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Collisional broadening and shifting of OCS rotational spectrum lines

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ABSTRACT

Broadening and shifting of carbonyl sulfide (OCS) rotational spectrum lines by pressure of N₂, O₂ and OCS were accurately studied in the frequency range 24–850 GHz at room temperature using a spectrometer with radio-acoustic detection of absorption. Rotational dependences of collisional widths of OCS spectrum lines were determined by a simple empirical polynomial fit of experimental data. Experimental uncertainties were analyzed. Results of supplementary test measurements of self-broadening of rotational OCS lines in the ν_2 excited vibrational state and carbon monoxide (CO) lines in the ground vibrational state are presented. Comparison of the obtained results with previously known measurements and theoretical calculations is given. The performed work allows for the first time development of accurate gaseous etalon of absorption for atmospheric applications and laboratory use, covering continuously the whole millimeter- and submillimeter-wave range.

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1. Introduction

Carbonyl sulfide (OCS) is an important laboratory, environmental and astrophysical molecule. The relatively strong dipole moment (0.715 D) and the quite dense rotational spectrum (12-GHz line spacing) make the molecule one of the most attractive objects in laboratory test measurements. OCS is one of the principal and most long-lived reservoirs of sulfur in the Earth's atmosphere [1] and has also been detected in different astrophysical objects (planets [2], molecular clouds [3], comets [4,5] and starburst galaxies [6,7]). The study of planetary atmospheres provides important information for understanding the origin, evolution, and more generally the formation processes of the Solar System planets. Volcanism (one of the Earth's OCS sources) and strong convection may suddenly induce disequilibrium leading to the presence of unexpected atmospheric components. Significant progress in study of such processes can be made by quantitative analysis of the trace atmospheric constituents. These measurements usually utilize molecular rotational lines or ro-vibrational bands [8] located in millimeter (MM), submillimeter (SubMM) and infrared (IR) spectral regions. Thus, accurate OCS line positions, intensities and pressure broadening and shifting coefficients are essential data for remote sensing and astrophysical needs as well as for laboratory calibration purposes. Any precise experimental information on collisional parameters of molecular spectral lines is also very much required for the development and improvement of the calculation of the intermolecular interaction potential by quantum chemistry methods.

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At the present time there are many databases compiling experimentally measured and/or theoretically calculated molecular line spectroscopic parameters. The most popular and commonly used are HITRAN [9], GEISA [10], JPL [11] and the more specialized MASTER [12] databases. However, due to the absence of necessary information, it is not uncommon for databases that spectroscopic information obtained for lines of some vibrational band is attributed to corresponding lines of other bands. For example, the air-broadening coefficients of OCS lines of all excited vibrational states tabulated in the HITRAN and the GEISA databases are based on the ν_1 band measurements performed in 1985 [13] and 1987 [14], while for all ground state lines one aggregate parameter is quoted. In addition, spectroscopic information contained in databases is still incomplete, e.g., line pressure shift and mixing parameters are often missing. This is likely caused by the lack of measurements and theoretical calculations or their inconsistencies. Thus, new accurate experimental data permit spectroscopic databases improvement.

OCS is a classical linear triatomic molecule. In addition to its simple structure and rigidity and consequently very clear regular spectrum the molecule is very useful from a spectroscopic point of view. Therefore it has been vigorously studied by many researchers. Precise laboratory measurements of OCS rotational line positions in MM–SubMM range were recently carried out by Lamb-dip, conventional line absorption and acoustic detection techniques [15]. The obtained experimental data were fit together with all previously known data that improved the accuracy of $^{16}\text{O}^{12}\text{C}^{32}\text{S}$ rotational constants in the ground vibrational state by one or two orders of magnitude in comparison with previously known ones. The achieved accuracy of the center frequency constitutes from tens of Hertz up to a few kilohertz for OCS lines with rotational quantum number J up to 92. Such precision is satisfactory for most of the aforementioned modern needs and allows using OCS lines as natural accurate frequency markers even in most demanding astrophysical applications.

Line intensity is still one of the most difficult parameters to measure due to various experimental uncertainties (radiation path length, apparatus baseline, etc.). At the same time it is the most crucial parameter for quantitative interpretation of planetary atmosphere and interstellar remote sensing data. Molecular line intensities can be calculated using the dipole moment μ and total internal partition sum Q_{tot} . Investigations of the dipole moment of $^{16}\text{O}^{12}\text{C}^{32}\text{S}$ in the ground vibrational state were performed by different techniques. Stark spectrometer measurements [16–18] were refined later by the molecular-beam electric-resonance method [19–21] that finally resulted in the value of $\mu_{\text{OCS}} = 0.71519(3)$ D [21]. Total partition sums for various molecules (including OCS) were calculated and are very well known (see, e.g., [22,23] and references therein). Thus, line intensities for OCS rotational transitions are supposed to be known with high accuracy and tabulated in spectroscopic databases. However, some casual systematic uncertainties in line intensities of some molecules in the JPL and HITRAN catalogs were pointed out in Ref. [12]. The JPL line intensities were generated without considering the vibrational contribution Q_{vib} to the total partition function. For the OCS molecule Q_{vib} is about 1.2 at 300 K [23]. The HITRAN intensities for the OCS rotational lines were adopted from the JPL. Thus, in both databases line intensities of the OCS transitions were overestimated by $\sim 20\%$. Corrected values are quoted in the MASTER database [12] and these are in good agreement with measurements by modern terahertz spectroscopy methods (averaged discrepancy is $\sim 0.7\%$, while averaged experimental uncertainty is $\sim 3.5\%$) [24]. However, line intensities itself are insufficient for quantitative analysis of observed spectra. For many practical applications the absorption coefficients at line center frequencies are more important. For their determination, the line pressure-broadening parameters are necessary in addition to the line intensity.

Collisional broadening and shifting parameters of the OCS rotational lines have been studied very little. In fact, the only systematic measurement of OCS line widths in the MM- and SubMM-wave range was recently performed using a conventional terahertz video spectrometer with two Ti:sapphire lasers mixed in GaAs photomixer [24]. Self pressure-broadening parameters were measured for a number of pure rotational transitions with J ranging from 10 to 90 with average accuracy of about 4.5% [24]. Self-broadening parameters of some individual OCS transitions with $J \leq 15$ were also measured by a number of authors (see, e.g., Table 1 from work of Dooze et al. [25] and references therein). To our knowledge, very few studies of the N_2 - and O_2 -pressure broadening and shift parameters of OCS lines have been undertaken and those only for the ν_1 [13,14], ν_3 [26] and $2\nu_3$ [27] vibration bands. Self-shift parameters for some of pure rotational OCS lines were analyzed both experimentally [28–30] and theoretically [31] leading to the conclusion that the self-shifting is negligible.

In this paper, we report the first comprehensive room temperature (298 ± 1 K) measurements of OCS-, N_2 - and O_2 -pressure broadening and shifting parameters of the $^{16}\text{O}^{12}\text{C}^{32}\text{S}$ pure rotational lines with J ranging from 1 up to 69 using a spectrometer with radio-acoustic detection of absorption (RAD spectrometer [32]). Nitrogen and oxygen were chosen as the most abundant atmospheric constituents. Measured pressure-broadening parameters determined a smooth regular dependence of line broadening on rotational quantum number. The combination of this dependence with known accurate centers and intensities allowed usage of OCS as an etalon of absolute absorption in MM and SubMM range. The experiment accuracy was verified by control measurements of the well-studied CO rotational lines within the frequency range of the investigation. The rigorous supplementary study of the self-broadening parameters of rotational transitions in the ν_2 excited vibrational state was carried out to check for possible systematic errors. The obtained parameters are compared with previously known data.

2. Experiment

The block-scheme and detailed description of modern version of the spectrometer can be found, e.g., in Ref. [33] and references therein. The operating frequency range of 24–850 GHz was covered by a series of backward-wave oscillators

(BWO) (“Istok”, Russia, <http://www.istok-mw.ru>) phase locked against harmonic of reference synthesizer of either 8–18 or 78–118 GHz range (“Kvarz”, Russia, <http://www.kvarz.com>). The synthesizer output was synchronized with rubidium frequency standard signal (5 MHz, $\Delta f/f = 10^{-11}$) and controlled by computer. Doubler (“Kvarz”, model 7006) of the 8–18 GHz synthesizer frequency was used to observe the R(1) transition at 24 GHz. The absorption gas cell (0.5–10 cm variable length, 2 cm in diameter) was coupled with a highly sensitive membrane microphone converting the acoustic wave into electrical signal. The cell was permanently connected to a vacuum system as well as vacuum pumps, gas samples and MKS Baratron pressure gauge (Type 627-B of 10-Torr range) with a declared accuracy of 0.12%.

Prior to each experiment, the cell was evacuated to a pressure of about 10^{-4} Torr. The choice of the OCS pressure in the cell was a result of a compromise between sufficient signal-to-noise ratio (SNR) of the observed line and minimal distortion of its shape by neighboring lines. The intensity of the studied lines varied by about three orders of magnitude (having a maximum near $J = 38$ at room temperature). Taking that into consideration, the maximal OCS pressure in the self-broadening experiments was varied from 3–4 Torr for more isolated high J lines down to 1.2–1.5 Torr for low J lines distorted by the v_2 state rotational transitions. On the contrary, in the foreign-gas broadening measurements the partial pressure of OCS in a mixture was varied from 0.02–0.03 Torr for the strong lines to about 0.6 Torr for the weaker lines to compensate the intensity reduction. Maximal total pressure of the mixture was the same as the aforementioned OCS pressure in the self-broadening measurements.

The measurement procedure was as follows. For the self-broadening study, the cell was filled by OCS up to the maximum pressure and the spectral line was recorded. Then the cell was stepwise evacuated and the line record was repeated at 8–10 pressures. The foreign-broadening experiment started with the low OCS partial pressure and then quantities of the perturber gas were added stepwise. At each step, the spectral line was recorded after equilibrium gas conditions were achieved. Each line record was repeated a few times to estimate statistical uncertainty of the measurement.

The BWO radiation beam was chopped at 180 Hz and the output signal from the RAD cell was demodulated by digital lock-in amplifier in 1-f mode. True absorption line shape was recorded via step-by-step frequency scan of the reference synthesizer. An example of the experimental spectrum nearby the R(1) transition of OCS is presented by points in Fig. 1. Two weak lines correspond to l -doublet of the same rotational transition in the thermally populated v_2 degenerate vibrational state.

An acoustic detection signal from spectral line is proportional to $I_0(1 - \exp(-\alpha L))$, where I_0 is an incident radiation power, α is the gas absorption coefficient and L is the optical path length, which coincides with geometrical length of absorption cell L_0 in the case of one passage of radiation through the cell. Such expression of the signal assumes that the width of the spectrometer spectral function (< 10 kHz) is negligible in comparison to the line width, which is true for our experiment. In the case of small optical depth $\alpha L \ll 1$, the signal expression can be simplified to $I_0 \alpha L$. We used the Lorentz and Voigt profiles for the line absorption coefficient $\alpha(\nu - \nu_0)$, where $(\nu - \nu_0)$ is the radiation frequency detuning relatively the line center ν_0 . At our conditions Doppler broadening constituted a very minor part of observed line width allowing use of the Lorentz profile for analysis of most records. However, at lowest experimental pressures and especially for high J lines the Doppler part became quite essential, forcing us to employ the Voigt profile. The RAD spectrometer baseline (frequency dependence of I_0 , radiation absorption in the cell windows, etc.) was taken into account by including multiplicative and additive constant- and linear-with-frequency terms into the model function describing the spectrometer output signal [33]. Collisional line width and line center were determined from the least-squares fit of the model function to experimental line

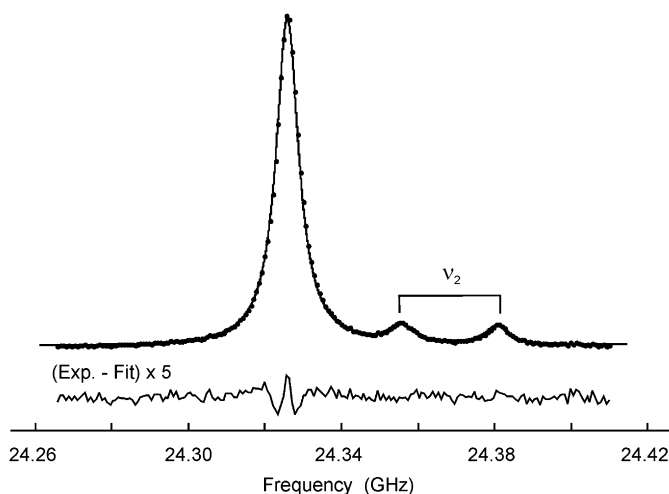


Fig. 1. Experimental record of the $^{16}\text{O}^{12}\text{C}^{32}\text{S}$ spectrum in the vicinity of R(1) transition at 0.6 Torr of pure OCS (points) and a result of its treatment by the model function (solid line). Residuals of the fit are displayed underneath on a $5 \times$ magnified scale.

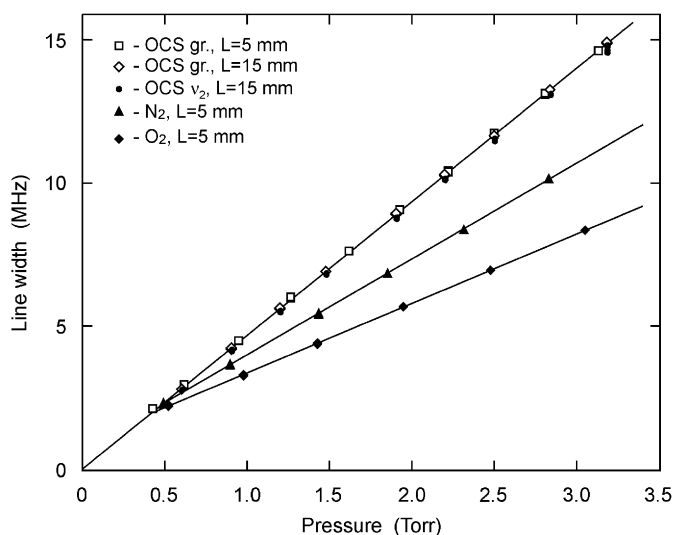


Fig. 2. Experimental pressure dependence of line width for the R(58) transitions at different cell lengths L_0 and perturbing molecules. Open squares and diamonds correspond to self-broadening of the ground state line measured at 5 and 15 mm cell lengths, respectively; self-broadening of the v_2 state doublet lines are shown by points; N_2 - and O_2 -broadenings are shown by filled triangles and diamonds, respectively. Solid lines are results of the linear regression of the experimental points. The only solid line for the self-broadening dependences is shown for clarity of the figure. It corresponds to the ground state line data measured at $L_0 = 15$ mm.

shape. Fixed calculated Doppler width was used in case of Voigt profile fittings. Values of the line shifting and broadening parameters were determined from a linear regression of observed widths and centers of the line at various pressures. An example of the line shape fit result is shown in Fig. 1 by solid line. The residual of the fit is presented in the lower part of the figure. Minor systematical deviations near the line center are observed constituting to about $\pm 1\%$ from the line amplitude. The nature of the deviations is unknown. They could not be reduced by variation of Gaussian component of the line shape. Typical SNR for the majority of the studied lines constituted 500–1500 providing good statistical accuracy of measurements. Test measurements of some well isolated l -doublets in the v_2 state with high J revealed similar collisional widths of the doublet lines. Therefore, in the fit procedure we used the same adjustable width parameter for both lines of the doublet but different from that for the neighboring ground state line.

A peak absorption coefficient $\alpha_0 = \alpha(0)$ for the OCS rotational transitions estimated using the MASTER database achieves $\sim 0.1 \text{ cm}^{-1}$ around $J = 40$. This means that the general expression of the model function considering the exponential dependence of the spectrometer signal on absorption coefficient should be used in the fit procedure. This leads to certain complications because of correlation between fitted parameters I_0 , L and line half width $\Delta\nu$ and increases the error of the line width determination. To minimize the error, a short cell length $L_0 = 0.5 \text{ cm}$ was used for the self-broadening measurements of the strongest OCS lines. To get higher SNR for weaker lines L_0 was enlarged up to 10 cm, keeping the value of optical depth $\alpha_0 L_0 \ll 10^{-2}$. The calculated optical depth was fixed in the line profile fit. Some lines were repeatedly studied varying the gas cell length. Coincidence within 1% of the self-broadening coefficients obtained even for essentially different cell lengths proves the consistency of our measurements. For the foreign-broadening measurements, the uncertainty related to the large optical depth is negligible due to strong dilution of the absorbing gas in a mixture, leading to essential decrease of a line-peak absorption coefficient α_0 , so the simplified expression of the model function could be used.

The self-broadening of the $^{16}\text{O}^{12}\text{C}^{32}\text{S}$ v_2 state pure rotational lines was studied for verification of the ground state measurements. This is justified because of the dominating contribution of molecular rotational relaxation to the line pressure broadening in comparison with the vibrational one, which was shown for other molecules (see, e.g., Ref. [34] and references therein). Thus, broadening data corresponding to the same rotational but different (at least first excited) vibrational state should be very similar. Moreover, the v_2 state lines are more than an order of magnitude weaker than those in the ground state, which allows using a simple expression of the model function thus excluding systematic errors related to large optical depth.

Fig. 2 shows a typical example of measured line width dependences versus total gas pressure for all studied perturbing molecules together with the result of their linear regressions. Results of the aforementioned test measurements of the same rotational transition in the v_2 state as well as measurements with a short length gas cell are also shown. Experimental points $1-\sigma$ error bars are less than symbol size. It is worth pointing out the practically perfect linearity of the experimental dependences, zero intercept of the self-broadening and consistency of the test measurements. Positions of the line center frequency corresponding to the self-pressure broadening experiment are shown in Fig. 3. This is a typical example of a line center versus gas pressure dependence for studied OCS transitions. One can see that no pressure-induced frequency shift is evident.

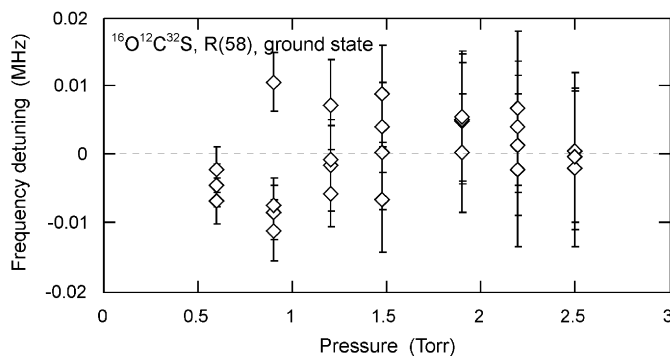


Fig. 3. The R(58) line center frequencies measured at different OCS pressures. Zero frequency corresponds to average over all experimental points value of 716546.542(5) MHz.

Table 1

Measured pressure-broadening parameters of the $^{16}\text{O}^{12}\text{C}^{32}\text{S}$ transitions in the ground and ν_2 vibrational state at 298 K for OCS, N_2 and O_2 perturbing molecules

Transition	Pressure broadening (MHz/Torr)			
	OCS		N_2	O_2
	Ground	ν_2		
R(1)	5.810(50)	5.795(200)	–	–
R(2)	5.930(35)	5.970(100)	4.255(20)	3.775(25)
R(3)	5.970(20)	5.815(170)	4.210(20)	3.740(20)
R(4)	6.075(20)	5.995(80)	4.215(20)	3.705(15)
R(6)	6.190(40)	6.190(100)	4.120(25)	3.650(25)
R(8)	6.330(50)	6.380(50)	4.090(25)	3.610(20)
R(10)	6.420(50)	6.390(60)	4.060(20)	3.570(15)
R(12)	6.500(25)	6.520(50)	4.020(15)	3.530(20)
R(13)	6.550(20)	6.540(45)	4.010(15)	3.510(15)
R(14)	6.605(15)	6.590(30)	3.990(20)	3.455(15)
R(15)	6.650(20)	6.650(35)	3.960(20)	3.445(15)
R(16)	6.675(20)	6.690(35)	3.930(20)	3.405(15)
R(19)	6.740(25)	6.730(50)	3.820(15)	3.330(15)
R(22)	6.780(20)	6.740(35)	3.760(15)	3.299(15)
R(25)	6.720(20)	6.700(20)	3.710(20)	3.230(15)
R(28)	6.655(35)	6.600(20)	3.655(20)	3.190(15)
R(32)	6.510(20)	6.415(50)	3.605(15)	3.125(15)
R(35)	6.290(25)	6.200(45)	3.560(20)	3.085(15)
R(38)	6.070(35)	5.980(50)	3.520(20)	3.050(15)
R(43)	5.710(15)	5.620(50)	3.475(25)	3.010(15)
R(48)	5.280(20)	5.200(30)	3.425(20)	2.945(20)
R(55)	4.810(20)	4.800(90)	3.370(25)	2.880(30)
R(58)	4.640(25)	4.615(35)	3.345(30)	2.855(25)
R(62)	4.430(25)	4.405(60)	3.335(25)	2.845(25)
R(66)	4.275(25)	4.195(50)	3.300(25)	2.810(25)
R(69)	4.165(20)	4.120(90)	3.280(30)	2.785(30)

Numbers in parenthesis after parameter values are $1-\sigma$ statistical uncertainties.

3. Results and discussions

3.1. Pressure-broadening parameters

Pressure-broadening coefficients measured in this work are collected in Table 1 and shown in Fig. 4 for the self-broadening for both studied ground and ν_2 vibrational states and in Fig. 5 for the foreign-broadening as a function of absolute value of quantum number m ($m = -j$ for P-branch and $m = j+1$ for R-branch). Previous measurements in MM/SubMM [24] and IR [26,35] ranges are also presented in the figures for comparison.

First of all, it is worth noting that our $1-\sigma$ statistical uncertainties of measured pressure-broadening parameters quoted in Table 1 constitute on average 0.5% of the parameter value for the ground state lines and about 1% for the ν_2 state lines. Moreover, the smooth dependence of the experimental points on m confirms a high statistical accuracy of the parameters

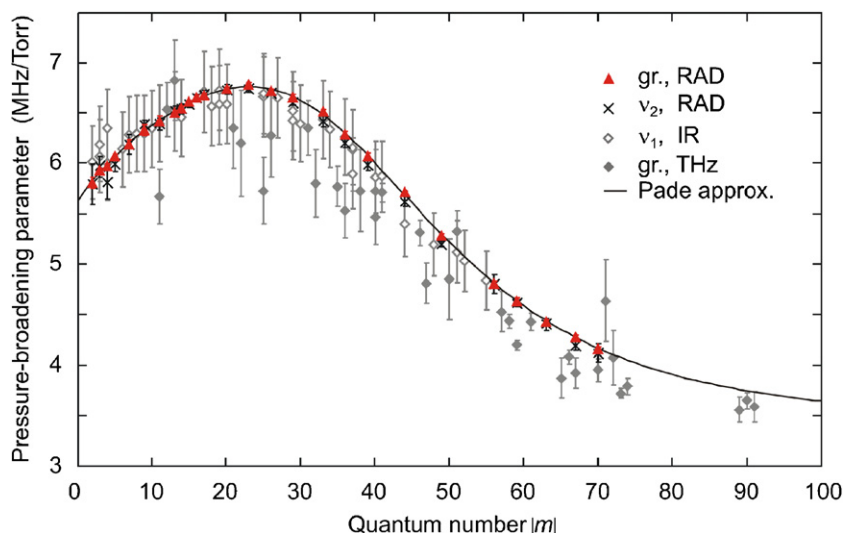


Fig. 4. Room temperature self-broadening parameters of OCS transitions. Filled triangles and crosses are results of our measurements for the ground and v_2 states, respectively; infrared data for the v_1 ro-vibrational band [35] are shown by open diamonds; ground state transitions measurements by conventional terahertz video spectrometer [24] are shown by filled diamonds. $1-\sigma$ uncertainty bars of our ground state data are less than the symbol size. Solid line is a result of the 4,4-Padé approximation of our data for the ground vibrational state.

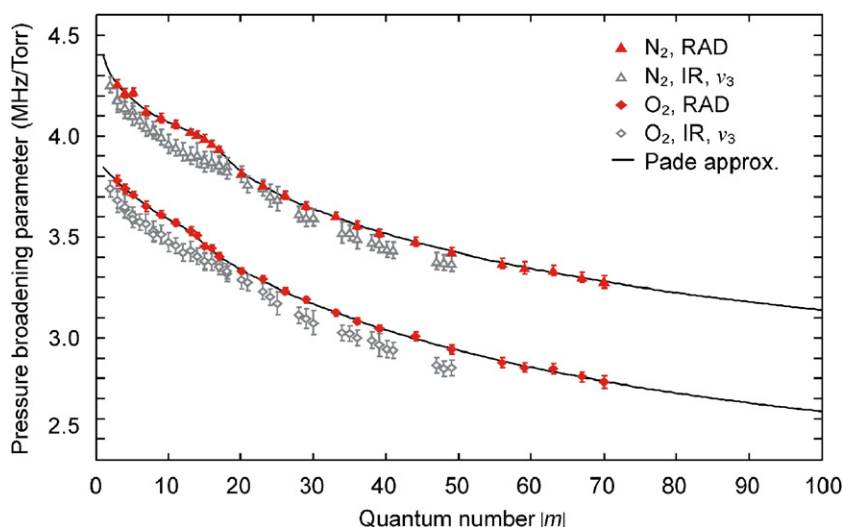


Fig. 5. Measured N_2 - (triangles) and O_2 - (diamonds) pressure broadening parameters of OCS lines. Filled symbols correspond to the ground state measurements by RAD spectrometer and open ones are IR data [26] for the v_3 band lines. Solid lines are results of the 4,4-Padé approximation of our data.

measured. Coincidence within experimental uncertainties of the self-broadening parameters for the ground and v_2 states proves minimization of systematic errors related to large optical depth. The obtained self-broadening parameters are in reasonable agreement with previous measurements of the ground state rotational lines by conventional terahertz video spectrometer [24] and reveal even better conformity with IR data for the v_1 ro-vibrational band [35]. Some previous measurements of the self-broadening parameters in MM-wave range [25,29,36] are not shown in Fig. 4 for the figure clarity. These data, together with our results, are collected in Table 2. One can see good general agreement of the presented parameters, taking into account quite large discrepancy between the data obtained by different authors for the same transition.

Broadening parameters of the OCS rotational spectrum lines by pressure of nitrogen and oxygen were measured for the first time. These data are shown in Fig. 5 together with corresponding v_3 ro-vibrational band data [26]. Comparison of the latter with other ro-vibrational bands data from works [13,14,27] can be found in Fig. 8 of work [26]. It is evident from Fig. 5

Table 2Measured self-broadening parameters of MM-range $^{16}\text{O}^{12}\text{C}^{32}\text{S}$ transitions in comparison with previously known data

Transition	Self-broadening (MHz/Torr)	Reference ^a
R(0)	5.728^b 5.97(1) 6.11(2) 5.52(15) 6.05(8)	Present study [25] (6) [25] (6) [25] (7) [25] (2)
R(1)	5.810(50) 5.795(200)^c 5.97(1) 5.89(1) 5.68(3) 5.92(3)	Present study Present study [25] (6) [25] (8) [25] (7) [25] (4)
R(2)	5.930(35) 5.970(100)^c 5.85(4) 5.80(11) 5.78(4) 5.96(3)	Present study Present study [25] (7) [25] (3) [25] (5) [29]
R(3)	5.970(20) 5.815(170)^c 5.98(6)	Present study Present study [25] (7)
R(6)	6.190(40) 6.190(100)^c 6.54(13)	Present study Present study [25]
R(7)	6.259^b 6.04(2)	Present study [25] (9)
R(8)	6.330(50) 6.380(50)^c 6.022(54)	Present study Present study [37]
R(11)	6.474^b 6.29(2)	Present study [25] (9)
R(15)	6.650(20) 6.650(35)^c 6.53(2)	Present study Present study [25] (9)

^a The table is based mainly on Table 1 from Ref. [25], so we decided not to extend our reference list but quoted in round parenthesis reference numbers from work [25] to distinguish between different authors.

^b Parameter obtained by the approximation of measured data (see text for details).

^c Parameter for the ν_2 vibrational state transition.

that two data sets are very close to each other both qualitatively and quantitatively. However, systematically lower values of the ν_3 data require some consideration because additional vibrational dephasing in the ν_3 state might contribute so lines should be equal or broader than in the ground state. Slightly lower values of the ν_3 state lines could appear as the result of not quite adequate line shape function used in [26], which we are going to consider and publish elsewhere. In any case, the high accuracy of both experiments reveals something else than just constant shift between the ground state and ν_3 data, which could be caused by the influence of molecular vibration on collisional relaxation mechanisms (e.g., vibrational energy transfer at the collision) [37].

As it was mentioned before, the HITRAN database [9] quotes the same value of 5.917 MHz/Torr for self-broadening and 2.761 MHz/Torr for air-broadening parameters of all pure rotational lines. Therefore, use of these data may lead up to 40% systematic error in pure gas measurements and 15–50% in air, indicating the necessity of the database upgrade.

Precise experimental information on pressure broadening of the OCS lines obtained in the present study is of interest for various spectroscopic applications, in particular for the Earth atmosphere remote sensing. Since not all transitions of the spectrum were studied, we followed Yamada et al. [38] and used a 4,4-Padé approximant as an empirical approach to

Table 3Fitted coefficients of the 4,4-Padé approximant for the OCS-, N₂- and O₂-broadening coefficients of the OCS rotational spectrum lines

Coefficient	Self-broadening	N ₂ -broadening	O ₂ -broadening
a_0	0.562533×10^1	0.677672×10^1	0.397370×10^1
a_1	0.447213	0.116867×10^3	0.300955×10^2
a_2	-0.407071×10^{-2}	-0.127406×10^2	-0.426736×10^1
a_3	0	0.290458	0.135284
a_4	0.244296×10^{-5}	0.687716×10^{-2}	0.203762×10^{-2}
b_1	0.602075×10^{-1}	0.270933×10^2	0.778203×10^1
b_2	-0.848500×10^{-3}	-0.271714×10^1	-0.102652×10^1
b_3	0	0.378000×10^{-1}	0.232901
b_4	0.712611×10^{-6}	0.260643×10^{-2}	0.997450×10^{-3}

obtain m -dependences of broadening parameters for all perturbers:

$$\gamma(m) = \frac{\sum_{i=0}^4 a_i m^i}{1 + \sum_{i=1}^4 b_i m^i} \quad (1)$$

where γ is pressure-broadening parameter, a_i and b_i are adjustable coefficients.

Strong correlation between a_i and b_i parameters and possible singularities of the rational function (1) are Padé approximant drawbacks pointed out in Ref. [38]. A good starting set of parameters was derived from the fit of the artificial data produced by interpolation of each five adjacent points using quadratic functions, as suggested in Ref. [38]. Results of the final fit of the rational function (1) to our broadening data are shown by solid lines in Figs. 4 and 5 for self- and foreign-broadening, respectively. Adjustable coefficients obtained from the fit are collected in Table 3. The mean discrepancy between our results and the fitting curve is only 0.1–0.2% for all three dependences that is essentially different from the results of Ref. [24] where this value is $\sim 7\%$ rising up to 10% for a few transitions.

Of course, the obtained set of parameters should be used mostly as a good interpolation between measured data. The extrapolating ability of this approach is weak, giving however, much better results in comparison with frequently employed power series, tending to infinity at $|m| \rightarrow \infty$. On the contrary, the Padé approximant gives finite value equal to a_4/b_4 that gives quite reasonable values of 3.428, 2.639 and 2.043 MHz/Torr for the self-, N₂- and O₂-pressure broadenings, respectively.

3.2. Pressure-shift parameters

Our study did not reveal any noticeable center frequency shift of the OCS pure rotational spectral lines due to collisions with OCS, N₂ and O₂ molecules but set the upper limit for the value of this effect constituting ± 15 kHz/Torr for all lines. This result agrees well with previous measurements [28–30] in the MM range and theoretical calculations [31]. The observed line center positions coincide within experimental accuracy (5–20 kHz) with the recent precise Lamb-dip measurements [15] that proves consistency of our data.

3.3. Data accuracy

The standard deviation of the parameter obtained from the least-squares fit is usually used as an estimation of the experimental uncertainty. However, it does not account for most of the systematic errors and this explains that very often the value of the same parameters measured by different authors differs much more than even summed $3-\sigma$ uncertainties given by these authors (see, e.g., Table 2). Only cross test measurements and comparison of results obtained by use of different techniques can reveal real experimental accuracy.

In the present study the main source of systematic error, in our opinion, is related to the gas cell optical depth and the most sensitive parameter is self-broadening. Despite minimization of this effect by using the short cell and general exponential expression of the model function, the error could arise from both the calculated intensity uncertainty and uncertainty in the cell length. In practice, uncontrolled interference pattern of MM-SubMM radiation beam and unavoidable reflections of radiation from a rear cell window and/or from other elements of spectrometer lead to an increase of the effective optical path length compare to geometrical cell length L_0 . Although this effect is relatively small, it must be taken into consideration for precise measurements. Our estimations showed that use of the exponential model function with the optical depth differing from the real one by 10% leads to systematic change up to $\sim 0.1\%$ for the self-broadening of the strongest OCS lines at the conditions of our experiment ($\gamma_0 L_0 \leq 0.06$). This value is comparable with the statistical accuracy of our experiments and the $3-\sigma$ statistical uncertainty appears to be a realistic estimation of the actual experimental error for the obtained broadening parameters.

Table 4

Measured central frequencies and self-broadening parameters of the MM-SubMM lines of CO together with precision data from work [39] and HITRAN

Transition	Central frequency (MHz)		Self-broadening (MHz/Torr)	
	Present study	Calculated in [39]	Present study	HITRAN
R(0)	115271.200 (5)	115271.20202 (6)	3.475(15)	3.408
R(1)	230537.996 (8)	230537.99996 (11)	3.280(15)	3.239
R(2)	345795.987 (5)	345795.98985 (16)	3.130(10)	3.097
R(3)	461040.764 (15)	461040.76798 (21)	2.990(25)	2.970
R(4)	576267.935 (10)	576267.93101 (25)	2.870(10)	2.868
R(5)	691473.085 (50)	691473.07609 (29)	2.780(30)	2.777
R(6)	806651.842 (40)	806651.80100 (30)	2.710(20)	2.702

To test the accuracy of our measurements, well-studied carbon monoxide ($^{12}\text{C}^{16}\text{O}$) molecular lines in the ground vibrational state were used as a secondary calibration standard for both pressure shift and pressure broadening, throughout the entire spectral range studied. Central frequencies and self-broadening parameters measured in our work in comparison with corresponding Lamb-dip measurements data [39] and with the HITRAN data are given in Table 4. The study did not reveal any CO line frequency pressure shifting within experimental accuracy. Measured centers coincide quite well with data from Ref. [39]. The studied CO lines are practically as intense as the OCS lines, so we used the same data treatment method for both molecules. An excellent agreement of measured CO lines self-broadening parameters with those from the HITRAN database proves consistency and high accuracy of our results for the OCS transitions.

Finally, coincidence of measured self-broadening parameters for two different vibrational states and their agreement with previous measurements proves that the systematic errors in our experiment are minimized.

3.4. Etalon of absorption

In closing of the discussion section we would like to point out that our work opens the possibility for development of a first gaseous etalon of absorption entirely covering MM- and SubMM-wave ranges. The value of the etalon absorption can vary from 10^{-1} to 10^{-2} cm^{-1} in the case of pure OCS, down to much smaller values corresponding to dilution of OCS by nitrogen. It should be recalled that nitrogen does not have absorption lines in MM–SubMM range. Of course, development of the rigorous OCS absorption model for any arbitrary pressure and temperature goes far beyond the present work bounds. Problems of adequate line profile, effect of line mixing, temperature dependences of collisional parameters, collision induced absorption, etc. should be solved in the course of the model development. However, even simplified absorption modeling in form of line-by-line sum of Lorentz profiles is worthy for practical applications such as quantitative analysis of gas mixtures, atmosphere monitoring, laboratory equipment calibrations, etc. The OCS rotational spectrum in the ground and lowest vibrational states for the most abundant isotopologues was studied well enough to predict positions of spectral lines [40–43]. Intensities of the $^{16}\text{O}^{12}\text{C}^{32}\text{S}$ ground state transitions are known [12]. Intensities of all other contributing spectral species can be scaled down from the ground state using isotope abundances and Boltzmann factor for population of vibrational states. It is known from studies of other molecules that change of isotopic composition as well as vibrational state does not significantly affect collisional broadening of corresponding lines [34,44]. Thus, broadening parameters measured in our work can be used for the calculation of total absorption of the OCS rotational spectrum either in pure gas or in a mixture with nitrogen and oxygen within a broad pressure range. An example of such calculation for pure OCS at 760 Torr and 298 K is presented in Fig. 6. For the calculation, we just summed contributions of all lines with J ranging from 0 to 100 for the $^{16}\text{O}^{12}\text{C}^{32}\text{S}$, $^{16}\text{O}^{12}\text{C}^{34}\text{S}$, $^{16}\text{O}^{13}\text{C}^{32}\text{S}$, $^{16}\text{O}^{12}\text{C}^{33}\text{S}$ and $^{18}\text{O}^{12}\text{C}^{32}\text{S}$ isotopologues in the ground vibrational state and lines of the $^{16}\text{O}^{12}\text{C}^{32}\text{S}$ isotopologue in the ν_2 vibrational state. To estimate possible inaccuracy of such a model related to extrapolation of the measured broadening data on higher J lines we assumed a smooth increase of the extrapolation error up to $\pm 10\%$ for the R(100) transition. The difference in the total contribution of wings of all lines with J ranging from 70 up to 100 for Fig. 6 conditions in the studied spectral range constituted on average about 0.03% and reached 0.1–0.2% near 850 GHz. Another source of inaccuracy of the model could be uncertainty in rotational constants of the isotopologues and vibrational states. In particular, the lowest ν_2 vibrational state and the second most abundant $^{16}\text{O}^{12}\text{C}^{34}\text{S}$ isotopologue should be considered. Their contribution to the total OCS absorption is about 20% and 4%, respectively. Summary contribution of all other isotopologues and vibrational states is less than 2%. To estimate the corresponding error we assumed that the line centers can be systematically shifted. The possible shift was estimated using information from Ref. [15], where accurate Lamb-dip measurements allowed improvement of the ground state rotational constants (previously known [40] with about the same accuracy as those for the ^{34}S -isotopologue and ν_2 state). Correction of systematical shift in line positions constituted about 200 kHz near 1 THz. We shifted by 1 MHz (increasing 200 kHz by factor of 5) frequencies of all lines of two aforementioned mostly contributing spectral species. This led to the OCS total absorption change within 10^{-3} – $10^{-4}\%$. Therefore, in the spectral range of our study (24–850 GHz), accuracy of the simple OCS spectrum absorption modeling is mainly determined by accuracy of line broadening parameters. To the best of our

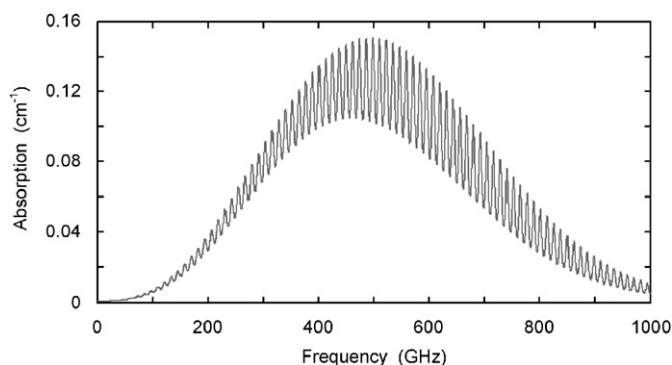


Fig. 6. OCS spectrum absorption at 24° C and 760 Torr, calculated for pure gas and natural isotopic abundances.

knowledge at present time there is no other molecule whose absorption spectrum could be calculated with comparable accuracy and continuously covers this wave range at reasonable pressures.

4. Conclusions

Broadening and shifting of the $^{16}\text{O}^{12}\text{C}^{32}\text{S}$ molecule ground state rotational spectrum lines by pressure of OCS, N_2 and O_2 were studied using the RAD spectrometer, which once again proved to be a very powerful instrument for accurate investigation of collisional parameters of molecular lines in a wide frequency range from tens of gigahertz up to terahertz. The N_2 - and O_2 -broadening and shifting were investigated for the first time. Dependences of the pressure-broadening parameter on the rotational quantum number were determined practically for all observable lines of the spectrum using simple empirical approximation of measured data. The obtained pressure-broadening parameters are in good agreement with previous data for rotational and ro-vibrational lines in MM, SubMM and IR ranges but have considerably higher accuracy. The negligibility of systematic errors of measured broadening parameters was confirmed by a supplementary study of the rotational transitions in the ν_2 excited vibrational state. Our measurements did not reveal any pressure shifting of the OCS lines, which was proved by coincidence of the measured centers with known precise values obtained by the Lamb-dip technique. The accuracy of the measurements was additionally verified by the test measurements of the well-known CO rotational lines within the studied spectral range. Excellent coincidence of the test measurement results with previously known data confirmed the accuracy and consistency of our experiments. The obtained accurate values of pressure-broadening and shifting parameters in combination with known accurate line centers and intensities allow using OCS as etalon of absolute absorption in MM and SubMM regions.

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