

CO₂-broadening and shift coefficients of sulfur dioxide near 4 μm

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ABSTRACT

The absorption spectra of the mixture of SO₂ and CO₂ at different partial pressures of both gases have been recorded at room temperature in the 4 μm region using the Bruker IFS 125 HR FTIR spectrometer. The multispectrum fitting procedure has been applied to these spectra to recover the CO₂-broadening and shift parameters of the sulfur dioxide spectral lines. The CO₂ broadening and the pressure induced shift coefficients for 1422 and 116 lines of the ν₁+ν₃ A-type band of ³²S¹⁶O₂ and ³⁴S¹⁶O₂, respectively, have been derived. Beside, these coefficients have been derived for 254 lines of the ν₁+ν₂+ν₃-ν₂ hot band of ³²S¹⁶O₂. The CO₂ pressure induced shift coefficients for this molecule are published for the first time. Our measured line intensities for the strong lines are 0.8% lower than those from the HITRAN2016 database. Our measured line positions are shifted to the blue side by 0.00008 cm⁻¹ for the principal isotopologue and by 0.00130 cm⁻¹ for the minor isotopologue ³⁴S¹⁶O₂ from the HITRAN2016 values.

EXPERIMENT

The SO₂ absorption spectra in the presence of CO₂ as a buffer gas have been recorded at V.E. Zuev Institute of Atmospheric Optics SB RAS using a Bruker IFS 125 HR high-resolution Fourier transform spectrometer in the 2450-2530 cm⁻¹ region. A sample of natural sulfur dioxide with a stated purity of 99.9% was used without further purification. Because of very low partial pressures of sulfur dioxide their measured values were corrected using the line intensities of the ν₁+ν₃ band taken from HITRAN2016 database [1,2]. For frequency calibration the absorption lines of the water originated from the small amounts of the residual water vapor present in the vacuum tank of the Fourier spectrometer were used. The water line parameters were taken from the HITRAN2016 database [1].

Experimental conditions

SNR ≈ 1500
Absorption path 960 cm
Temperature 295.6 K

#	Aperture diameter mm	Spectral resolution cm ⁻¹	SO ₂ pressure atm	CO ₂ pressure atm
1	1	0.0020	0.00036	0.00748
2	1	0.0020	0.00048	0.01281
3	1	0.0020	0.00068	0.01604
4	1.15	0.0024	0.00087	0.01963
5	1.15	0.0030	0.00084	0.02576
6	1.15	0.0024	0.00101	0.03001
7	1.15	0.0030	0.00116	0.03780
8	1.15	0.0030	0.00113	0.05040

REFERENCES

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LINE PARAMETERS RETRIEVAL

The spectral line parameters were retrieved using the multispectrum fitting procedure in which the nonlinear least-squares method is applied simultaneously to the spectra recorded at different experimental conditions. The spectral line shape was modeled with the Voigt and the quadratic Speed Dependent Voigt (qSDV) [3,4] profiles. Due to a very small SO₂ partial pressure in the used samples the self-broadening coefficients were fixed to the HITRAN values [1] and self pressure induced shifts were neglected in all fits. The Doppler line width was calculated using the standard equation. The apparatus function was modeled with sinc function. The baseline was modeled with a straight line.

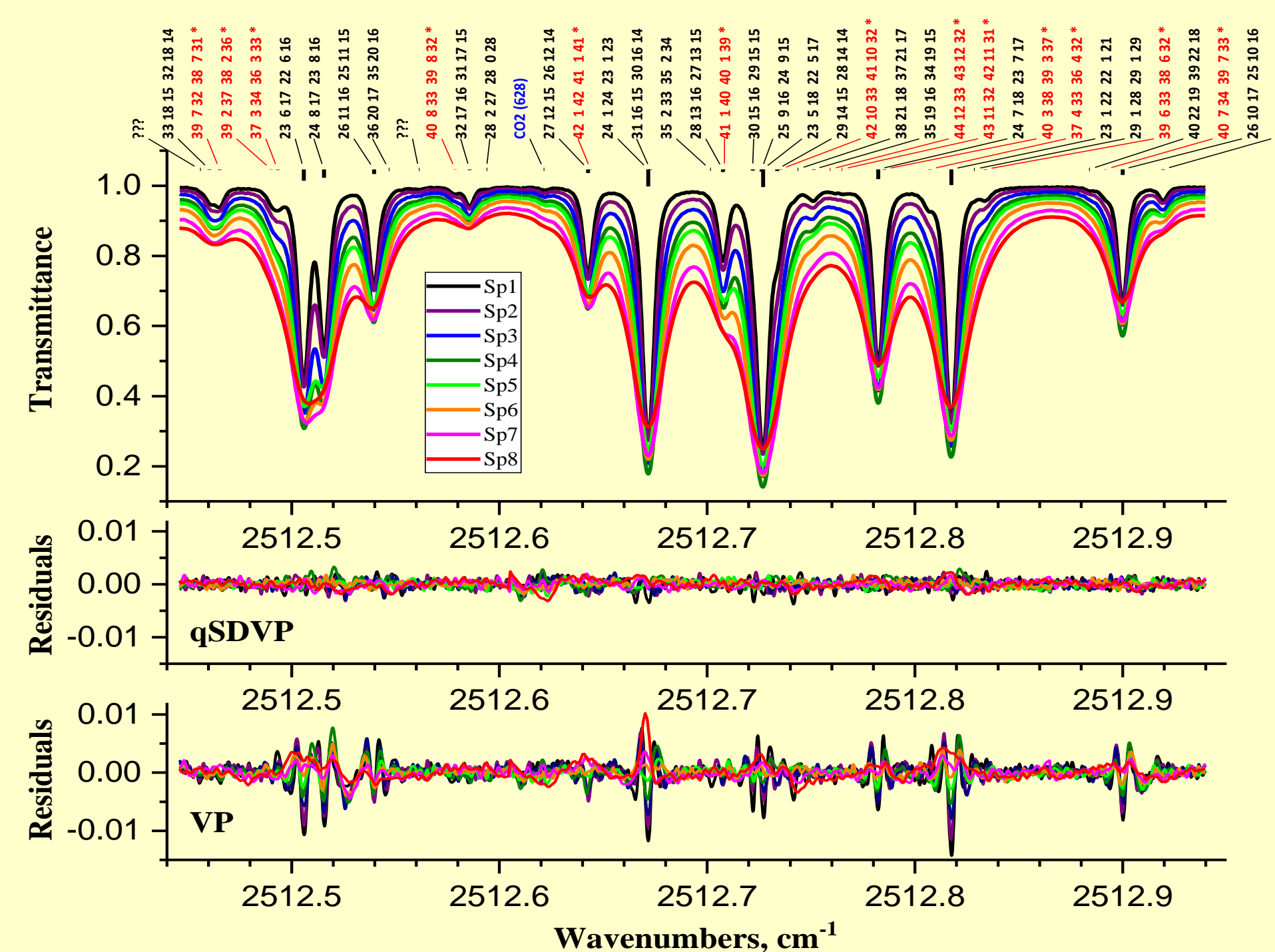


Fig.1. Multispectrum fit of the SO₂ spectra perturbed by the CO₂ pressure in the 2512.44 - 2512.94 cm⁻¹ range. *Transmittance* – the experimental spectra. The spectrum numbers (Sp1, Sp2, ..., Sp8) correspond to the spectrum numbers in the table. The line assignment is also presented. The line labels of the ν₁+ν₃ band of ³²S¹⁶O₂ are given in black and those of the lines of the ν₁+ν₂+ν₃-ν₂ hot band of ³²S¹⁶O₂ are given in red. ??? mark unassigned SO₂ lines. *Lower panels* – the residuals between the experimental spectra and the fitted spectra, respectively, with the quadratic speed dependent Voigt profile (qSDVP) and with the Voigt profile (VP).

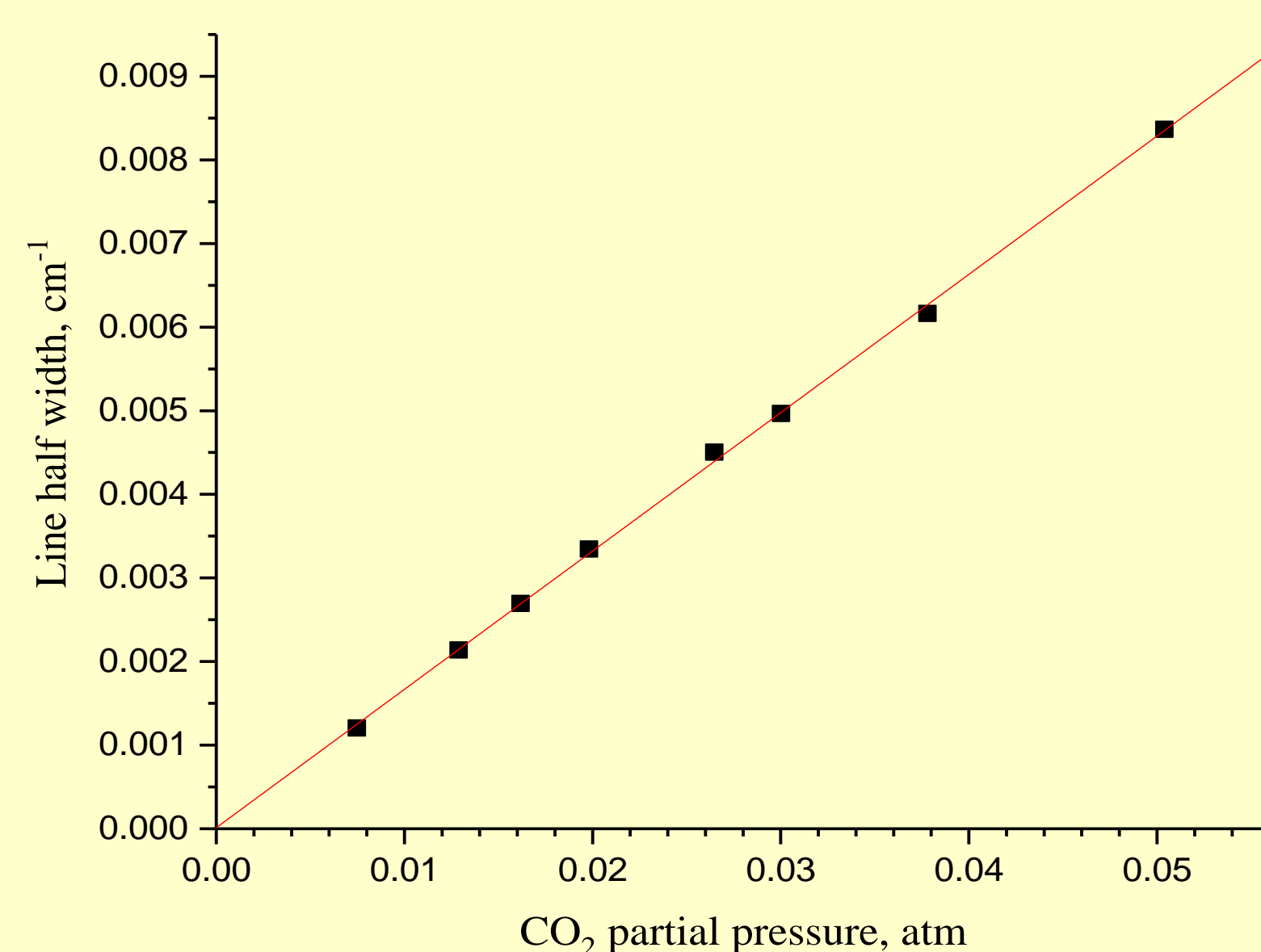


Fig.2. Linear dependence on the carbon dioxide partial pressure of the measured half width of the (26 10 17 ← 25 10 16) line of the ν₁+ν₃ band of ³²S¹⁶O₂ situated at 2512.900 cm⁻¹.

CO₂ PRESSURE INDUCED SHIFT COEFFICIENTS

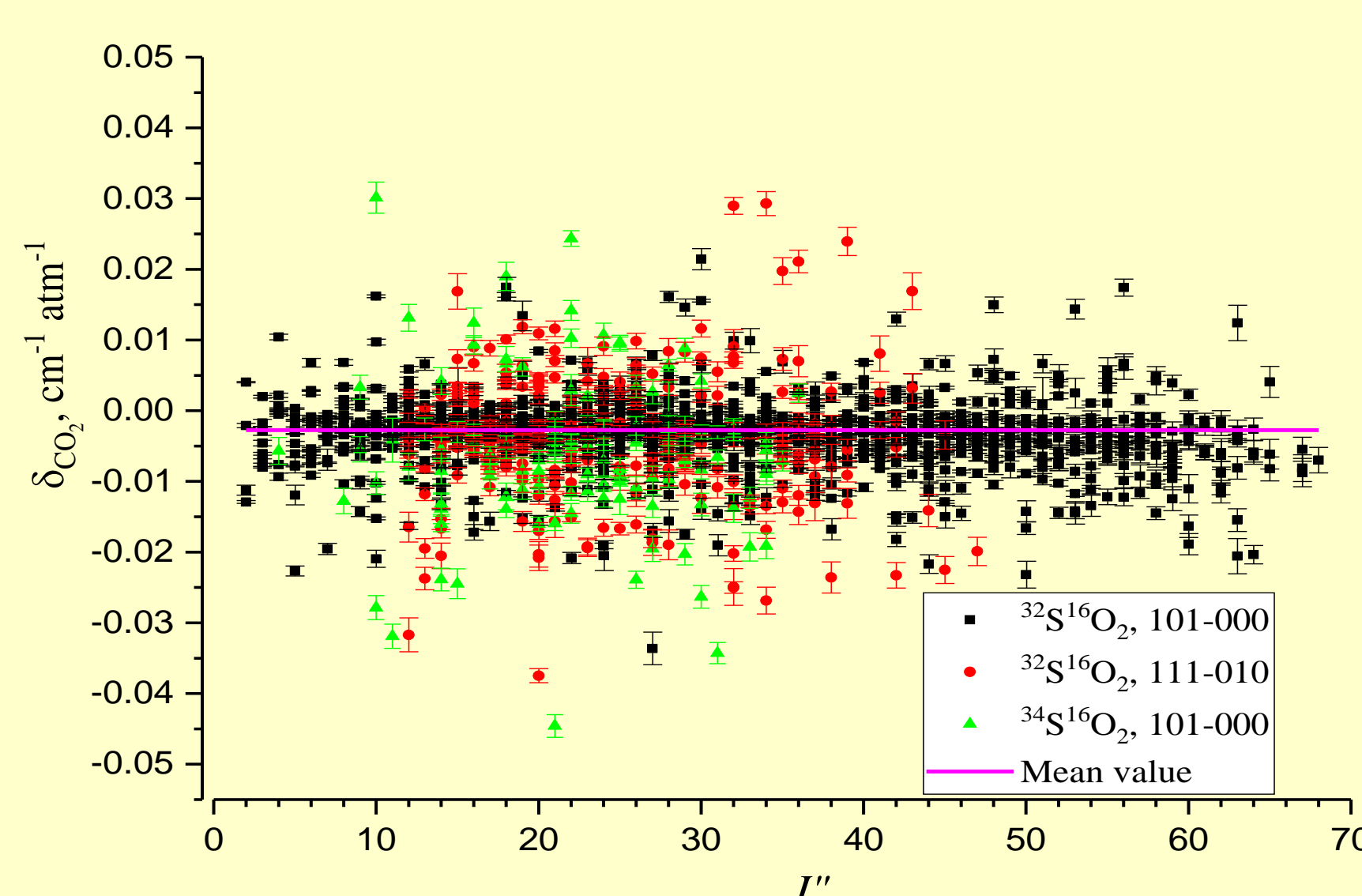


Fig.7. CO₂ pressure induced shift coefficients of the sulfur dioxide in the 4 μm region versus the rotational quantum number. The mean value of the shift coefficients is -0.0027 cm⁻¹ atm⁻¹.

CO₂-BROADENING COEFFICIENTS

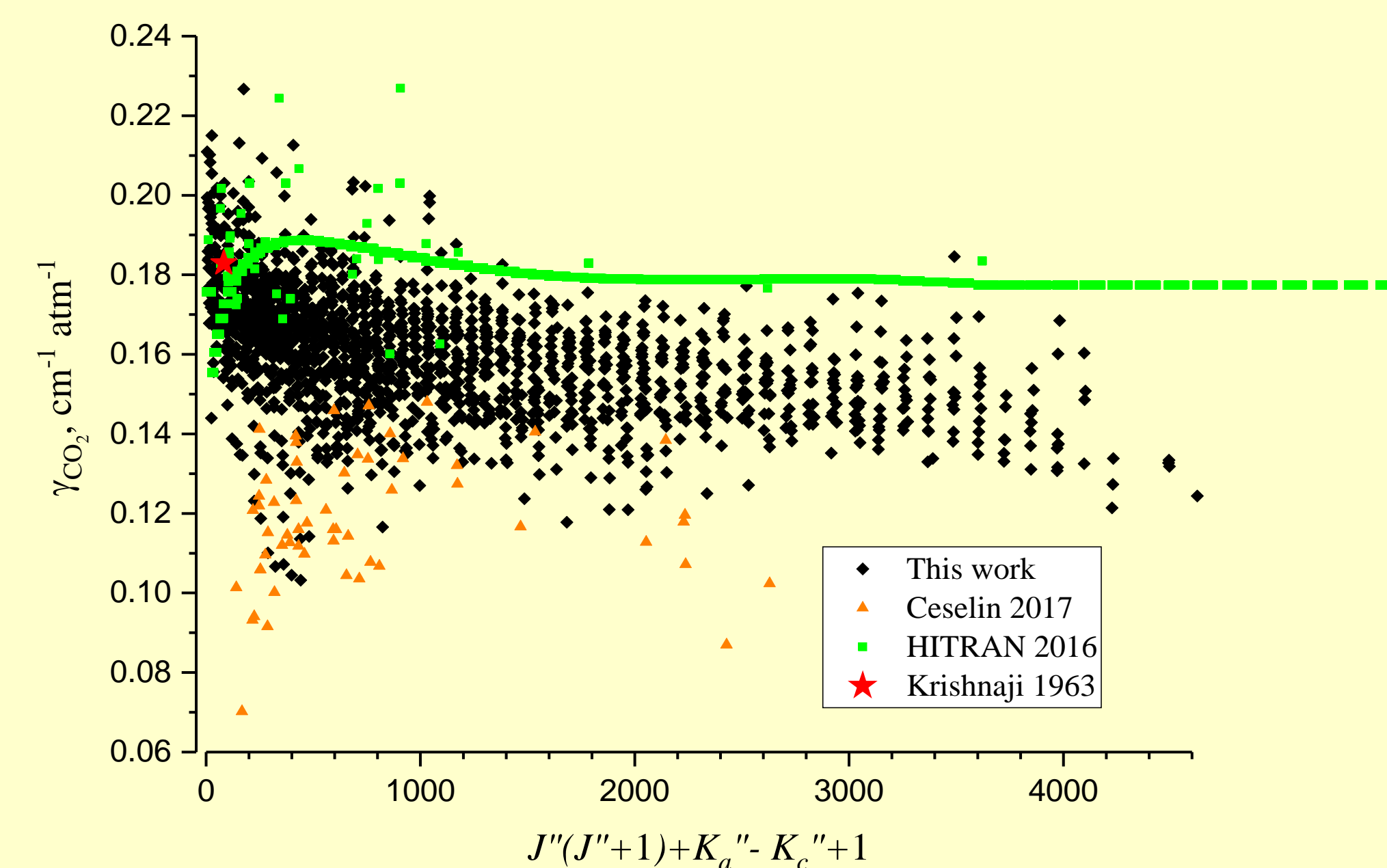


Fig.3. CO₂-broadening coefficients of the SO₂ lines. The black full rhombs – this work, the brown full triangles – Ref.[5], the full green squares – the HITRAN2016 values, the star – the value from Ref.[6].

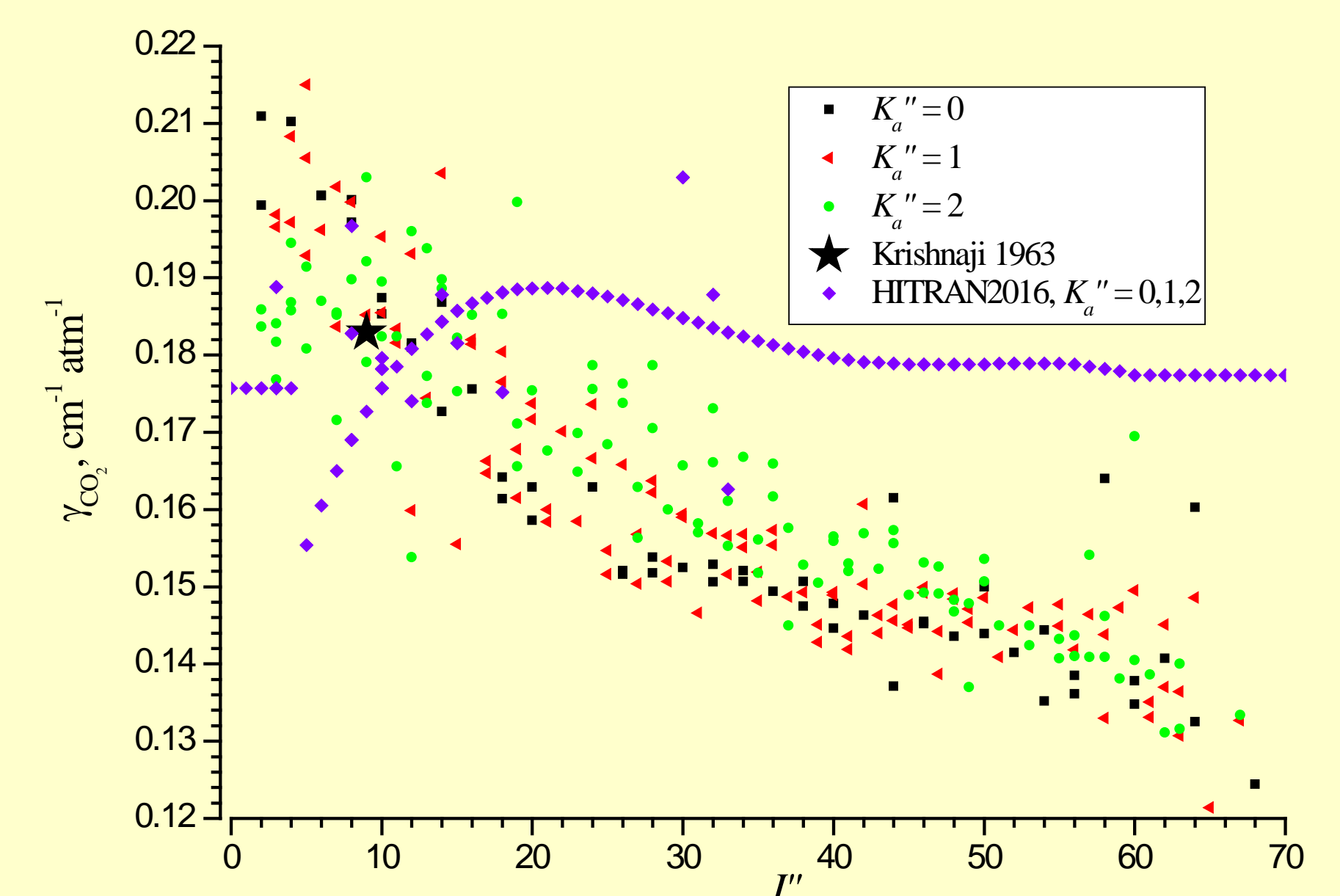


Fig.4. SO₂-CO₂ broadening coefficients for small values of the rotational quantum number versus the rotational quantum number. The value of the CO₂-broadening coefficient for the rotational line (8 2 8 ← 9 1 9) from Ref.[6] is plotted with a star.

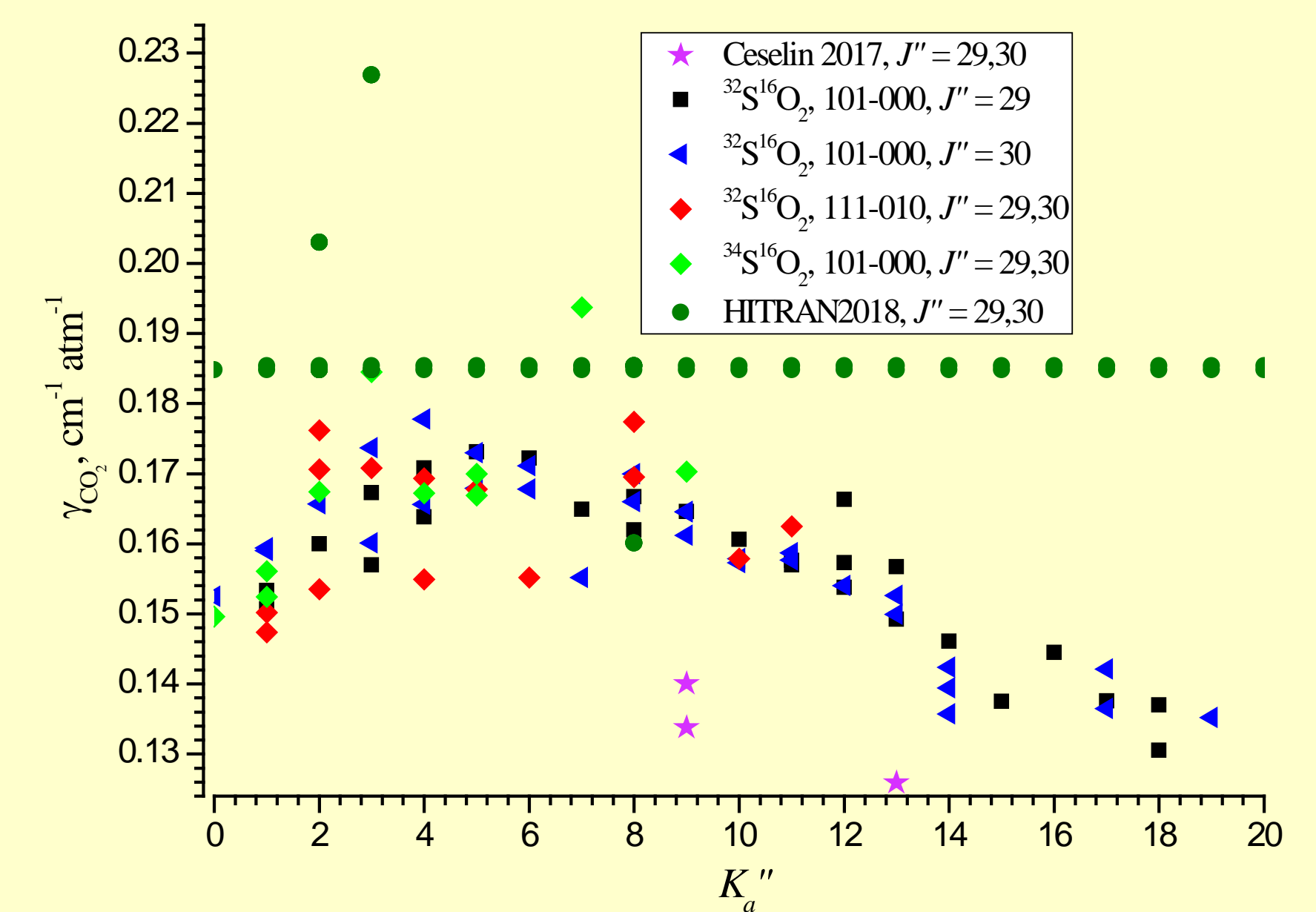


Fig.5. SO₂-CO₂ broadening coefficients versus the rotational quantum number Ka''.

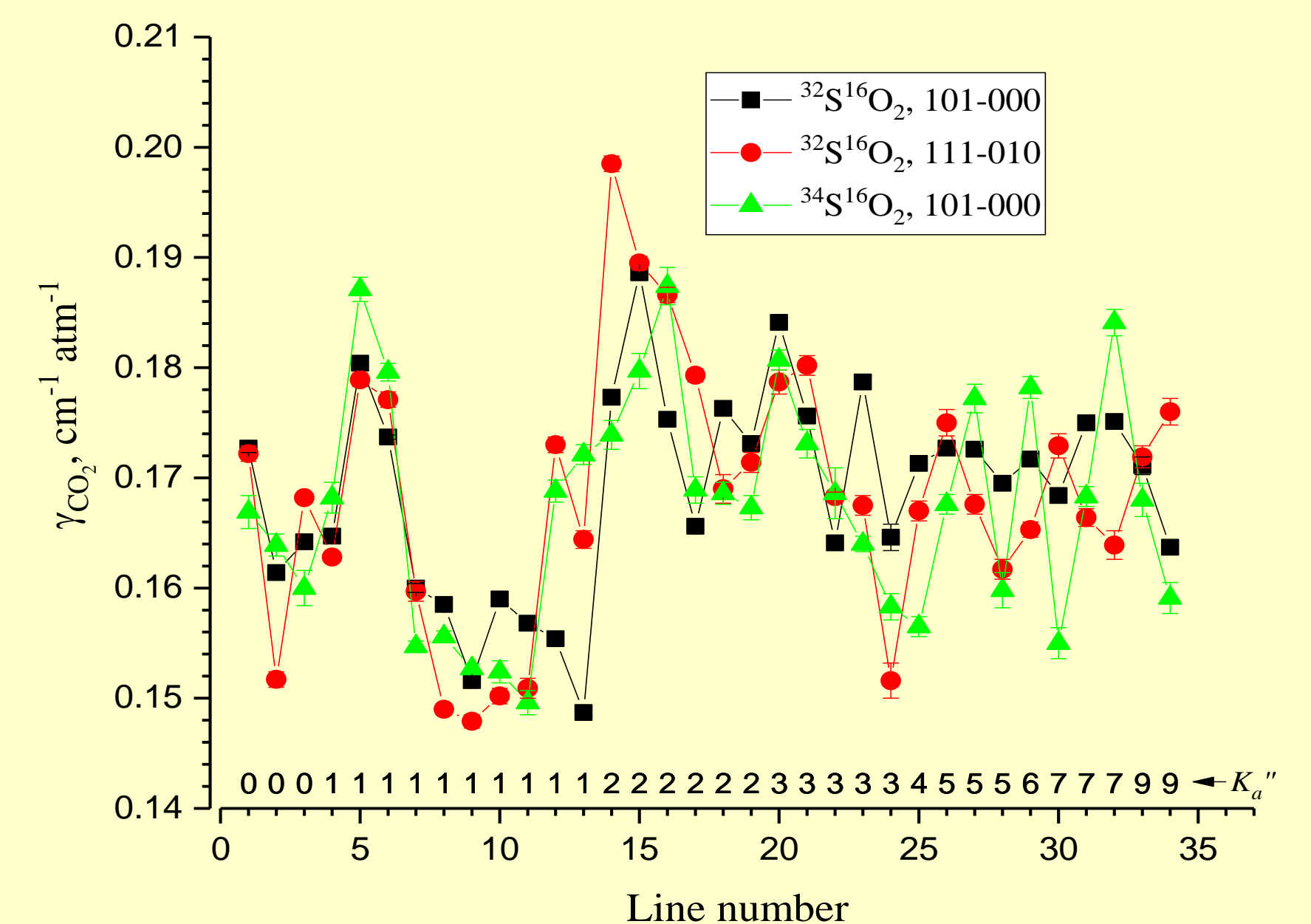


Fig.6. SO₂-CO₂ broadening coefficients for the lines with the same rotational quantum numbers of the ν₁+ν₃ and ν₁+ν₂+ν₃-ν₂ bands of the principal isotopologue ³²S¹⁶O₂ and for the lines of the minor ³⁴S¹⁶O₂ isotopologue.

ACKNOWLEDGMENTS

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