Supplementary Information (SI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Material
High-Accuracy Theoretical Rate Coefficients for the Reaction of H_2S with OH

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[3]*In loving memory of Prof. John F. Stanton (1961-2025).*

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Optimized geometries of various stationary points on the PES calculated for the H_2S + OH reaction

OH ($C_{\infty v}$, $X^2\Pi$): optimized at ae-CCSD(T)/cc-pCVQZ

O
H 1 B1*

B1 = 0.968898865501339

H_2S (C_{2v}, $^1A_1$): optimized at ae-CCSD(T)/cc-p(w)CVQZ

S
H 1 R1*
H 1 R1* 2 A1*

R1 = 1.334844500676897
A1 = 92.305601609130591

H_2O (C_{2v}, $^1A_1$): optimized at ae-CCSD(T)/cc-pCVQZ

O
H 1 R1*
H 1 R1* 2 A1*

R1 = 0.957119039087896
A1 = 104.224678631849955

SH ($C_{\infty v}$, $X^2\Pi$): optimized at ae-CCSD(T)/cc-pCVQZ

H
S 1 R1*

R1 = 1.339287033028603

PRC (C_s, $^2A''$): optimized at ae-CCSD(T)/cc-p(w)CVQZ

S
H 1 R1*
X 2 R0 1 A1*
O 2 R2* 3 A1* 1 D180
H 1 R3* 2 A2* 3 D1*
H 1 R3* 2 A2* 3 D2*

R1 = 2.538739373469334
R0 = 1.000000409314806
A1 = 87.509878306034153
R2 = 0.972925934567063
D180 = 180.000000000000000
R3 = 1.335617940603538
A2 = 94.402733338337299

D1 = 46.359125118069628
D2 = -46.359125118069628

PRC (C_s, $^2A'$): optimized at ae-CCSD(T)/cc-p(w)CVQZ

S
H 1 R1*
X 2 R0 1 A1*
O 2 R2* 3 A1* 1 D180
H 1 R3* 2 A2* 3 D1*
H 1 R3* 2 A2* 3 D2*

R1 = 2.526687220900317
R0 = 1.000000613972272
A1 = 87.652594713462122
R2 = 0.972915584738110
D180 = 180.000000000000000
R3 = 1.335510586878342
A2 = 95.617204582180662
D1 = 46.545857285385708
D2 = -46.545857285385708

TS1-Habs (C_1, ^2A): optimized at ae-CCSD(T)/cc-p(w)CVQZ

H
S 1 B1
H 2 B2 1 A1
O 2 B3 1 A2 3 D1
H 4 B4 2 A3 1 D2

B1 = 1.335768767794827
B2 = 1.399813002373515
A1 = 92.094502015269683
B3 = 2.684984993012950
A2 = 84.665827704711958
D1 = 20.130254780497946
B4 = 0.968878015348230
A3 = 86.092922719659455
D2 = 110.003826998270441

PPC (C_s, $^2A''$): optimized at ae-CCSD(T)/cc-p(w)CVQZ

O
H 1 R1*
X 2 R0 1 A1*
S 2 R2* 3 A1* 1 D180
H 1 R3* 2 A2* 3 D1*
H 1 R3* 2 A2* 3 D2*

R1 = 2.215350685343787
R0 = 1.000000409314806
A1 = 91.699053038566163

R2 = 1.343444417861273
D180 = 180.000000000000000
R3 = 0.957788542632208
A2 = 117.447570857816615
D1 = 117.009995098174187
D2 = -117.009995098174187

PPC (C_s, $^2A'$): optimized at ae-CCSD(T)/cc-p(w)CVQZ
O
H 1 R1*
X 2 R0 1 A1*
S 2 R2* 3 A1* 1 D180
H 1 R3* 2 A2* 3 D1*
H 1 R3* 2 A2* 3 D2*

R1 = 2.179302672689876
R0 = 1.000000409314806
A1 = 90.156539942534337
R2 = 1.343023029999567
D180 = 180.000000000000000
R3 = 0.957616489919152
A2 = 122.577829350531317
D1 = 109.986771256247621
D2 = -109.986771256247621

Rovibrational parameters and anharmonic constants for various species

OH ($C_{\infty v}$, $X^2\Pi$)
Har. Frequency = 3744.3495 cm^{-1} (at ae-CCSD(T)/aCVQZ)
Rot. constant (2D) = B = 18.9033 cm^{-1}
Diagonal anharmonic constant = X_{11} = -81.8586 cm^{-1}.

H_2S (C_{2v}, $^1A_1$)

Type	a(w)CVTZ	a(w)CVQZ
vib	1215.5803	1214.7303
vib	2725.8539	2727.8389
vib	2741.3853	2743.7046
A (cm^{-1})	10.3678	10.3884
B (cm^{-1})	9.0191	9.0127
C (cm^{-1})	4.8233	4.8259

ANHARMONICITY CONSTANTS X(ij)
(cm-1)

I J	X(IJ)
1 1	-4.5035
1 2	-16.4015
1 3	-21.1508
2 2	-24.8476
2 3	-97.7996
3 3	-25.1034

TS1-Habs (C_1, ^2A)

TS1	a(w)CVTZ	a(w)CVQZ
Imag. Freq.	886.5594i	882.1304i
vib (1DHR)	179.5274	182.4127
vib	256.9044	258.7588
vib	328.2326	326.9791
vib	722.6762	723.2198
vib	1112.7796	1113.5639
vib	1746.7351	1784.5287
vib	2727.9765	2730.2056
vib	3726.4982	3750.0040
A (cm^{-1})	5.7893	5.7606
B	0.2047	0.2067
C	0.2026	0.2045

Anharmonic constants (cm^{-1}) calculated at ae-CCSD(T)/aug-cc-p(w)CVTZ

-158.9944								
17.7775i	-0.8536							
55.4765i	-9.7032	-5.014						
70.5420i	-8.9065	-14.1008	-2.265					
197.0470i	6.5518	6.295	15.0855	4.3284				

-60.7993i	-3.6071	6.5158	-70.9875	-5.8012	-7.0626			
-795.2279i	-48.992	-75.7391	-41.8364	-102.5795	62.5581	184.5609		
-3.0615i	-1.9293	-2.1804	-4.5216	-2.1618	-16.1339	-2.5901	-48.9071	
0.8527i	-0.7833	-2.4177	-1.3283	-13.2878	-1.6046	-14.7632	-0.0185	-80.3884

PRC (C_s, ^{2}A' and 2A")

Type	2A"	2A'	2A"
vib	106.1955	108.4179	106.0422
vib	112.3121	119.3376	112.3121
vib	134.9614	137.4804	141.7712
vib	395.9341	337.5055	337.6787
vib	421.3900	424.7174	421.3900
vib	1212.0301	1212.4990	1212.8331
vib	2728.9062	2729.5466	2729.0228
vib	2743.6849	2744.6341	2743.6849
vib	3682.6639	3682.8482	3682.7411
A (cm^{-1})	4.8320	4.8599	4.8320
B	0.1214	0.1220	0.1214
C	0.1212	0.1217	0.1212

Table S1a: Ro-vibrational parameters and relative energies of grid points along the association path of H_2S and OH leading to a van der Waals complex, PRC.

Type	2.8 Angstrom	3.0 A	3.2 A	3.4 A	3.6 A	3.8 A
vib	91.7190	83.5469	70.0061	51.3788	57.0636	57.2244
vib	117.1867	102.9070	88.6359	75.5153	64.8107	70.2816
vib	276.0055	236.0703	202.7561	175.7633	154.7506	138.5624
vib	343.6855	292.1625	252.4134	215.6393	191.1527	172.7698
vib	1212.7605	1212.9639	1213.1214	1213.2358	1213.3224	1213.3837
vib	2729.9425	2730.3956	2730.7019	2731.0076	2731.2633	2731.4619
vib	2745.1375	2745.5175	2745.8150	2746.1008	2746.5262	2746.6222
vib	3640.2992	3653.0772	3660.9278	3665.9615	3669.1417	3671.0394
A (cm^{-1})	4.8353	4.8133	4.7875	4.7633	4.7454	4.7380
B (cm^{-1})	0.1062	0.0962	0.0876	0.0801	0.0735	0.0675
C (cm^{-1})	0.1061	0.0961	0.0875	0.0801	0.0734	0.0675

Rel energy (kJ mol^{-1})	0.00	0.97	1.96	2.81	3.66	4.42

Table S1b: (Continued)

Type	4.0 Angstrom	4.2 A	4.4 A	4.6 A	4.8 A	5.0 A
vib	52.2195	48.6922	45.5710	42.7182	39.8775	37.3164
vib	58.8656	62.6322	54.9683	48.4783	46.2571	39.5980
vib	125.6080	114.7305	105.1589	96.6900	89.0533	82.2699
vib	143.1124	156.6328	128.0601	114.0244	108.8986	100.5782
vib	1213.4250	1213.4486	1213.4532	1213.4424	1213.4130	1213.3686
vib	2731.6095	2731.6911	2731.7323	2731.7256	2731.6859	2731.5990
vib	2746.8535	2747.0222	2747.1710	2747.2878	2747.3971	2747.4808
vib	3672.1051	3672.6485	3672.9689	3673.1811	3673.3158	3673.3445
A (cm^{-1})	4.7413	4.7534	4.7712	4.7928	4.8186	4.8483
B	0.0622	0.0574	0.0531	0.0493	0.0459	0.0428
C	0.0622	0.0574	0.0531	0.0493	0.0458	0.0427
Rel energy (kJ mol^{-1})	4.85	5.45	5.67	5.88	6.09	6.21

Table S1c: (Continued)

Type	5.2 Angstrom	5.4 A	5.6 A	5.8 A	6.0 A	6.2 A
vib	35.2437	33.1669	28.2050	29.6024	28.0221	20.8961
vib	37.1603	34.1776	33.9552	31.0639	28.5073	30.4232
vib	76.3352	70.9337	67.6758	61.8106	58.1258	56.2596
vib	93.2539	86.2560	78.6972	75.0498	69.7179	64.4025
vib	1213.3148	1213.2460	1213.2326	1213.0847	1213.0007	1212.9549
vib	2731.4829	2731.3375	2731.2575	2730.9845	2730.7922	2730.6582
vib	2747.5398	2747.5909	2747.5699	2747.6604	2747.6743	2747.6435
vib	3673.2776	3673.1770	3672.9734	3672.9181	3672.7992	3672.5670
A (cm^{-1})	4.8823	4.9196	4.9509	5.0009	5.0435	5.0864
B	0.0400	0.0374	0.0351	0.0331	0.0311	0.0294
C	0.0399	0.0374	0.0351	0.0330	0.0311	0.0294
Rel energy (kJ mol^{-1})	6.32	6.40	6.45	6.51	6.54	6.56

Table S1d: (Continued)

Type	6.4 Angstrom	6.6 A	6.8 A	7.0 A	7.2 A
vib	25.0946	23.8690	19.8669	21.4285	15.9417

vib	25.4519	24.2723	23.9991	22.0188	23.8188
vib	51.2770	48.5743	46.4270	43.4511	42.2977
vib	61.8319	58.6084	55.0925	52.8951	49.6273
vib	1212.8167	1212.7138	1212.7350	1212.4857	1212.4247
vib	2730.3867	2730.1545	2730.1920	2729.6591	2729.5073
vib	2747.7105	2747.7140	2747.7052	2747.7300	2747.7071
vib	3672.6641	3672.4527	3673.2956	3672.1816	3672.0220
A (cm^{-1})	5.1257	5.1756	5.1612	5.2806	5.3227
B	0.0278	0.0263	0.0250	0.0237	0.0225
C	0.0278	0.0263	0.0250	0.0237	0.0225
Rel energy (kJ mol^{-1})	6.58	6.60	6.60	6.61	6.61

Table S2: Collisional parameters and energies are used in the E,J-resolved 2DME model.

Parameters	Values
Air (80% N_2 and 20% O_2)	Mass = 28.8 g/mol, σ = 3.668 Å, ε/k_B = 86.2 K
H_3OS (PRC)	Mass = 51 g/mol, σ = 5.46 Å, ε/k_B = 401 K
E_{max}	10,000 cm^{-1} above H_3OS (PRC)
ΔE_{grain}	2 cm^{-1}
$<\Delta E_d>$	= temperature (in cm^{-1}) when T ≤ 100 K
J_{max}	100
ΔJ	2

Table S3: Calculated LPL rate coefficients ($cm^3\ s^{-1}$) for the reaction of H_2S + OH as a function of temperature

T (K)	ab initio	Va + 0.5 kJ mol^{-1}
	k(T,p=0)	k(T,p=0)
10	1.11E-10	8.16E-11
15	7.90E-11	5.61E-11
20	6.00E-11	4.16E-11
25	4.77E-11	3.25E-11

30	3.90E-11	2.63E-11
35	3.27E-11	2.18E-11
40	2.78E-11	1.84E-11
45	2.40E-11	1.59E-11
50	2.09E-11	1.38E-11
55	1.85E-11	1.22E-11
60	1.65E-11	1.09E-11
65	1.48E-11	9.78E-12
70	1.34E-11	8.88E-12
75	1.22E-11	8.13E-12
80	1.12E-11	7.50E-12
85	1.04E-11	6.97E-12
90	9.67E-12	6.51E-12
95	9.04E-12	6.12E-12
100	8.50E-12	5.79E-12
105	8.03E-12	5.50E-12
110	7.63E-12	5.25E-12
115	7.27E-12	5.04E-12
120	6.95E-12	4.85E-12
125	6.68E-12	4.68E-12
130	6.44E-12	4.54E-12
135	6.22E-12	4.42E-12
140	6.03E-12	4.31E-12
145	5.86E-12	4.22E-12
150	5.72E-12	4.14E-12
155	5.58E-12	4.06E-12
160	5.47E-12	4.00E-12
165	5.37E-12	3.95E-12
170	5.28E-12	3.91E-12
175	5.20E-12	3.87E-12
180	5.13E-12	3.84E-12
185	5.07E-12	3.82E-12
190	5.02E-12	3.80E-12
195	4.97E-12	3.79E-12
200	4.94E-12	3.78E-12
210	4.88E-12	3.77E-12
220	4.84E-12	3.78E-12
230	4.83E-12	3.80E-12
240	4.83E-12	3.83E-12

250	4.84E-12	3.87E-12
260	4.87E-12	3.92E-12
270	4.91E-12	3.98E-12
280	4.95E-12	4.05E-12
290	5.01E-12	4.12E-12
300	5.08E-12	4.20E-12
310	5.15E-12	4.29E-12
320	5.24E-12	4.38E-12
330	5.33E-12	4.48E-12
340	5.43E-12	4.58E-12
350	5.53E-12	4.70E-12
360	5.64E-12	4.81E-12
370	5.76E-12	4.93E-12
380	5.88E-12	5.06E-12
390	6.01E-12	5.19E-12
400	6.15E-12	5.33E-12
410	6.29E-12	5.47E-12
420	6.44E-12	5.62E-12
430	6.59E-12	5.77E-12
440	6.75E-12	5.93E-12
450	6.92E-12	6.09E-12
460	7.09E-12	6.26E-12
470	7.26E-12	6.43E-12
480	7.44E-12	6.61E-12
490	7.63E-12	6.79E-12
500	7.82E-12	6.98E-12
510	8.02E-12	7.17E-12
520	8.22E-12	7.37E-12
530	8.42E-12	7.57E-12
540	8.64E-12	7.78E-12
550	8.85E-12	7.99E-12
560	9.08E-12	8.21E-12
570	9.30E-12	8.43E-12
580	9.53E-12	8.66E-12
590	9.77E-12	8.89E-12
600	1.00E-11	9.12E-12
625	1.06E-11	9.72E-12
650	1.13E-11	1.03E-11
675	1.19E-11	1.10E-11

700	1.26E-11	1.17E-11
725	1.34E-11	1.24E-11
750	1.41E-11	1.31E-11
775	1.49E-11	1.38E-11
800	1.56E-11	1.46E-11
825	1.64E-11	1.54E-11
850	1.73E-11	1.62E-11
875	1.81E-11	1.70E-11
900	1.89E-11	1.78E-11
925	1.98E-11	1.86E-11
950	2.06E-11	1.95E-11
975	2.15E-11	2.03E-11
1000	2.24E-11	2.12E-11
1025	2.32E-11	2.20E-11
1050	2.41E-11	2.29E-11
1075	2.50E-11	2.38E-11
1100	2.58E-11	2.46E-11
1125	2.67E-11	2.55E-11
1150	2.76E-11	2.63E-11
1175	2.84E-11	2.72E-11
1200	2.93E-11	2.80E-11
1225	3.02E-11	2.89E-11
1250	3.10E-11	2.97E-11
1275	3.18E-11	3.05E-11
1300	3.27E-11	3.14E-11
1325	3.35E-11	3.22E-11
1350	3.43E-11	3.30E-11
1375	3.51E-11	3.38E-11
1400	3.59E-11	3.46E-11
1425	3.67E-11	3.53E-11
1450	3.74E-11	3.61E-11
1475	3.82E-11	3.68E-11
1500	3.89E-11	3.76E-11
1525	3.96E-11	3.83E-11
1550	4.03E-11	3.90E-11
1575	4.10E-11	3.97E-11
1600	4.17E-11	4.04E-11
1625	4.24E-11	4.10E-11
1650	4.30E-11	4.17E-11

1675	4.37E-11	4.23E-11
1700	4.43E-11	4.29E-11
1725	4.49E-11	4.35E-11
1750	4.55E-11	4.41E-11
1775	4.60E-11	4.47E-11
1800	4.66E-11	4.53E-11
1825	4.71E-11	4.58E-11
1850	4.77E-11	4.63E-11
1875	4.82E-11	4.69E-11
1900	4.87E-11	4.74E-11
1925	4.92E-11	4.78E-11
1950	4.96E-11	4.83E-11
1975	5.01E-11	4.88E-11
2000	5.05E-11	4.92E-11
2050	5.14E-11	5.01E-11
2100	5.21E-11	5.09E-11
2150	5.29E-11	5.16E-11
2200	5.35E-11	5.23E-11
2250	5.42E-11	5.29E-11
2300	5.47E-11	5.35E-11
2350	5.52E-11	5.40E-11
2400	5.57E-11	5.45E-11
2450	5.61E-11	5.49E-11
2500	5.65E-11	5.53E-11
2550	5.69E-11	5.57E-11
2600	5.72E-11	5.60E-11
2650	5.74E-11	5.63E-11
2700	5.76E-11	5.65E-11
2750	5.78E-11	5.67E-11
2800	5.80E-11	5.69E-11
2850	5.81E-11	5.70E-11
2900	5.82E-11	5.71E-11
2950	5.82E-11	5.72E-11
3000	5.83E-11	5.72E-11

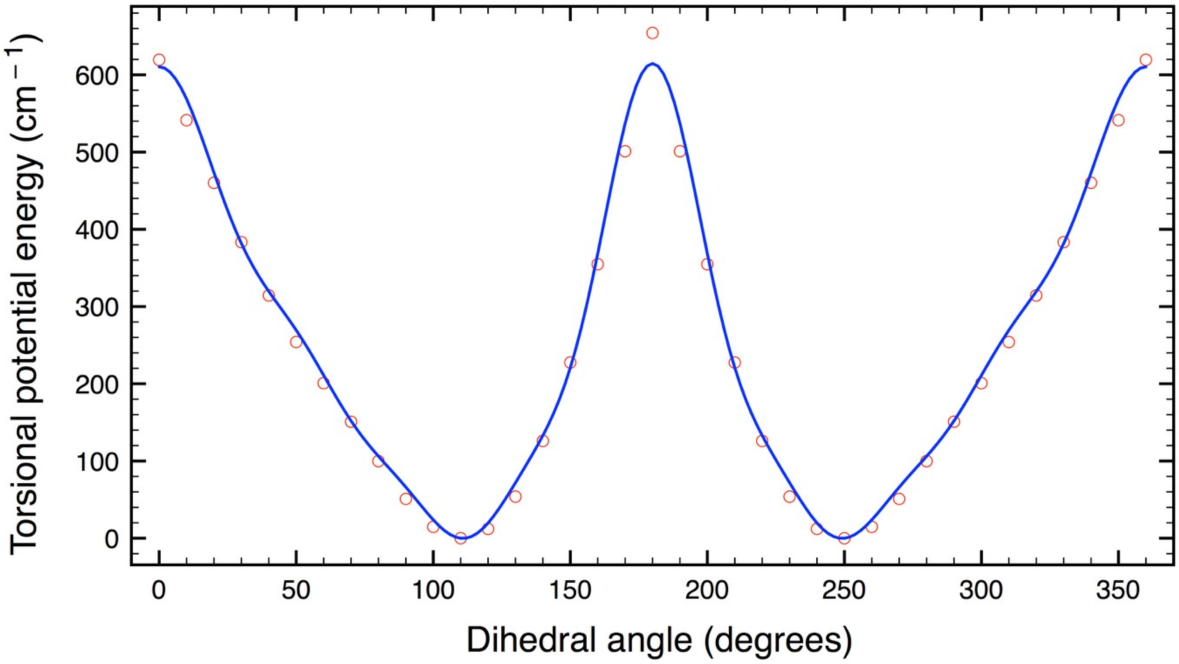

Figure S1: Torsional potential energy (in cm^{-1}) calculated as a function of torsional dihedral angle (∠ HOSH) using ae-CCSD(T)/aug-cc-p(w)CVQZ level of theory, and it is then fitted to the following equation:

$$
\begin{aligned}
V(x\ in\ rad) &= 251.941 - 77.6125\cos(x-\pi) + 244.119\cos(2(x-\pi)) + 61.2026\cos(3(x-\pi)) + 70.5907\cos(4 \\
&+ 8.18076\cos(5(x-\pi)) + 29.1142\cos(6(x-\pi)) + 7.05877\cos(7(x-\pi)) + 16.7772 \\
&\cos(8(x-\pi)) + 3.268\cos(9(x-\pi))
\end{aligned}
$$

, in cm^{-1}.

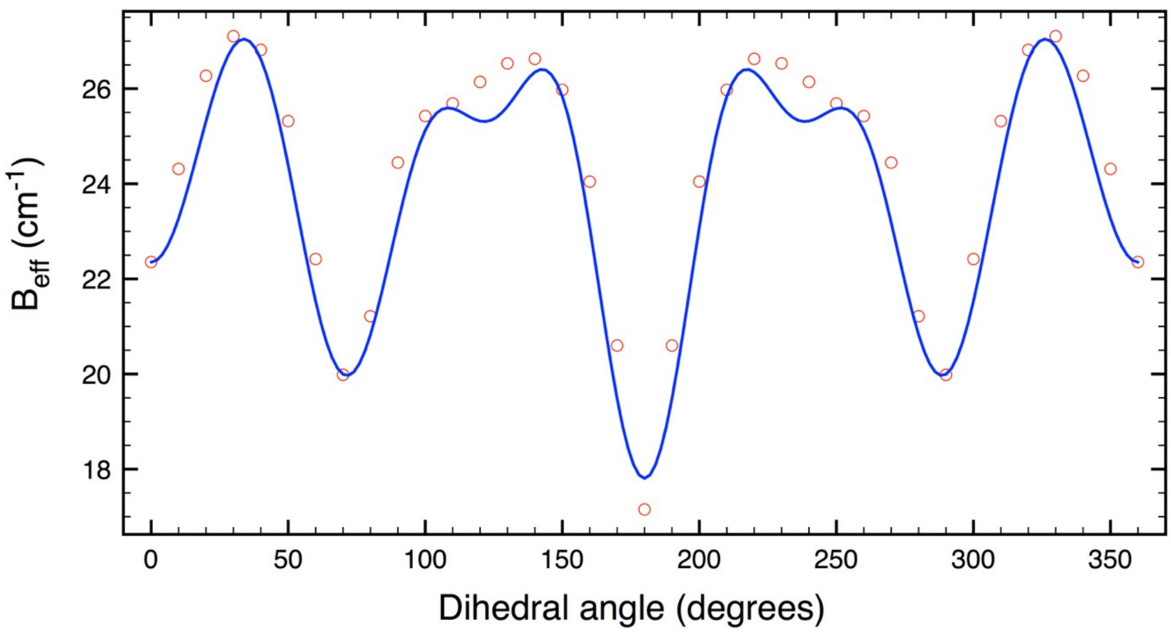

Figure S2: Effective rotational constant (in cm^{-1}) calculated as a function of torsional dihedral angle (∠ HOSH) using ae-CCSD(T)/aug-cc-p(w)CVQZ level of theory, and it is then fitted to the following equation:

$$B_{eff}(x\ in\ rad) = 23.8053 - 0.430331\cos(x-\pi) - 0.0551531\cos(2(x-\pi)) - 2.04226\cos(3(x-\pi)) - 2.11488\cos(4(x-\pi)) + 0.790369\cos(5(x-\pi)) - 1.49623\cos(6(x-\pi)) - 0.612716\cos(7(x-\pi)) - 0.0599316\cos(8(x-\pi)) + 0.0216401\cos(9(x-\pi))$$

, in cm^{-1}.

A vector of eigenvalues (cm-1) for the 1D-HIR in TS1

Index	Eigenvalue (cm^{-1})
1	103.945593811482 (**ZPE of 1D-HIR**)
2	104.539882299500
3	281.036338993284
4	286.190673445122
5	417.031754851664
6	440.547974417222
7	553.751080855778
8	626.830652154044
9	699.747454562451
10	852.340659865728
11	881.281840156165
12	1115.33170754771
13	1122.76962958776
14	1421.01869343650
15	1422.43377603692
16	1773.17120705677
17	1773.42747910120

18	2172.91479257905
19	2172.94375579093
20	2620.24723900225
21	2620.24741802068
22	3115.06867733519
23	3115.06942535482
24	3657.29133707767
25	3657.29140093336
26	4246.85220604681
27	4246.85234037378
28	4883.71238731773
29	4883.71240343927
30	5567.84566832406
31	5567.84566917612
32	6299.23423504569
33	6299.23423643545
34	7077.86551010796
35	7077.86551019470
36	7903.73040422886
37	7903.73040431788
38	8776.82221821556
39	8776.82221823515
40	9697.13592175965
41	9697.13592176035
42	10664.6676769975
43	10664.6676769988
44	11679.4145136060
45	11679.4145136067
46	12741.3741030248
47	12741.3741030253
48	13850.5445985723
49	13850.5445985728
50	15006.9245202776
51	15006.9245202777
52	16210.5126706639
53	16210.5126706642
54	17461.3080723062
55	17461.3080723067
56	18759.3099209492
57	18759.3099209493
58	20104.5175498920
59	20104.5175498922
60	21496.9304026542
61	21496.9304026545
62	22936.5480117803
63	22936.5480117805
64	24423.3699822577
65	24423.3699822579
66	25957.3959784361
67	25957.3959784364
68	27538.6257136226
69	27538.6257136229
70	29167.0589417471
71	29167.0589417473
72	30842.6954506399
73	30842.6954506399

74	32565.5350565714
75	32565.5350565714
76	34335.5775997941
77	34335.5775997942
78	36152.8229408790
79	36152.8229408793
80	38017.2709576882
81	38017.2709576885
82	39928.9215428624
83	39928.9215428626
84	41887.7746017248
85	41887.7746017248
86	43893.8300505235
87	43893.8300505236
88	45947.0878149515
89	45947.0878149516
90	48047.5478288962
91	48047.5478288965
92	50195.2100333789
93	50195.2100333791

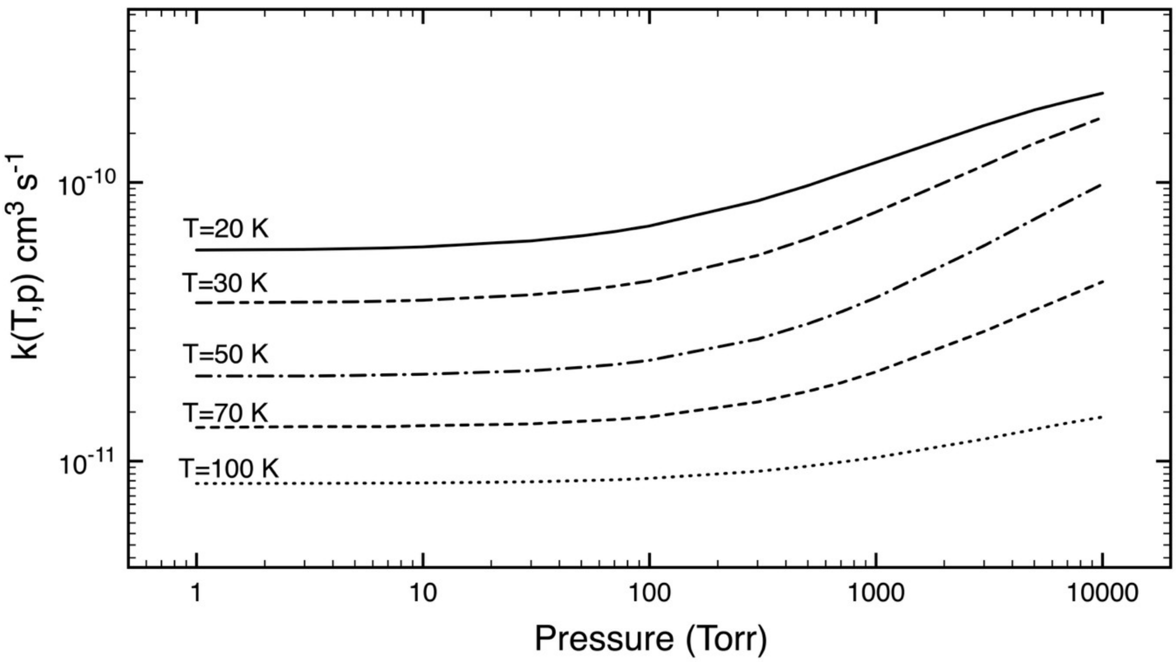

Figure S3: Falloff curves for the H_2S + OH reaction calculated as a function of pressure at different low temperatures.