which determines the range of its possible applications for resolving both fundamental and applied problems. High resolution of the gas spectrometers permits one to observe the lines which characterize unambiguously, as fingerprints, the particular molecules. This opens up huge opportunities, on the one hand, for a molecular-level understanding of the world and, on the other hand, for a quantitative and qualitative analysis of the gas mixtures. The higher the sensitivity, the higher the accuracy of measurement of the spectral line parameters and the greater the number of lines that can be observed in the experiment (the smaller the number of molecules in a gas mixture needed for their lines to appear in the spectrum) and the higher the accuracy with which the properties of the molecules can be explored. High sensitivity of the spectrometer can significantly extend the range of studied objects. Apart from the conventional electric- and/or magnetic-dipole transitions of the molecules, there is a huge number of the so-called forbidden transitions, including those which become allowed due to a centrifugal disturbance in symmetric top and spherical molecules, as well as quadrupole transitions, which are even weaker. The latter are currently little studied and only the observation of several lines of a few molecules confirms their existence. For example, a record sensitivity of about $5 \cdot 10^{-13}$ cm^{-1} (with a signal accumulation time of 4.5 days) was achieved in the IR range by the method of CRD (Cavity Ring Down) spectroscopy [1], which made it possible to perform for the first time highly accurate line shape study [2] of a series of the electric-quadrupole transitions of the hydrogen molecule and demonstrate necessity of further refinement of the most popular nowadays HTP model [3].

One can recall quite a large number of currently known wideband spectrometers used for a study of the spectra of various molecules in the mm/submm wave range. They can be divided into two types according to the principle of molecular spectra registering: from variations in the characteristics of either radiation or the gas being studied [4].

For most of the mm/submm spectrometers, in which either the radiation transmitted through a cell with gas or the radiation re-radiated by the gas is detected, a sensitivity close to the limit determined by fundamental physical principles is achieved (see, e.g. [5], chapter 15, p. 414). The only method that permits one to advance in solving the problem of high sensitivity achievement is known as optoacoustic (photoacoustic or radioacoustic) detection of absorption [6]. For example, a twentyfold increase in sensitivity of the optoacoustic spectroscopic method with the radiated power increased from 0.7 to 15 mW was demonstrated in the IR region [7]. The development of the technology and methods of photoacoustic spectroscopy has found wide practical application, in particular, for the problems of micro-impurity analysis (see, e.g., a

* Corresponding author.
E-mail address: koma@ipfran.ru (M.A. Koshelev).
URL: http://www.mwl.sci-nnov.ru (M.A. Koshelev).

http://dx.doi.org/10.1016/j.jms.2016.10.014
0022-2852/

review paper [8]). On the basis of this method, a spectrometer with radioacoustic detection of absorption signal (RAD spectrometer) was developed more than forty years ago, and has successfully been operated up to now, in the mm/submm range [4,9,10].

The sensitivity of any spectrometer is determined by several factors. The most crucial ones are radiation power, detection system noise (which may depend on the mean radiation power), and spectral purity of the radiation (directly related to the radiation noise). In spectrometers of the first type (e.g., classical video-spectrometer), the sensitivity increases with increasing radiation power until the detection system noise becomes surpassed by the radiation noise. The further increase in power is not practical because a useful signal starts increasing simultaneously with noise, while the sensitivity remains the same. For example, one does not need more than an about 1-mW radiation power in the mm-submm wavelength range if the source is referenced by the phase locking system to a contemporary ultralow-noise microwave synthesizer, and a liquid helium-cooled bolometer serves as a radiation detector. The situation is radically different in spectrometers of the second type (e.g., in a RAD spectrometer). In this case, the detection noise is defined by thermal fluctuations of a microphone membrane in the gas (both due to the inherent Brownian motion of the membrane and the Brownian motion of the gas). The limiting sensitivity of the spectrometer is obtained when thermal fluctuations of the membrane are defined preferably by the Brownian motion of the gas. These fluctuations do not depend on the radiation power passing through the gas cell. Meanwhile, the useful signal amplitude is directly proportional to the radiation power absorbed by the gas and, therefore, linearly increases with the power. Thus, the RAD sensitivity of RAD, or, in other words, the signal-to-noise ratio of the spectral lines observed by the RAD, is also linearly increasing.

In this paper, we report on the step towards the super-sensitive detection in the mm-submm wavelength range by increasing the radiation power by orders of magnitude. This is a mutual feature of any spectrometer of the second type. This is absolutely impossible in spectrometers of the first type, namely, because of the detector noise increase (followed by the detector burning) with increasing power. We demonstrate the feasibility of significant (several orders of magnitude) improvement of RAD spectrometer sensitivity by using high-power coherent radiation sources. The sensitivity achieved in the spectrometer permitted us, in particular, to observe the weak transitions predicted earlier in the rotational spectrum of the SO_2 molecule.

2. Spectrometer with radioacoustic detection: principles

A detailed description of the modern version of the RAD spectrometer and methods for studying the spectral properties of gases can be found in [11]. We will give only a short description of the device. A simplified diagram of the RAD spectrometer is shown in Fig. 1.

By tradition, backward-wave oscillators (BWOs) are used as radiation sources in the RAD spectrometers, a series of which covers a very wide range of 35–1500 GHz ([12,13], http://www.istokmw.ru/). The BWO power can vary from a fraction to tens of mW (reaching more than 100 mW in the best tubes) within the operating frequency range. High stability, low level of the phase noise, and exact knowledge of the frequency are provided due to the use of a phase-locked loop (PLL) system of the BWO radiation referenced by a microwave frequency synthesizer signal, which is synchronized with a frequency and time standard signal [14,15]. The detector of absorbed radiation power is a cell with gas and a microphone connected to it. If the radiation frequency coincides with the molecular transition frequency, then the gas absorbs the radiation, is heated, and expanded. Pressure variations are registered by a microphone. Radiation frequency or amplitude modulation and the synchronous detection of absorption signal are used for increasing the spectrometer sensitivity. The output signal of the spectrometer is directly proportional to the power of the radiation absorbed by the gas. The signal can be expressed as a product of the incident power of the radiation, gas absorption coefficient and optical path length, if the Beer-Lambert law is taken into account and the case of a small optical depth is considered.

Thus, there are two methods to improve the sensitivity of the RAD spectrometer, namely, to increase the effective optical path length and/or radiation power. Let us examine both methods.

A standard approach for improving the sensitivity of any spectrometer is to increase the optical path length in the gas. This is commonly done by using gas cells of different length (from a few centimeters to tens of meters) and configurations (e.g., White and Heriott multipass cells, resonator-type cells, etc.). A sensitivity increase in the RAD spectrometer with increasing effective path length was examined in [16–18]. As a result, a record sensitivity of $3 \cdot 10^{-11}$ cm^{-1} of the RAD spectrometer for a synchronous detection time constant of 1 s and a radiation power of about 50 mW was demonstrated in [17] by observation of pure rotational lines of the N_2O molecule in excited vibrational states (030) and (040) in a resonator-type gas cell. The main drawback of using high-Q resonators, unlike the multipass cells employed in the IR range, is the need to adjust the resonance frequency to the scanned radiation frequency. This method is difficult to use when unknown low-intensity lines are sought, but it can be fully utilized in a particular gas analysis since the frequency of the marker line is well known in advance. In addition, the resonance cell significantly complicates the interference pattern in the wave channel of the spectrometer and hence complicates the spectrometer baseline. This makes it virtually impossible to use resonant cells for a high-precision analysis of the molecular line profiles.

Another way for improving the sensitivity of the radioacoustic method is to increase the radiation power. However, unlike the IR range, the choice of mm/submm radiation sources is not as wide even at present. The following paragraph presents a short review of available powerful generators.

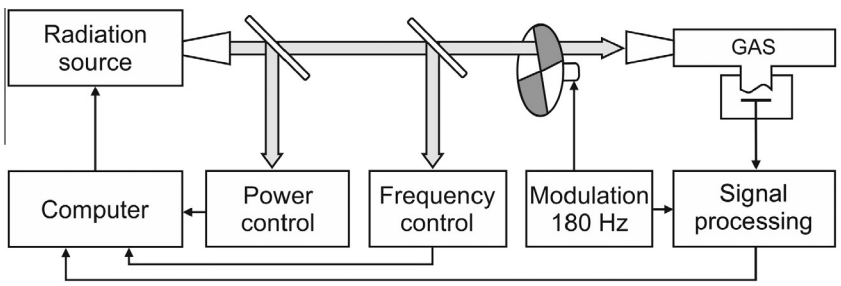

Fig. 1. Simplified diagram of the RAD spectrometer.

3. High-power millimeter and submillimeter wave sources: capabilities and applications

Among the existing sources, the well-known and long-developed electronic devices, in particular, backward-wave oscillators (BWOs), free-electron lasers (FELs), and gyrotrons, hold a prominent place. Terahertz BWOs with low electron energies of up to 5 keV, which were developed many years ago, provide a milliwatt radiation power of up to the maximum radiation frequency 1.5 THz. Free-electron lasers are able to ensure many orders of magnitude higher radiation powers in an unprecedented wide range from centimeter to X-ray waves. However, the realization of FELs at the terahertz waves requires electron beams with particle energies more than 1 MeV, which can only be obtained with fairly large facilities. The gyrotrons, which are many orders of magnitude inferior to FELs in the maximum usable frequency, are able to ensure the same or even a much higher level of average power with a much lower energy of electrons, namely tens of keV, at wavelengths of up to 1 THz. However, it should be noted that such high-frequency gyrotrons require very strong magnetic fields, which was and is the main obstacle to their wide spread. For example, a field of more than 36 T is required to obtain a radiation frequency of 1 THz at the main cyclotron resonance. At most, such fields can only be created by pulsed magnets. However, for effective operation at cyclotron harmonics (2, 3, ...), one can use, correspondingly lower magnetic field, which can be provided by the existing and rapidly developing cryomagnetic systems, if the required level of the spurious mode discrimination is achieved in the gyrotron.

Generation of submillimeter waves by weakly relativistic electron beams moving in a strong magnetic field was first mentioned in the paper [19] belonging even to the pre-gyrotron experiments, in which a power of about 1 mW was demonstrated at a frequency of 316 GHz for a pulse length of 100 μs. Successful experiments with high-frequency gyrotrons, in which CW generation at the second cyclotron harmonic at separate frequencies in the range 0.25–0.35 THz for a power level of about 1 kW were carried out at the Institute of Applied Physics (IAP) in 1970–1980 [20]. A pulsed oscillator at the main cyclotron resonance with a power of 40–100 kW in 100-μs pulses at frequencies of up to 0.65 THz was demonstrated [21]. These outstanding achievements are far ahead of their time and have not been used effectively for applications. Successful demonstration of the possibility of stable single-mode oscillation at the second harmonic of gyrofrequency with relatively high operating modes (e.g., $TE_{6,5}$ in a gyrotron with conventional cylindrical resonator [22]) and the realization of broadband mechanical frequency adjustment [23] should be admitted the main outcome of the first experiments. Later, successful experiments with high-frequency gyrotrons were also carried out at the Massachusetts Institute of Technology (MIT), Boston, USA [24], University of Sydney, Australia [25], and University of Fukui, Japan [26]. Experiments on using relatively low-power high-frequency gyrotrons for high-field EPR (electron paramagnetic resonance) spectroscopy and dynamic nuclear polarization in NMR (nuclear magnetic resonance) spectroscopy were conducted at the MIT. This application is rapidly developed in some institutions, including the IAP [27,28], and is at present the most important stimulus for the development of the whole line of research. A frequency frontier of 1 THz, which had been inaccessible to the gyrotrons, was achieved and then surpassed in the experiments performed at the IAP [29] and University of Fukui [30]. To date, progress in the creation of strong magnetic fields makes prospects for the achievement of even higher frequencies quite apparent. The corresponding relatively powerful and compact sources may appear most convenient and accessible for many of the already existing and emerging new applications.

4. Using the gyrotron for radioacoustic detection

The possibility of improving the RAD spectrometer sensitivity by increasing the radiation power was experimentally demonstrated for the first time in [31] where an up to 1-kW gyrotron operated in CW regime at a frequency of about 34 GHz was employed. Formic acid (HCOOH) was used as a test gas. One of the predicted lines of the rotational spectrum of the acid was chosen to fit a narrow spectral range that was accessible for the gyrotron. Rough tuning of the gyrotron frequency was possible due to a slight mechanical variation of the cavity sizes. Smooth sweeping of the source frequency was not possible. An absorption signal was detected (Fig. 2) at one frequency near the maximum of the predicted $J_{Ka,Kc} = 6_{1,5}–6_{1,6}$ rotational line of the ground vibrational state at 34378.8 MHz in a single pass of radiation through a cell 10 cm long. The signal amplitude showed a linear dependence on the radiation power. Based on the absorption coefficient estimate $8.4 \cdot 10^{-8}$ cm^{-1} at the maximum of the chosen line in the HCOOH and N_2O mixture and the experimental signal to noise ratio, the corresponding value of the RAD spectrometer sensitivity was estimated as $(1–2) \cdot 10^{-11}$ cm^{-1} for a synchronous detection time constant of 1 s. As a result, the gain in the spectrometer sensitivity was estimated as 3–4 orders of magnitude when a more powerful (than BWO) radiation source was used.

A drawback of this work is that the absorption spectrum of a sample, in its classical understanding, was not recorded because of the impossibility of smooth tuning of the radiation frequency. Correspondingly, all the possible "parasitic" signals that occur, in particular, due to absorption of radiation in the cell elements and are synchronous with the absorption signal in a gas contributed to the observed signal. The presence of a parasitic signal, which is smaller than the signal from the line was mentioned in [31], but this was neglected in the data interpretation. Note that the useful-to-parasitic signal ratio decreases with decreasing absorption coefficient in the line maximum and increasing power of the radiation source and can reach up to 1/10 or less (see, e.g., Fig. 5). Thus, the interpretation of results obtained in [31] can be somewhat ambiguous. A true estimate of the sensitivity can only be obtained from observations of the absorption line and analysis of their profiles.

Progress in the development of high-power mm/submm radiation sources, which was achieved in recent years, made it possible to return to the problem of increasing the RAD sensitivity by the "power" method. In particular, an automated facility [32] based on a gyrotron operated at a frequency of about 263 GHz in the CW regime with a radiation power of up to ~1 kW was developed at the IAP RAS. This gyrotron permits smooth tuning of the radiation frequency, although within small (in terms of spectroscopy standards) limits of the order of 0.2 GHz due to varying the operating voltage and temperature of the gyrotron cavity. The gyrotron radiation spectrum width Δf is about 0.5 MHz ($\Delta f/f \sim 10^{-6}$) and is mostly determined by the instabilities of the accelerating power-supply voltage with a characteristic time of about 10 μs. The spectrum could be further improved, as in the case with a BWO, by phase locking to a highly stable signal of the reference synthesizer (see, e.g., Ref. [33]), but this was not done in this study. Instead, there was continuous monitoring of the gyrotron radiation frequency, as in Ref. [34], by the heterodyne method using a harmonic multiplier-mixer. An Anritsu MG3692C frequency synthesizer (2–20 GHz) served as the heterodyne. The beat frequency signal between the 18th harmonic of the synthesizer frequency and the fundamental gyrotron frequency was controlled using an Agilent N9320B spectrum analyzer in the frequency range 250–400 MHz. The uncertainty of determining the frequency with allowance for the gyrotron radiation spectrum bandwidth was about ±0.2 MHz. The gyrotron radiation power was measured by

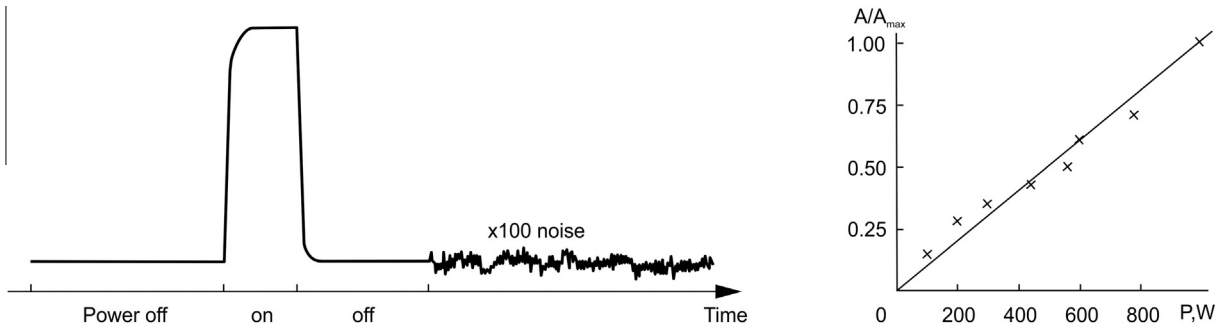

Fig. 2. (Based on Figs. 1 and 2 from [31].) Left: Output signal of the RAD spectrometer, which was observed with the gyrotron switched on at a frequency near the maximum of the $J_{Ka,Kc} = 6_{1,5}–6_{1,6}$ line of HCOOH. The radiation power is 10^3 W. Noise is shown on a 100 times enlarged scale. Right: Spectrometer signal amplitude (in relative units) as a function of radiation power.

the calorimetric method with an uncertainty of about ±5 W. The radiation beam is rather close to the Gaussian one with a characteristic diameter of about 10 mm at the point of the plane phase front [32], which makes its use for spectroscopy fairly simple.

5. Results and discussion

In this paper, to demonstrate the capabilities of the RAD spectrometer, as the test gas we used sulfur dioxide (SO_2), which has a fairly dense, well-studied spectrum in the mm/submm range. This factor was decisive in the choice due to the limited possibility of the gyrotron frequency tuning. An example of the calculated spectrum of SO_2 (according to [35]) in the gyrotron generation range is shown in Fig. 3A for the SO_2 and Ar mixture. In the spectrum modeling we used a Lorentz profile. The coefficients of collisional line broadening by the SO_2 and Ar pressure were taken 13 MHz/Torr [36] and 2.5 MHz/Torr [37], respectively.

Typical recordings of the SO_2 and Ar mixture spectra, which were obtained using the RAD spectrometer for several pressures and at a single pass of radiation through a 10 cm long and 2 cm diameter gas cell are shown in Fig. 3B. Identification and quantitative characteristics of the experimentally observed lines taken from [35] are given in Table 1. The spectrometer absorption sensitivity corresponding to the BWO recordings was determined from the absorption coefficient at the line maximum divided by the signal-to-noise ratio, which yielded about $3 \cdot 10^{-7}$ cm^{-1} for a synchronous detection time constant of 1 s. In the calculations, it was taken into account that SO_2 was diluted 1:50 in the mixture. It should be mentioned that such sensitivity is routine for most of the mm/submm spectrometers.

A relatively high gas pressure in the experiment allowed eliminating the influence of the radiation noise related to fast frequency fluctuations. Indeed, the collisional line width at these pressures is much larger than the radiation spectrum bandwidth. Thus, the latter factor influence on the observed line shape becomes negligibly small.

Fig. 4 shows the experimental spectra recorded at a constant gas pressure and different levels of radiation power from 2 to 25 W. These recordings clearly demonstrate the spectrometer sensitivity increase with increasing power of the scanning radiation from fractions of a watt to a few watts. The achieved sensitivity made it possible to observe the theoretically predicted [35] transitions in the SO_2 molecule at frequencies near 263.151 GHz and 263.161 GHz (Fig. 4, bottom) with an absorption coefficient of about 10^{-8} cm^{-1} at the line center. The transition frequencies measured in this paper using the RAD spectrometer and the gyrotron are given in Table 1. The measurement error (1σ) is about ±0.2 MHz. The maximum absorption sensitivity of the spectrometer corresponding to the spectra in Fig. 4 was determined as $6 \cdot 10^{-10}$ cm^{-1} for a synchronous detection time constant of 1 s. Thus, an increase in the scanning radiation power by about three orders of magnitude leads to a proportional increase in the sensitivity of the RAD spectrometer, showing the efficiency of the "power" method.

Unfortunately, an increase in the radiation power leads not only to an increase in the spectrometer sensitivity, but also limits the latter. This is due to the spectral line saturation effect. The effect is that under the action of a high-power resonant field the molecules that absorbed the energy do not have time to return fast enough to the initial state via collisions with other molecules (the probability of relaxation due to the spontaneous emission is negligibly small). As a result, the energy level populations become equal, the transition is saturated, and the gas becomes transparent for radiation at the transition frequency. The effect is characterized by the Rabi frequency corresponding to oscillation of the population difference between the transition levels. Although we did not study the parameters of the radiation coming into the cell (beam size, field distribution, etc.) the Rabi frequency can be roughly estimated for the lines observed in Fig. 4 at 2 W power level as 5 MHz for 263.15-GHz line and 35 MHz for 263.16-GHz line, respectively. For a higher level of power, the Rabi frequency increases as a square root of power. In the calculations, we assumed a 1-cm radius of the gyrotron radiation beam inside the cell. Note that at these wavelengths the real distribution of the field power is essentially unknown because of the unavoidable interference effects. Thus, the calculations present more likely a lower limit of the Rabi frequency. The collision rate calculated for the conditions from Fig. 4 is about 1 MHz, which is essentially smaller than the Rabi frequency. This means that the saturation effect appeared for the observed lines even with the lowest power under study.

The manifestation of the effect is well seen in, e.g., Fig. 4 from the 263.161-GHz line profile variation as the radiation power is increased. It is evident that a further increase in the scanning radiation power will not help to improve the sensitivity of the radioacoustic method for observation of this line at a given pressure (the Rabi frequency is higher than the collision rate). The line at 263.151 GHz becomes saturated with increasing power a little bit slower due to a 6-times smaller matrix element of the dipole moment of the transition with $\Delta K_a = 3$, but essentially this does not resolve the problem.

The degree of saturation of the transition depends on both the radiation parameters (intensity) and the parameters of the line itself (matrix element of the dipole moment of the transition and collisional width of the corresponding line, i.e., the rate of the collisional relaxation processes). That is why, for the SO_2 molecule having a large dipole moment (about 1.6 Debye), the saturation

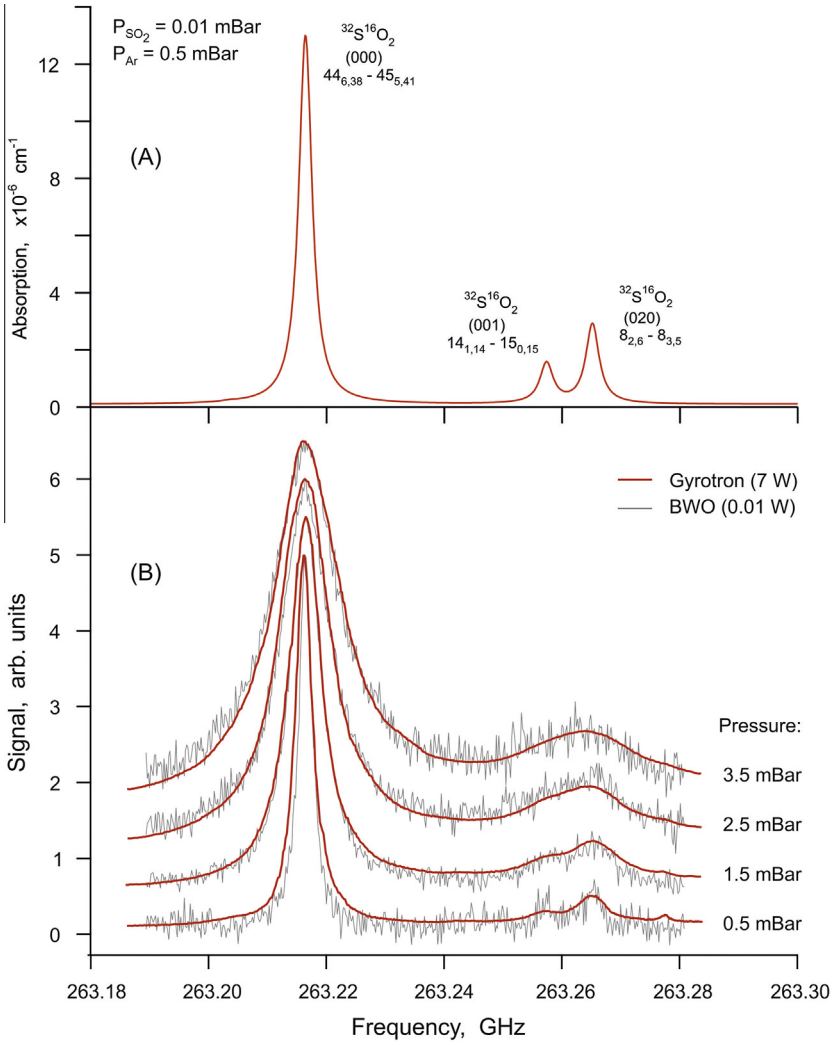

Fig. 3. Top (A): calculated spectrum of the SO_2 (0.01 mBar) and Ar (0.5 mBar) mixture. Bottom (B): an example of the experimental spectra of the SO_2 and argon mixture obtained using the RAD spectrometer for different pressures of gas in the cell at a constant level of radiation power. Partial pressure of SO_2 in the mixture is 0.01 mBar. The total gas pressure in the cell is shown in the figure near the corresponding spectrum. For the figure clarity, each spectrum is shifted vertically to a constant value with respect to the previous one. The spectra obtained using a BWO with a radiation power of about 0.01 W (typical power of an OB-24 type tube) and using a gyrotron with about 7 W power are shown by gray broken and red smooth lines, respectively. The synchronous detection time constant is 1 s.

Table 1
Identification and quantitative characteristics of the observed lines.

Frequency, MHz		α_{max}, cm^{-1}[b]	Molecule	Vib. state	Transition, $J'_{K'a,K'c} \leftarrow J_{Ka,Kc}$
Predicted [35]	Observed (this work)				
263151.527	263151.47	$1.97 \cdot 10^{-7}$	$^{32}SO_2$	(0 0 1)	$25_{1,24}$–$24_{4,21}$
263161.805[a]	263160.89	$2.43 \cdot 10^{-7}$	$^{34}SO_2$	(0 0 0)	$64_{11,53}$–$65_{10,56}$
263216.416[a]	263216.14	$1.67 \cdot 10^{-4}$	$^{32}SO_2$	(0 0 0)	$44_{6,38}$–$45_{5,41}$
263257.353	263256.68	$1.81 \cdot 10^{-5}$	$^{32}SO_2$	(0 0 1)	$14_{1,14}$–$15_{0,15}$
263265.148	263264.90	$3.60 \cdot 10^{-5}$	$^{32}SO_2$	(0 2 0)	$8_{2,6}$–$8_{3,5}$

[a] The lines included in [36].
[b] Absorption coefficient at the line center in pure SO_2 at T = 293 K under the assumption of Lorentz profile.

effect is strong enough even at a significant broadening. The effect manifestation can be minimized by selection of an appropriate molecule and choosing the transition (with a smaller matrix element of the dipole moment), as well as by optimization of the conditions of its observation (line broadening by pressure, cross section of the radiation interaction with gas). Thus, for achieving the record spectrometer sensitivity limited by thermal fluctuations of the gas pressure in the cell, it is needed to choose carefully the molecule, the transition, and experimental conditions.

In the actual facilities, the manifestation of a non-informative background signal of the spectrometer (the so-called baseline), which is due to absorption of radiation in the cell elements (see Fig. 5) remains a fundamental constraint of the RAD method. Note that this background signal is not noise in its usual appearance. The closest analog of this signal is synchronous with the modulation frequency pick-up, which may take place in the detection system employing a lock-in amplifier. The pick-up manifestation in the output signal of the amplifier is an additional signal. The amplitude

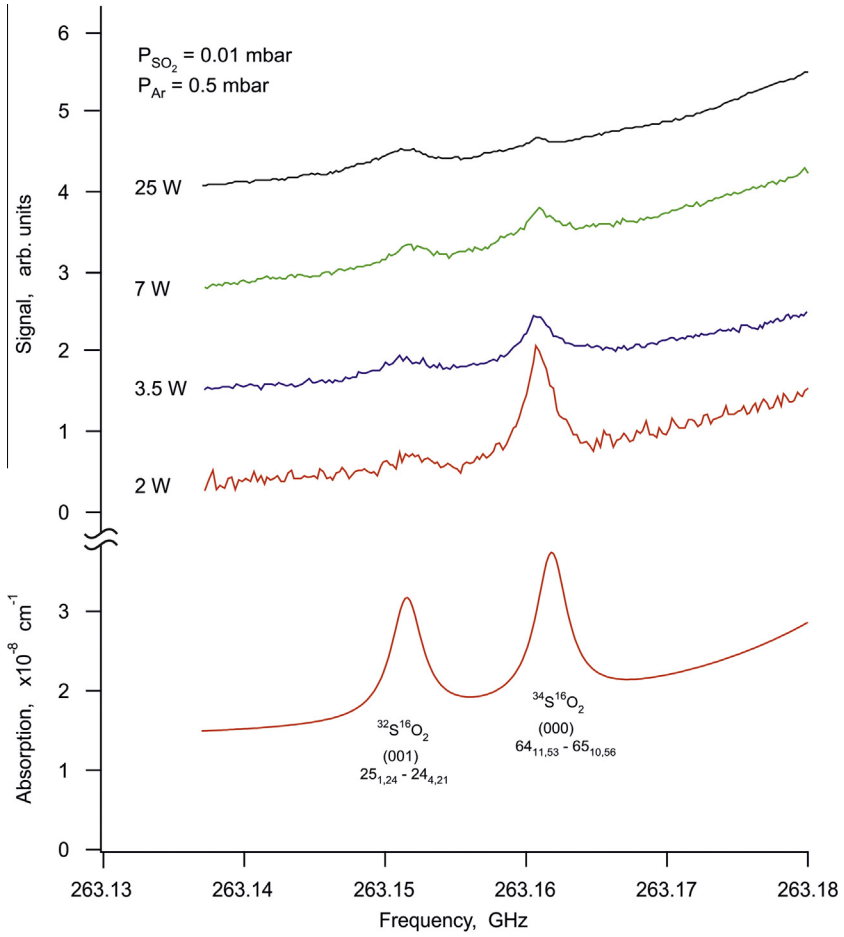

Fig. 4. Bottom: calculated spectrum of the SO_2 (0.01 mBar) and Ar (0.5 mBar) mixture. Top: examples of the experimental spectra of the SO_2 and argon mixture obtained using the RAD spectrometer with the gyrotron at room temperature and constant pressure for different levels of the radiation power (shown in the figure near the corresponding spectrum). Partial pressure of the SO_2 in the mixture is 0.01 mBar and argon is 0.5 mBar. For the figure clarity, the records were normalized by the observed 263.15-GHz line amplitude, and each spectrum was shifted vertically to a constant value with respect to the previous one. The synchronous detection time constant is 1 s. This figure demonstrates an increase in the signal-to-noise ratio with increasing radiation power until the line saturation.

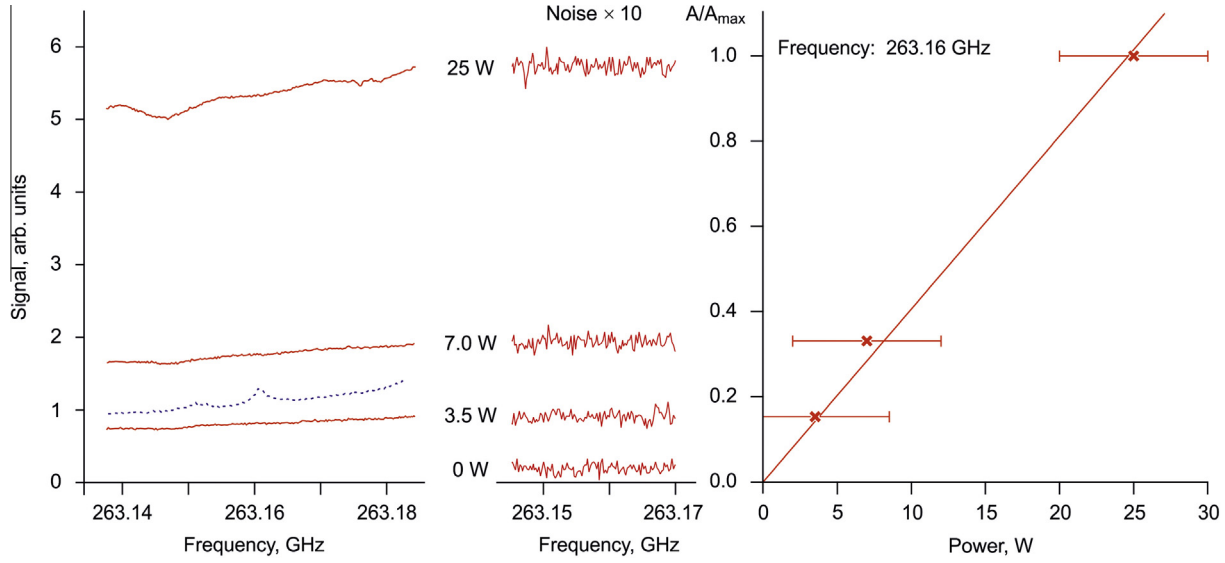

Fig. 5. Left: spectrometer baseline signal obtained for different radiation powers (indicated in the figure) when the cell is filled up with pure argon (solid red lines) up to a pressure of 0.5 mBar. A spectrum recording of the SO_2 and Ar mixture (0.01/0.5 mBar, dotted blue line) for a power of 3.5 W adopted from Fig. 4 is shown for comparison. Middle: Part of the tenfold enlarged noise residuals after the fit of the baselines by a polynomial function. The "0 W" residual corresponds to acoustic noise of the cell without radiation. Right (same as Fig. 2): crosses show the relative values of the baseline amplitude A(P)/A(25 W) at a frequency of 263.16 GHz as functions of the power P. Solid line is approximation of the points by a function $y(P) = a \cdot P$. Horizontal bars at the points show the uncertainty of measurement of the power (±5 W).

of this parasitic signal is constant if the pick-up amplitude is constant with time. In the RAD spectrometer, this signal is radiation frequency dependent. The dependence is mainly determined by the radiation power variation caused by standing waves in the source-to-cell wave channel. The presence of this signal significantly impedes measuring the low-power variations caused by absorption of the radiation in the studied medium. However, the baseline signal can be taken into account at the stage of the line shape analysis if the gas pressure is small enough and the characteristic frequency scale of these baseline variations is larger than the observed line width. An additional term that is linear or quadratic in frequency with variable parameters included in the line shape model resolves the problem. Thus, the presence of this parasitic signal does not affect the signal-to-noise ratio of the observed line.

It was mentioned above that the useful-to-parasitic signal ratio decreases with increasing source power, as was demonstrated in Fig. 5. In particular, for a radiation power of 3.5 W, the absorption signal at the center of the 263.151-GHz line was about 10% of the baseline signal, decreasing down to 1.5% for 25 W. Moreover, the radiation power dependence demonstrated by the baseline signal at a given frequency (Fig. 5, right) is very similar to that obtained earlier in [31] and interpreted as an absorption signal from the HCOOH line (Fig. 2). The obtained dependences clearly show that without the frequency tuning of the source, i.e., without recording of the molecular line profile, the baseline signal can erroneously be taken for a signal from the line, and the error of determining the spectrometer sensitivity may achieve up to tenfold or even more. This error can be avoided if instead of the radiation intensity modulation, the frequency modulation is used.

The middle part of Fig. 5 demonstrates a portion of tenfold enlarged residual noise after the fit of each baseline by a polynomial function. It is seen that an increase in radiation power does not reveal any noticeable change in noise (at least within the power limits of the current study) in comparison with the acoustic noise of the cell marked by "0 W" and recorded in the absence of the radiation. This proves the high-power gyrotron to be a promising radiation source for achieving a high sensitivity of the gas molecular spectroscopy using radio-acoustic detection.

6. Conclusions

In this paper, we study the "power" approach to improve the sensitivity of the radio-acoustic detection method. A gyrotron was used as the source of high-power continuous monochromatic radiation in the spectrometer. As a result of analysis of experimental profiles of the spectral lines of the well-studied SO_2 spectrum, it was demonstrated for the first time that an increase of radiation power by about three orders of magnitude leads to a proportional increase of sensitivity of the RAD spectrometer. The achieved sensitivity of the spectrometer is not a limit. The spectrometer sensitivity obtained in this study is determined only by the SO_2 line saturation effect, which can be substantially reduced by proper selection of the molecule, the transition, and experimental conditions. Among the possible research subjects, forbidden spectra of the polar and non-polar molecules, including quadrupole transitions, for which the saturation effect with powers of the existing mm/submm radiation sources is insignificant, seem to be most interesting. It is essential that the use of a gyrotron does not exclude utilizing the conventional method to achieve high RAD spectrometer sensitivity by increasing the effective optical path length, which, as the previous studies showed [16–18], provides an absorption sensitivity of 10^{-9}–10^{-11} cm^{-1} even when the BWO radiation is employed. This gives a hope that a record-breaking sensitivity can be achieved if these two methods are combined and opens up tremendous opportunities for both fundamental studies of molecular spectra and practical applications, particularly in the field of highly sensitive micro-impurity gas analysis.

Acknowledgements

We would like to thank E.S. Bekhtereva and O.N. Ulenikov for help with calculation of the dipole matrix elements of SO_2. Authors are grateful to G.Yu. Golubiatnikov for technical support and suggestions and to A.F. Krupnov for careful reading the manuscript and his valuable comments. Development of the spectrometer components was partly supported by RFBR (project No. 15-02-07887), the gyrotron development supported by RSF grant 14-12-00887.

References

[1] S. Kassi, A. Campargue, Cavity ringdown spectroscopy with 510^{-13} cm^{-1}, J. Chem. Phys. 137 (2012) 234201.
[2] P. Wcisło, I.E. Gordon, H. Tran, Y. Tan, S.-M. Hu, A. Campargue, S. Kassi, D. Romanini, C. Hill, R.V. Kochanov, L.S. Rothman, The implementation of non-Voigt line profiles in the HITRAN database: H2 case study, J. Quant. Spectrosc. Radiat. Transf. 177 (2016) 75–91.
[3] J. Tennyson, P.F. Bernath, A. Campargue, et al., Recommended isolated-line profile for representing high-resolution spectroscopic transitions (IUPAC technical report), Pure Appl. Chem. 86 (12) (2014) 1931–1943.
[4] A.F. Krupnov, A.V. Burenin, New methods in submillimeter microwave spectroscopy, in: K.N. Rao (Ed.), Molecular Spectroscopy: Modern Research, Academic Press, N.Y., 1976, pp. 93–126.
[5] C.H. Townes, A.L. Schawlow, Microwave Spectroscopy, McGraw-Hill, New York-London-Toronto, 1955.
[6] Y.-H. Pao (Ed.), Optoacoustic Spectroscopy and Detection, Academic Press, London, 1977.
[7] L.B. Kreuzer, Ultralow gas concentration infrared absorption spectroscopy, J. Appl. Phys. 42 (1971) 2934–2943.
[8] A. Elia, P.M. Lugara, C. Di Franco, V. Spagnolo, Photoacoustic techniques for trace gas sensing based on semiconductor laser sources, Sensors 9 (2009) 9616–9628.
[9] A.F. Krupnov, L.I. Gershtein, V.G. Shustrov, S.P. Belov, Microwave spectrometer in millimeter and submillimeter wave range with acoustic detection, Izv. VUZov. Radiofiz. 13 (1970) 1403–1405.
[10] A.F. Krupnov, Modern submillimeter microwave scanning spectroscopy, in: G. W. Chantry (Ed.), Modern Aspects of Microwave Spectroscopy, Academic Press, London, 1979, pp. 217–256.
[11] M.Yu. Tretyakov, M.A. Koshelev, D.S. Makarov, M.V. Tonkov, Precise measurements of collision parameters of spectral lines with a spectrometer with radioacoustic detection of absorption in the millimeter and submillimeter ranges, Instrum. Exp. Tech. 51 (2008) 78–88.
[12] M.B. Golant, R.L. Vilenkin, E.A. Zulina, Z.F. Kaplun, A.A. Negirev, V.A. Parilov, T. B. Rebrova, V.S. Saveliev, A series of low power broad-band oscillators operating in millimeter and submillimeter wave ranges, Prib. Tech. Eksp. 4 (1959) 136–139 (in Russian; English translation of journal available under the title "Sovjet Physics - Pribory").
[13] M.B. Golant, Z.T. Alekseenko, Z.S. Korotkova, L.A. Lunkina, A.A. Negirev, O.P. Petrova, T.B. Rebrova, V.S. Savel'ev, Wide-range oscillators for the submillimeter wavelengths, Prib. Tekh. Eksp. 3 (1969) 231–237 (In Russian; English translation of journal available under the title "Sovjet Physics - Pribory").
[14] A.F. Krupnov, Phase lock-in of MM/SUBMM backward wave oscillators: development, evolution and applications, Int. J. IR MM Waves 22 (1) (2001) 1–18.
[15] A.F. Krupnov, M.Yu. Tretyakov, S.P. Belov, G.Yu. Golubiatnikov, V.V. Parshin, M. A. Koshelev, D.S. Makarov, E.A. Serov, Accurate broadband rotational BWO-based spectroscopy, J. Mol. Spectrosc. 280 (2012) 110–118.
[16] V.P. Kazakov, Increasing the sensitivity of the scanning RAD spectrometer by using of non-tunable resonator, Izv. VUZov. Radiofiz. 23 (7) (1980) 877–879 (in Russian).
[17] V.P. Kazakov, V.V. Parshin, Yu.A. Dryagin, Increasing the sensitivity of the scanning RAD spectrometer by using quasioptical resonator, Izv. VUZov. Radiofiz. 29 (1986) 240–243 (in Russian).
[18] V.P. Kazakov, A.F. Krupnov, V.N. Saveliev, O.N. Ulenikov, Submillimeter spectrum and constants of AsH_3, J. Mol. Spectrosc. 123 (1987) 340–355.
[19] I.B. Bott, Tunable source of millimeter and submillimeter electromagnetic radiation, Proc. IEEE 52 (3) (1964) 330–332.
[20] N.I. Zaytsev, T.B. Pankratova, M.I. Petelin, V.A. Flyagin, Millimeter-and submillimeter-wave gyrotrons, Radio Eng. Electron. Phys. 19 (1974) 103–107.
[21] V. Flyagin, A. Luchinin, G. Nusinovich, Submillimeter-wave gyrotrons: theory and experiments, Int. J. Infrared Millim. Waves 4 (4) (1983) 629–637.
[22] T.B. Pankratova, G.S. Nusinovich, Experimental study of a diagnostic gyrotron, Sov. Phys. Tech. Phys. 34 (8) (1989) 912–914.
[23] I.I. Antakov, V.A. Gintzburg, L.I. Zagryadskaya, L.V. Nikolaev, Mechanically tunable CRM oscillators, Electron. Tekh. Ser. Elektron. SVCh 8 (1975) 20–25 (in Russian).

[24] M.K. Hornstein, V.S. Bajaj, R.G. Griffin, K.E. Kreischer, I. Mastovsky, M.A. Shapiro, J.R. Sirigiri, R.J. Temkin, Second harmonic operation at 460 GHz and broadband continuous frequency tuning of a gyrotron oscillator, IEEE Trans. Electron. Dev. 52 (2005) 798–807.
[25] K. Hong, F. Brand, T. Idehara, A 150–600 GHz step-tunable gyrotron, J. Appl. Phys. 74 (8) (1993) 5250–5258.
[26] T. Idehara, S. Mitsudo, S. Sabchevski, M. Glyavin, I. Ogawa, Gyrotron FU series – current status of development and applications, Vacuum 62 (2001) 123–132.
[27] V.L. Bratman, M.Yu. Glyavin, Yu.K. Kalynov, A.G. Litvak, A.G. Luchinin, A.V. Savilov, V.E. Zapevalov, Terahertz gyrotrons at IAP RAS: status and new designs, J. Infrared Millim. Terahertz Waves 32 (3) (2001) 371–379.
[28] M.Yu. Glyavin, T. Idehara, S.P. Sabchevski, Development of THz gyrotrons at IAP RAS and FIR UF and their applications in physical research and high−power THz technologies, IEEE Trans. Terahertz Sci. Technol. 5 (5) (2015) 788–797.
[29] M.Yu. Glyavin, A.G. Luchinin, G.Yu. Golubiatnikov, Generation of 1.5-kW, 1-THz coherent radiation from a gyrotron with a pulsed magnetic field, Phys. Rev. Lett. 100 (2008) 015101.
[30] T. Idehara, H. Tsuchiya, O. Watanabe, S..Mitsudo. LaAgusu, The first experiment of a THz gyrotron with a pulse magnet, Int. J. IR MM Waves 27 (3) (2006) 319–331.
[31] I.I. Antakov, S.P. Belov, L.I. Gershtein, V.A. Ginzburg, A.F. Krupnov, G.S. Parshin, Use of large powers of resonant radiation for enhancing the sensitivity of microwave spectrometers, JETP Lett. 19 (1974) 634–637.
[32] M.Yu. Glyavin, A.V. Chirkov, G.G. Denisov, A.P. Fokin, V.V. Kholoptsev, A.N. Kuftin, A.G. Luchinin, G.Yu. Golubyatnikov, V.I. Malygin, M.V. Morozkin, V.N. Manuilov, M.D. Proyavin, A.S. Sedov, E.V. Sokolov, E.M. Tai, A.I. Tsvetkov, V.E. Zapevalov, Experimental tests of 263 GHz gyrotron for spectroscopy applications and diagnostic of various media, Rev. Sci. Instr. 86 (5) (2015) 054705.
[33] G.Yu. Golubiatnikov, A.F. Krupnov, L.V. Lubyako, A.G. Luchinin, A.B. Pavelyev, M.I. Petelin, A. Fernandez Curto, Gyrotron frequency control by a phase lock system, Tech. Phys. Lett. 32 (8) (2006) 650–652.
[34] M.Yu. Tretyakov, Yu.K. Kalynov, Measurements of the radiation frequency of a pulsed subMM-wave gyrotron using beat-note signals with the harmonics of a millimeter-wave frequency synthesizer, Instrum. Exp. Tech. 49 (5) (2006) 661–668.
[35] S.P. Belov, M.Yu. Tretyakov, I.N. Kozin, E. Klisch, G. Winnewisser, J.-M. Flaud, W.J. Lafferty, High frequency transitions in the rotational spectrum of SO_2, J. Mol. Spectrosc. 191 (1998) 17–27.
[36] L.S. Rothman, I.E. Gordon, Y. Babikov, et al., The HITRAN 2012 molecular spectroscopic database, J. Quant. Spectrosc. Radiat. Transf. 130 (2013) 4–50. <http://hitran.org>.
[37] B. Sumpf, M. Schone, O. Fleischmann, Y. Heiner, H.D. Kronfeldt, Quantum number and temperature dependence of foreign gas-broadening coefficients in the nu(1) and nu(3) bands of SO_2: collisions with H-2, Air, He, Ne, Ar, Kr, and Xe, J. Mol. Spectrosc. 183 (1997) 61–71.