

The broadening coefficients of H₂S

The air-broadening coefficients of hydrogen sulfide (H₂S) in the HITRAN database were set to a constant value, $\gamma_{\text{air}}=0.0740 \text{ cm}^{-1}$ for most of the transitions (since HITRAN2004) based on the average value of available experimental data while just few half-widths were based on the experimental values. Since then more measurements have been made of both the air-broadening and self-broadening coefficients of H₂S. This enables improvements for the HITRAN2016 edition of the database. All the available experimental results have been collected in Table1. A slow decrease of the air-broadening coefficients with increasing ($J''+0.2Ka''$) lower-state quantum number combination can be seen in Fig.1. Similar decrease pattern for the self-broadening coefficients was found, as shown in Fig.2. The vibrational dependence of the broadening parameters is neglected and we use the semi-empirical method based on the linear fit to the available experimental data to compute both air- and self-broadening coefficients of H₂S for all the isotopologues.

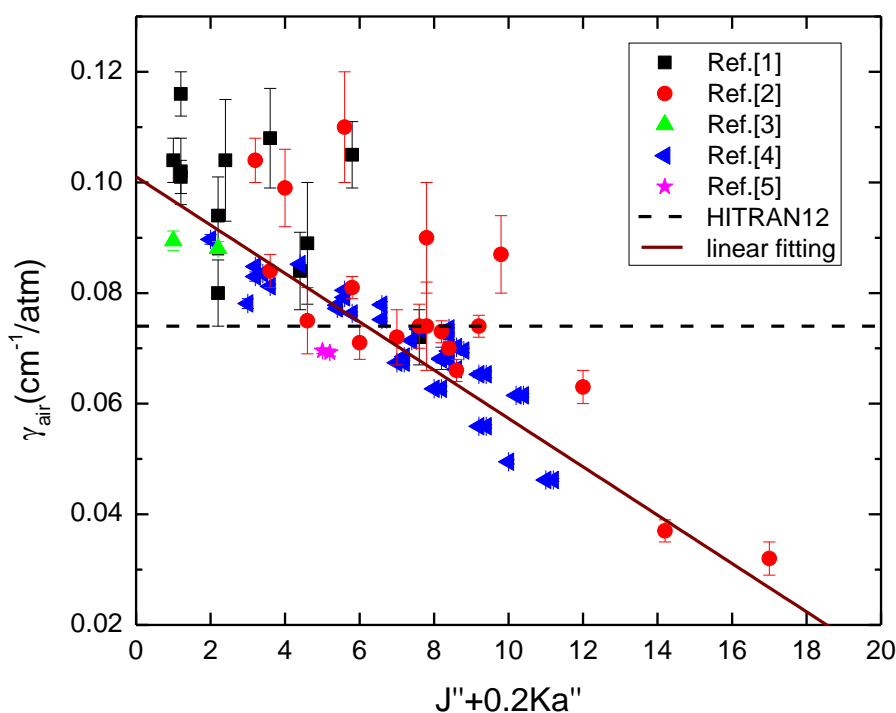


Fig. 1. The air-broadening coefficients plotted as a function of the lower-state rotational quantum number ($J''+0.2Ka''$)

Linear fit: $Y= a+b*X$	value	Standard Error
Intercept	0.10103	0.00212
Slope	-0.00437	2.6752E-4

Table1

H₂S air-broadening coefficients (in cm⁻¹/atm)

J''	Ka''	γ_{air}	error	Reference
1	0	0.104	0.004	Ref.[1]
1	1	0.116	0.004	
1	1	0.101	0.003	
1	1	0.102	0.006	
2	1	0.08	0.006	
2	1	0.094	0.007	
2	2	0.104	0.011	
3	3	0.108	0.009	
4	2	0.084	0.007	
4	3	0.089	0.011	
5	4	0.105	0.006	
7	3	0.072	0.005	
3	3	0.084	0.003	Ref.[2]
4	0	0.099	0.007	
4	3	0.075	0.006	
5	3	0.11	0.010	
5	4	0.081	0.002	
6	5	0.072	0.005	
7	3	0.074	0.004	
7	4	0.074	0.008	
7	6	0.073	0.002	
8	3	0.066	0.002	
8	6	0.074	0.002	
9	4	0.087	0.007	
11	5	0.063	0.003	
14	1	0.037	0.002	
17	0	0.032	0.003	
3	1	0.104	0.004	
5	5	0.071	0.003	
7	4	0.09	0.010	
7	7	0.07	0.001	
1	0	0.08945	0.00178	Ref.[3]
2	1	0.08805	0.00127	
8	1	0.068	0.00062	Ref.[4]
8	0	0.0627	0.00046	
8	1	0.0627	0.00046	
2	0	0.0897	0.00088	
3	2	0.0835	0.00028	

3	3	0.0812	0.00040	
4	2	0.0852	0.00030	
5	3	0.0792	0.00038	
5	3	0.0805	0.00038	
5	4	0.0763	0.00030	
6	3	0.0752	0.00028	
7	2	0.0714	0.00020	
7	3	0.0735	0.00028	
8	2	0.0725	0.00118	
8	3	0.0662	0.00076	
8	4	0.0696	0.00038	
9	2	0.0559	0.00030	
9	1	0.0559	0.00030	
10	0	0.0495	0.00038	
11	1	0.0462	0.00030	
11	0	0.0462	0.00030	
7	1	0.0685	0.00036	
8	1	0.0682	0.00201	
8	2	0.0736	0.00074	
9	1	0.0653	0.00062	
9	2	0.0653	0.00062	
10	1	0.0615	0.00030	
10	2	0.0615	0.00030	
5	0	0.06956	0.00048	<i>Ref. [5]</i>
5	0	0.06956	0.00048	
5	1	0.06923	0.00064	
5	1	0.06923	0.00064	

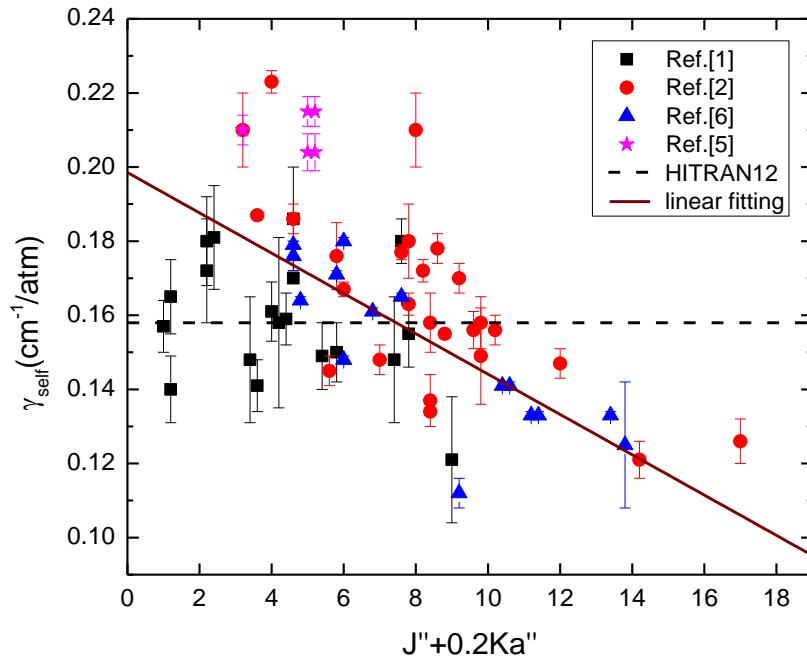


Fig.2. The self-broadening coefficients plotted as a function of the lower-state rotational quantum number ($J''+0.2Ka''$)

Linear fit: $Y = a + b \cdot X$	value	Standard Error
Intercept	0.19852	0.0043
Slope	-0.00544	5.32577E-4

Table2

H₂S self-broadening coefficients (in cm⁻¹/atm)

J''	Ka''	γ_{self}	error	Reference
1	0	0.157	0.007	Ref.[1]
1	1	0.14	0.009	
1	1	0.165	0.010	
2	1	0.172	0.014	
2	1	0.18	0.012	
2	2	0.181	0.014	
3	2	0.148	0.017	
3	3	0.141	0.007	
4	0	0.161	0.008	
4	1	0.158	0.023	
4	2	0.159	0.007	

4	3	0.17	0.001	
4	3	0.186	0.014	
5	2	0.149	0.009	
5	4	0.15	0.001	
5	4	0.15	0.008	
7	2	0.148	0.017	
7	3	0.18	0.006	
7	4	0.155	0.009	
8	5	0.121	0.017	
3	3	0.187	0.001	<i>Ref.[2]</i>
4	0	0.223	0.003	
4	3	0.186	0.004	
5	3	0.145	0.004	
5	4	0.176	0.009	
6	5	0.148	0.004	
7	3	0.177	0.002	
7	4	0.163	0.003	
7	5	0.21	0.010	
7	6	0.172	0.003	
8	2	0.158	0.008	
8	3	0.178	0.004	
8	6	0.17	0.004	
9	4	0.158	0.007	
11	5	0.147	0.004	
14	1	0.121	0.005	
17	0	0.126	0.006	
3	1	0.21	0.010	
5	5	0.167	0.002	
7	4	0.18	0.010	
7	7	0.134	0.001	
7	7	0.137	0.007	
8	4	0.155	0.001	
9	3	0.156	0.005	
9	4	0.149	0.013	
9	6	0.156	0.004	
4	3	0.179	0.001	<i>Ref.[6]</i>
4	4	0.164	0.001	
5	5	0.18	0.001	
5	5	0.148	0.001	
5	4	0.171	0.001	
6	4	0.161	0.001	
7	3	0.165	0.001	

10	3	0.141	0.001	
10	2	0.141	0.001	
11	1	0.133	0.001	
11	2	0.133	0.001	
13	2	0.133	0.001	
13	4	0.125	0.017	
4	3	0.176	0.004	
9	1	0.112	0.004	
3	1	0.21	0.004	Ref.[5]
5	1	0.204	0.005	
5	0	0.204	0.005	
5	0	0.215	0.004	
5	1	0.215	0.004	

This linear approaching value could only be used within the range probed by experiments. So for lower state rotational quantum number $J'' < 12$, the error code was 4 for both self- and air-broadening coefficients; for $12 \leq J'' \leq 18$, the error code was 3; and for $J'' > 18$, the value of both self- and air-broadening coefficients was set to be the corresponding results for $J'' = 18$, and the error code was 2. And all the reference code for air-broadening was 9 and 6 for self-broadening.

- [1] Waschull J, Kuhnemann F, Sumpf B. Self-, Air, and Helium Broadening in the ν_2 Band of H₂S. *J Mol Spectrosc* 1994;165:150–8. doi:10.1006/jmsp.1994.1117.
- [2] Sumpf B, Meusel I, Kronfeldt H-D. Self- and Air-Broadening in the ν_1 and ν_3 Bands of H₂S. *J Mol Spectrosc* 1996;177:143–5. doi:10.1006/jmsp.1996.0126.
- [3] BALL CD, DUTTA JM, BEAKY MM, GOYETTE TM, DE LUCIA FC. VARIABLE-TEMPERATURE PRESSURE BROADENING OF H₂S BY O₂ AND N₂. *J Quant Spectrosc Radiat Transf* 1999;61:775–80. doi:10.1016/S0022-4073(98)00065-X.
- [4] Kissel A, Sumpf B, Kronfeldt H-D, Tikhomirov B., Ponomarev Y. Molecular-Gas-Pressure-Induced Line-Shift and Line-Broadening in the ν_2 -Band of H₂S. *J Mol Spectrosc* 2002;216:345–54. doi:10.1006/jmsp.2002.8630.
- [5] Ciaffoni L, Cummings BL, Denzer W, Peverall R, Procter SR, Ritchie GAD. Line strength and collisional broadening studies of hydrogen sulphide in the 1.58 μm region using diode laser spectroscopy. *Appl Phys B* 2008;92:627–33. doi:10.1007/s00340-008-3119-y.
- [6] Sumpf B. Experimental Investigation of the Self-Broadening Coefficients in the $\nu_1 + \nu_3$ Band of SO₂ and the $2\nu_2$ Band of H₂S. *J Mol Spectrosc* 1997;181:160–7. doi:10.1006/jmsp.1996.7168.

The new HITRAN ref table for H₂S:

Half-widths (air)

[GlobRef 519] 2. J. Waschull, F. Kuhnemann, B. Sumpf, “Self-, Air, and Helium Broadening in the ν_2 Band of H₂S”, *J Mol Spectrosc* 1994;165:150–8. doi:10.1006/jmsp.1994.1117.

[GlobRef 520] 3. B. Sumpf, I. Meusel, H-D. Kronfeldt, “Self- and Air-Broadening in the ν_1 and ν_3 Bands of H_2S ”, J Mol Spectrosc 1996;177:143–5. doi:10.1006/jmsp.1996.0126.

[GlobRef 521] 4. A. Kissel, B. Sumpf, H. D. Kronfeldt, B. Tikhomirov, Y. Ponomarev, “Molecular-Gas-Pressure-Induced Line-Shift and Line-Broadening in the ν_2 -Band of H_2S ”, J Mol Spectrosc 2002;216:345–54. doi:10.1006/jmsp.2002.8630.

[GlobRef 1106] 7. C.D. Ball, J. M. Dutta, M.M Beaky, T. M. Goyette, F. C. De Lucia, “Variable-Temperature Pressure Broadening of H_2S by O_2 and N_2 ”, J Quant Spectrosc Radiat Transf 1999;61:775–80. doi:10.1016/S0022-4073(98)00065-X.

[GlobRef 1108] 8. L. Ciaffoni, B. L. Cummings, W. Denzer, R. Peverall, S. R. Procter, G. A. D. Ritchie, “Line strength and collisional broadening studies of hydrogen sulphide in the 1.58 μm region using diode laser spectroscopy”, Appl Phys B 2008;92:627–33. doi:10.1007/s00340-008-3119-y.

[GlobRef 1109] 9. this report.

Half-widths (self)

[GlobRef 519] 1. J. Waschull, F. Kuhnemann, B. Sumpf, “Self-, Air, and Helium Broadening in the ν_2 Band of H_2S ”, J Mol Spectrosc 1994;165:150–8. doi:10.1006/jmsp.1994.1117.

[GlobRef 520] 2. B. Sumpf, I. Meusel, H-D. Kronfeldt, “Self- and Air-Broadening in the ν_1 and ν_3 Bands of H_2S ”, J Mol Spectrosc 1996;177:143–5. doi:10.1006/jmsp.1996.0126.

[GlobRef 525] 3. B. Sumpf, “Experimental Investigation of the Self-Broadening Coefficients in the $\nu_1 + \nu_3$ Band of SO_2 and the $2\nu_2$ Band of H_2S ”, J Mol Spectrosc 1997;181:160–7.

[GlobRef 1108] 5. L. Ciaffoni, B. L. Cummings, W. Denzer, R. Peverall, S. R. Procter, G. A. D. Ritchie, “Line strength and collisional broadening studies of hydrogen sulphide in the 1.58 μm region using diode laser spectroscopy”, Appl Phys B 2008;92:627–33. doi:10.1007/s00340-008-3119-y.

[GlobRef 1109] 6. this report.

The line positions and intensities of H₂S

Line positions for 654 transitions in the (010)-(000) band, were updated using experimental upper state energy levels for H₂³²S, H₂³³S, and H₂³⁴S isotopologues reported in Ulenikov et al. [ref.1] while the lower state energy levels were calculated using the rotational constants of Flaud et al. [ref.2].

The line positions and intensities of the transitions in the triad bands were replaced with the new corrected line list from Naumenko [ref.3].

Finally, The line intensities of some of the transitions in the 4471-11329 cm⁻¹ region were found to be overestimated, and they were replaced with new calculated results from Naumenko [ref.3].

The new HITRAN ref table for H₂S:

Positions

[GlobRef 1112] **12.** Transitions wavenumbers are evaluated from the upper experimental energy levels of Ref.[1] and calculated lower energy levels based on the rotational constants of Flaud et al. [2].

[GlobRef 1113] **13.** private communication from Olga. V. Naumenko 2016.

Intensity

[GlobRef 1112] **11.** Transitions wavenumbers are evaluated from the upper experimental energy levels of Ref.[1] and calculated lower energy levels based on the rotational constants of Flaud et al. [2].

[GlobRef 1113] **12.** private communication from Olga. V. Naumenko 2016.

[1] Ulenikov O. N., Malikova A. B., Koivusaari M., Alanko S., Anttila R.
High Resolution Vibrational–Rotational Spectrum of H₂S in the Region of the ν₂ Fundamental Band // J. Mol. Spectrosc. 1996. V 176. № 2. P. 229-235.

[2] Flaud J-M., Camy-Peyret C., and J.W.C. Johns.
The far-infrared spectrum of hydrogen sulphide. The (000) rotational constants of H₂³²S, H₂³³S and H₂³⁴S // Can. J. Phys. 1983. V.61. P. 1462-1473.

[3] private communication from Olga V. Naumenko 2016