Ab initio treatment of molecular Coster-Kronig decay using complex-scaled equation-of-motion coupled-cluster theory

Supplementary Information

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Table 1: Exponents of complex-scaled basis functions.

H	S	Ar	H	S	Ar
s-shells			p-shells		
0.33027132	2.38134993	2.20531200	1.32938926	9.58527386	8.87669400
0.21397640	1.54283057	1.42877900	0.86200227	6.21528098	5.75582400
0.10698820	0.77141529	0.71438900	0.43100117	3.10764077	2.87791200
0.05349410	0.38570764	0.35719500	0.21550055	1.55382011	1.43895600
0.02674705	0.19285382	0.17859750	0.10775027	0.77691005	0.71947800
0.01337352	0.09642691	0.08929875	0.05387514	0.38845503	0.35973900
0.00668676	0.04821346	0.04464938	0.02693757	0.19422751	0.17986950
0.00334338	0.02410673	0.02232469	0.01346878	0.09711376	0.08993475
d-shells					
1.80846418	13.0395400	12.0756100	0.07992358	0.57627173	0.53367150
0.63938860	4.61017327	4.26937200	0.03996179	0.28813586	0.26683575
0.31969434	2.30508691	2.13468600	0.01998090	0.14406793	0.13341788
0.15984717	1.15254345	1.06734300	0.00999045	0.07203397	0.06670894

Table 2: Optimal complex scaling angles.

	Method	Basis	Angle
Ar	CS-EOM-CCSD	aug-cc-pCVQZ	16°
Ar	CS-EOM-CCSD	aug-cc-pCV5Z	17°
Ar	CBF-EOM-CCSD	aug-cc-pCV5Z+4(spd)	14°
Ar	CBF-EOM-CCSD	aug-cc-pCV5Z+6(spd)	32°
Ar	CBF-EOM-CCSD	aug-cc-pCV5Z+8(spd)	34°
H_2S	CBF-EOM-CCSD	aug-cc-pCVTZ(5sp)+4(spd)	17°
H_2S	CBF-EOM-CCSD	aug-cc-pCVTZ(5sp)+6(spd)	27°
H_2S	CBF-EOM-CCSD	aug-cc-pCVTZ(5sp)+8(spd)	14°

Table 3: Partial Auger decay widths in meV for the $2s^{-1}$ state of argon computed with CS-EOM-CCSD and CBF-EOM-CCSD using different basis sets. Results from Phys. Rev. A 103, 063102 (2021) obtained using multiconfigurational Dirac-Hartree-Fock (MCDHF) theory are shown as well.

	CS-EOM-CCSD		CBF-EOM-CCSD			MCDHF
	aug-cc-	aug-cc-	aug-cc-pCV5Z			[Phys. Rev. A 103
Decay channel	pCVQZ	pCV5Z	4(spd)	6(spd)	8(spd)	063102 (2021)]
$L_{2,3}M$ channels						
^1P ($2p^{-1}3s^{-1}$)	969.6	1040.7	85.5	612.4	1146.1	414.7
^3D ($2p^{-1}3p^{-1}$)	586.6	569.8	251.0	587.9	492.2	125.1/198.8/337.7[a]
^1S ($2p^{-1}3p^{-1}$)	357.6	389.0	318.3	427.1	361.6	267.9
^1D ($2p^{-1}3p^{-1}$)	229.0	219.1	82.9	399.4	126.5	223.8
^3S ($2p^{-1}3p^{-1}$)	144.5	154.2	83.7	143.7	148.5	143.5
^3P ($2p^{-1}3p^{-1}$)	0.0	0.0	0.0	0.0	0.0	7.2/26.8/18.9[a]
^1P ($2p^{-1}3p^{-1}$)	0.0	0.0	0.0	0.0	0.0	23.6
^3P ($2p^{-1}3s^{-1}$)	-14.1	0.5	–1.4	45.9	–15.9	5.3/213.9/30.3[a]
MM channels						
^1P ($3s^{-1}3p^{-1}$)	44.2	46.6	28.6	47.8	45.1	15.3
^3P ($3s^{-1}3p^{-1}$)	18.4	18.9	8.2	17.5	19.1	3.4/10.1/17.1[a]
^1S ($3s^{-2}$)	13.9	13.7	10.7	14.0	13.6	8.2
^1S ($3p^{-2}$)	4.1	4.1	3.7	3.7	4.0	0.7[b]
^1D ($3p^{-2}$)	-6.5	–6.4	1.2	–4.8	–6.5	
^3P ($3p^{-2}$)	0.0	0.0	0.0	0.0	0.0	

[a] Widths of the $^3P_0/^3P_1/^3P_2$ or $^3D_1/^3D_2/^3D_3$ channels, respectively.

[b] Combined width of the $3p^{-2}$ channels (^1S, ^1D, ^3P).

Table 4: Partial Auger decay widths in meV for the $2a_1^{-1}$ state of hydrogen sulfide computed with CBF-EOM-CCSD using the aug-cc-pCVTZ(5sp) basis set augmented by 4, 6, or 8 complex-scaled shells.

Decay channel	aug-cc-pCVTZ(5sp) 4(spd)	6(spd)	8(spd)	Decay channel	aug-cc-pCVTZ(5sp) 4(spd)	6(spd)	8(spd)
	$L_{2,3}M$ channels				MM channels		
$^1B_2$ $(4a_1^{-1}1b_2^{-1})$	215.2	225.6	244.3	$^1B_2(4a_1^{-1}2b_2^{-1})$	10.3	9.3	9.3
$^1B_1$ $(4a_1^{-1}1b_1^{-1})$	236.1	224.9	208.7	$^1A_1(4a_1^{-2})$	8.7	7.7	7.5
$^1A_1$ $(3a_1^{-1}4a_1^{-1})$	216.9	212.8	236.4	$^1A_1(4a_1^{-1}5a_1^{-1})$	8.8	7.5	7.2
$^1A_1$ $(1b_2^{-1}2b_2^{-1})$	124.8	101.9	97.8	$^1B_1(4a_1^{-1}2b_1^{-1})$	8.6	6.0	5.9
$^1A_1$ $(3a_1^{-1}5a_1^{-1})$	–45.5	100.2	97.2	$^3B_2(4a_1^{-1}2b_2^{-1})$	5.0	3.9	3.8
$^3A_1$ $(1b_2^{-1}2b_2^{-1})$	54.1	73.4	76.1	$^3A_1(4a_1^{-1}5a_1^{-1})$	4.6	3.3	3.2
$^1A_1$ $(1b_1^{-1}2b_1^{-1})$	57.2	57.9	65.2	$^1A_1(5a_1^{-2})$	3.1	2.6	2.7
$^3A_1$ $(3a_1^{-1}5a_1^{-1})$	–21.7	54.9	57.3	$^3B_1(4a_1^{-1}2b_1^{-1})$	3.6	2.6	2.4
$^3A_1$ $(1b_1^{-1}2b_1^{-1})$	37.8	47.4	59.8	$^1B_2(5a_1^{-1}2b_2^{-1})$	1.1	0.7	0.8
$^1B_2$ $(5a_1^{-1}1b_2^{-1})$	9.7	42.2	43.0	$^1B_1(5a_1^{-1}2b_1^{-1})$	1.1	0.6	0.6
$^3B_1$ $(3a_1^{-1}2b_1^{-1})$	23.0	38.3	34.1	$^3B_2(5a_1^{-1}2b_2^{-1})$	0.6	0.5	0.5
$^1B_1$ $(5a_1^{-1}1b_1^{-1})$	29.8	35.9	33.6	$^1A_1(2b_2^{-2})$	0.6	0.4	0.4
$^3A_2$ $(1b_1^{-1}2b_2^{-1})$	8.3	31.4	32.6	$^3B_1(5a_1^{-1}2b_1^{-1})$	0.3	0.3	0.3
$^3B_2$ $(3a_1^{-1}2b_2^{-1})$	11.3	37.7	32.2	$^1A_1(2b_1^{-2})$	0.5	0.1	0.1
$^3A_2$ $(2b_1^{-1}1b_2^{-1})$	10.6	28.6	30.6	$^3A_2(2b_1^{-1}2b_2^{-1})$	0.0	0.0	0.0
$^3B_2$ $(5a_1^{-1}1b_2^{-1})$	–4.2	25.0	26.7	$^1A_2(2b_1^{-1}2b_2^{-1})$	0.0	–0.6	–0.6
$^3B_1$ $(5a_1^{-1}1b_1^{-1})$	16.8	18.9	22.9				
$^1B_1$ $(3a_1^{-1}2b_1^{-1})$	–3.2	21.2	9.2				
$^1A_2$ $(2b_1^{-1}1b_2^{-1})$	–8.8	9.8	8.8				
$^1A_2$ $(1b_1^{-1}2b_2^{-1})$	–1.2	0.3	8.3				
$^1B_2$ $(3a_1^{-1}2b_2^{-1})$	2.9	11.2	6.3				
$^3B_2$ $(4a_1^{-1}1b_2^{-1})$	–3.6	–6.7	–5.3				
$^3A_1$ $(3a_1^{-1}4a_1^{-1})$	1.4	–13.2	–13.7				
$^3B_1$ $(4a_1^{-1}1b_1^{-1})$	–4.3	–17.2	–15.6				

Table 5: Partial Auger decay widths in meV for the $2a_1^{-1}$ state of hydrogen sulfide computed with Fano-EOM-CCSD using the aug-cc-pCVTZ(5sp) basis set and freezing the $1a_1$ and $2a_1$ orbitals. Total energies of the doubly ionized target states are given in Hartree. The ground state of neutral hydrogen sulfide is at -399.16457 a.u.

Decay channel	Total energy	Decay width	Decay channel	Total energy	Decay width
	$L_{2,3}M$ channels			MM channels	
$^1B_1$ ($4a_1^{-1}$ $1b_1^{-1}$)	-391.50805	94.0	$^1A_1$ ($4a_1^{-2}$)	-397.06871	2.5
$^1A_1$ ($3a_1^{-1}$ $4a_1^{-1}$)	-391.50812	94.4	$^1B_1$ ($4a_1^{-1}$ $2b_1^{-1}$)	-397.29553	0.2
$^1B_2$ ($4a_1^{-1}$ $1b_2^{-1}$)	-391.51614	69.5	$^1A_1$ ($4a_1^{-1}$ $5a_1^{-1}$)	-397.48515	2.8
$^3B_1$ ($4a_1^{-1}$ $1b_1^{-1}$)	-391.53342	589.1	$^3B_1$ ($4a_1^{-1}$ $2b_1^{-1}$)	-397.51107	0.4
$^3A_1$ ($3a_1^{-1}$ $4a_1^{-1}$)	-391.54028	617.2	$^1B_2$ ($4a_1^{-1}$ $2b_2^{-1}$)	-397.56269	0.7
$^3B_2$ ($4a_1^{-1}$ $1b_2^{-1}$)	-391.54571	510.0	$^3A_1$ ($4a_1^{-1}$ $5a_1^{-1}$)	-397.59880	0.4
$^1A_1$ ($1b_1^{-1}$ $2b_1^{-1}$)	-391.89365	53.1	$^3B_2$ ($4a_1^{-1}$ $2b_2^{-1}$)	-397.68791	0.5
$^1B_1$ ($3a_1^{-1}$ $2b_1^{-1}$)	-391.92273	76.1	$^1A_1$ ($2b_1^{-2}$)	-397.70788	0.4
$^1A_2$ ($2b_1^{-1}$ $1b_2^{-1}$)	-391.93410	43.8	$^1B_1$ ($5a_1^{-1}$ $2b_1^{-1}$)	-397.82839	0.6
$^3B_1$ ($3a_1^{-1}$ $2b_1^{-1}$)	-391.94041	102.1	$^3B_1$ ($5a_1^{-1}$ $2b_1^{-1}$)	-397.88710	0.2
$^3A_1$ ($1b_1^{-1}$ $2b_1^{-1}$)	-391.94593	255.1	$^1A_1$ ($5a_1^{-2}$)	-397.89703	0.5
$^3A_2$ ($2b_1^{-1}$ $1b_2^{-1}$)	-391.94798	60.9	$^1A_2$ ($2b_1^{-1}$ $2b_2^{-1}$)	-397.96118	0.5
$^1A_1$ ($3a_1^{-1}$ $5a_1^{-1}$)	-391.94873	73.1	$^3A_2$ ($2b_1^{-1}$ $2b_2^{-1}$)	-397.99345	0.0
$^1B_2$ ($5a_1^{-1}$ $1b_2^{-1}$)	-391.98548	64.4	$^1B_2$ ($5a_1^{-1}$ $2b_2^{-1}$)	-398.02620	0.6
$^3B_1$ ($5a_1^{-1}$ $1b_1^{-1}$)	-392.00506	199.9	$^3B_2$ ($5a_1^{-1}$ $2b_2^{-1}$)	-398.07858	0.2
$^1B_1$ ($5a_1^{-1}$ $1b_1^{-1}$)	-392.00615	18.0	$^1A_1$ ($2b_2^{-2}$)	-398.11993	0.6
$^3B_2$ ($5a_1^{-1}$ $1b_2^{-1}$)	-392.00696	139.2			
$^3A_1$ ($3a_1^{-1}$ $5a_1^{-1}$)	-392.01102	283.0			
$^1A_1$ ($1b_2^{-1}$ $2b_2^{-1}$)	-392.04610	86.7			
$^1A_2$ ($1b_1^{-1}$ $2b_2^{-1}$)	-392.10138	28.4			
$^3A_2$ ($1b_1^{-1}$ $2b_2^{-1}$)	-392.10779	129.2			
$^1B_2$ ($3a_1^{-1}$ $2b_2^{-1}$)	-392.11116	22.5			
$^3B_2$ ($3a_1^{-1}$ $2b_2^{-1}$)	-392.11196	144.0			
$^3A_1$ ($1b_2^{-1}$ $2b_2^{-1}$)	-392.12382	269.2			

Table 6: Total energies of dicationic states of argon in Hartree computed with EOM-DIP-CCSD and the aug-cc-pCV5Z basis set. The ground state of the neutral argon atom is at -527.50192261 a.u.

State	Energy	State	Energy
$^1S(2s^{-2})$	-502.11953780	$^1S(2p^{-1}3p^{-1})$	-516.93623795
$^1P(2s^{-1}2p^{-1})$	-504.15162313	$^1D(2p^{-1}3p^{-1})$	-517.00415593
$^3P(2s^{-1}2p^{-1})$	-504.99960172	$^3P(2p^{-1}3p^{-1})$	-517.05644742
$^1S(2p^{-2})$	-506.71950954	$^3S(2p^{-1}3p^{-1})$	-517.08070346
$^1D(2p^{-2})$	-507.04763959	$^3D(2p^{-1}3p^{-1})$	-517.10768441
$^3P(2p^{-2})$	-507.32726971	$^1P(2p^{-1}3p^{-1})$	-517.12890315
$^1S(2s^{-1}3s^{-1})$	-513.64440003	$^1S(3s^{-2})$	-524.63993328
$^3S(2s^{-1}3s^{-1})$	-513.75903219	$^1P(3s^{-1}3p^{-1})$	-525.15594198
$^1P(2s^{-1}3p^{-1})$	-514.30769076	$^3P(3s^{-1}3p^{-1})$	-525.33962206
$^3P(2s^{-1}3p^{-1})$	-514.56199259	$^1S(3p^{-2})$	-525.73558656
$^1P(2p^{-1}3s^{-1})$	-516.40222113	$^1D(3p^{-2})$	-525.82512212
$^3P(2p^{-1}3s^{-1})$	-516.44380731	$^3P(3p^{-2})$	-525.88588074

Table 7: Total energies of dicationic states of hydrogen sulfide in Hartree computed with EOM-DIP-CCSD and the aug-cc-pCVTZ(5sp) basis set. The ground state of neutral hydrogen sulfide is at -399.29963301 a.u.

State	Energy	State	Energy	State	Energy
$^1B_1(4a_1^{-1}1b_1^{-1})$	-391.50805055	$^3B_1(5a_1^{-1}1b_1^{-1})$	-392.00505733	$^1B_2(4a_1^{-1}2b_2^{-1})$	-397.56268737
$^1A_1(3a_1^{-1}4a_1^{-1})$	-391.50812376	$^1B_1(5a_1^{-1}1b_1^{-1})$	-392.00614771	$^3A_1(4a_1^{-1}5a_1^{-1})$	-397.59880345
$^1B_2(4a_1^{-1}1b_2^{-1})$	-391.51614467	$^3B_2(5a_1^{-1}1b_2^{-1})$	-392.00695775	$^3B_2(4a_1^{-1}2b_2^{-1})$	-397.68790891
$^3B_1(4a_1^{-1}1b_1^{-1})$	-391.53341771	$^3A_1(3a_1^{-1}5a_1^{-1})$	-392.01102152	$^1A_1(2b_1^{-2})$	-397.70787930
$^3A_1(3a_1^{-1}4a_1^{-1})$	-391.54027728	$^1A_1(1b_2^{-1}2b_2^{-1})$	-392.04610035	$^1B_1(5a_1^{-1}2b_1^{-1})$	-397.82838608
$^3B_2(4a_1^{-1}1b_2^{-1})$	-391.54571226	$^1A_2(1b_1^{-1}2b_2^{-1})$	-392.10138109	$^3B_1(5a_1^{-1}2b_1^{-1})$	-397.88709715
$^1A_1(1b_1^{-1}2b_1^{-1})$	-391.89364688	$^3A_2(1b_1^{-1}2b_2^{-1})$	-392.10778991	$^1A_1(5a_1^{-2})$	-397.89702856
$^1B_1(3a_1^{-1}2b_1^{-1})$	-391.92272791	$^1B_2(3a_1^{-1}2b_2^{-1})$	-392.11116374	$^1A_2(2b_1^{-1}2b_2^{-1})$	-397.96117751
$^1A_2(2b_1^{-1}1b_2^{-1})$	-391.93409866	$^3B_2(3a_1^{-1}2b_2^{-1})$	-392.11196153	$^3A_2(2b_1^{-1}2b_2^{-1})$	-397.99345391
$^3B_1(3a_1^{-1}2b_1^{-1})$	-391.94040548	$^3A_1(1b_2^{-1}2b_2^{-1})$	-392.12382102	$^1B_2(5a_1^{-1}2b_2^{-1})$	-398.02619840
$^3A_1(1b_1^{-1}2b_1^{-1})$	-391.94593051	$^1A_1(4a_1^{-2})$	-397.06870917	$^3B_2(5a_1^{-1}2b_2^{-1})$	-398.07858230
$^3A_2(2b_1^{-1}1b_2^{-1})$	-391.94797578	$^1B_1(4a_1^{-1}2b_1^{-1})$	-397.29553406	$^1A_1(2b_2^{-2})$	-398.11993149
$^1A_1(3a_1^{-1}5a_1^{-1})$	-391.94872814	$^1A_1(4a_1^{-1}5a_1^{-1})$	-397.48514587		
$^1B_2(5a_1^{-1}1b_2^{-1})$	-391.98547668	$^3B_1(4a_1^{-1}2b_1^{-1})$	-397.51106502		

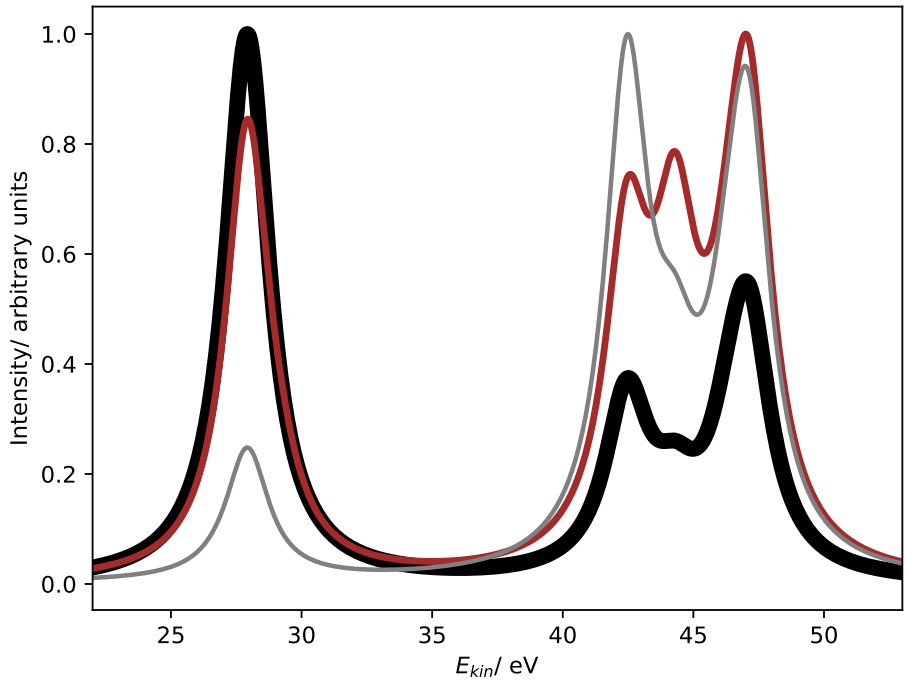

Figure 1: $L_1L_{2,3}M$ Coster-Kronig spectrum of argon. Partial decay widths were computed with CBF-EOM-CCSD and the aug-cc-pCV5Z basis set augmented by 4 (gray), 6 (brown), and 8 (black) complex-scaled s, p, and d shells.

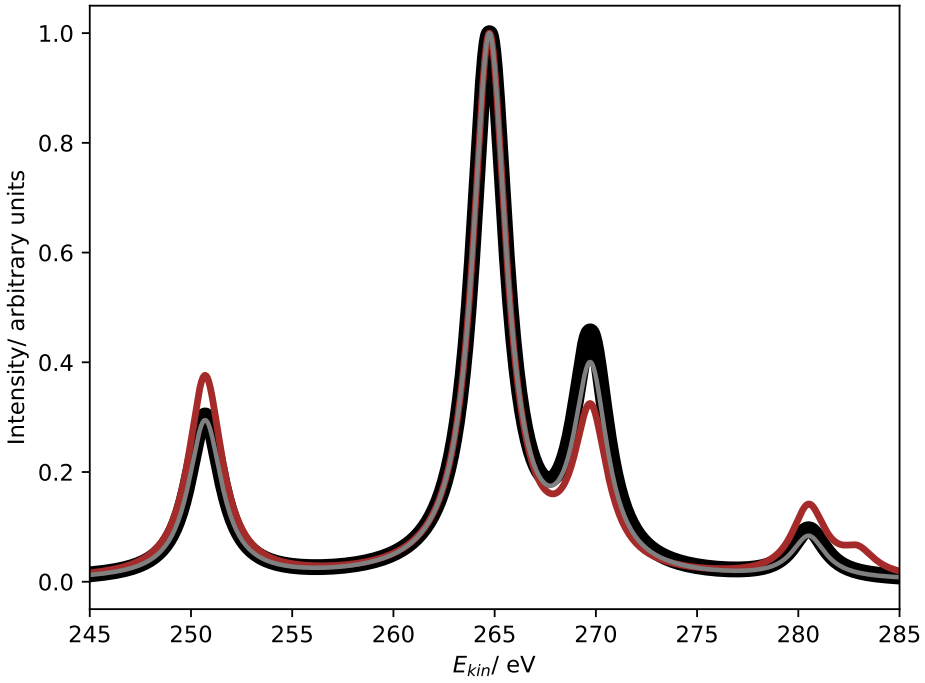

Figure 2: L_1MM Auger spectrum of argon. Partial decay widths were computed with CBF-EOM-CCSD and the aug-cc-pCV5Z basis set augmented by 4 (gray), 6 (brown), and 8 (black) complex-scaled s, p, and d shells.

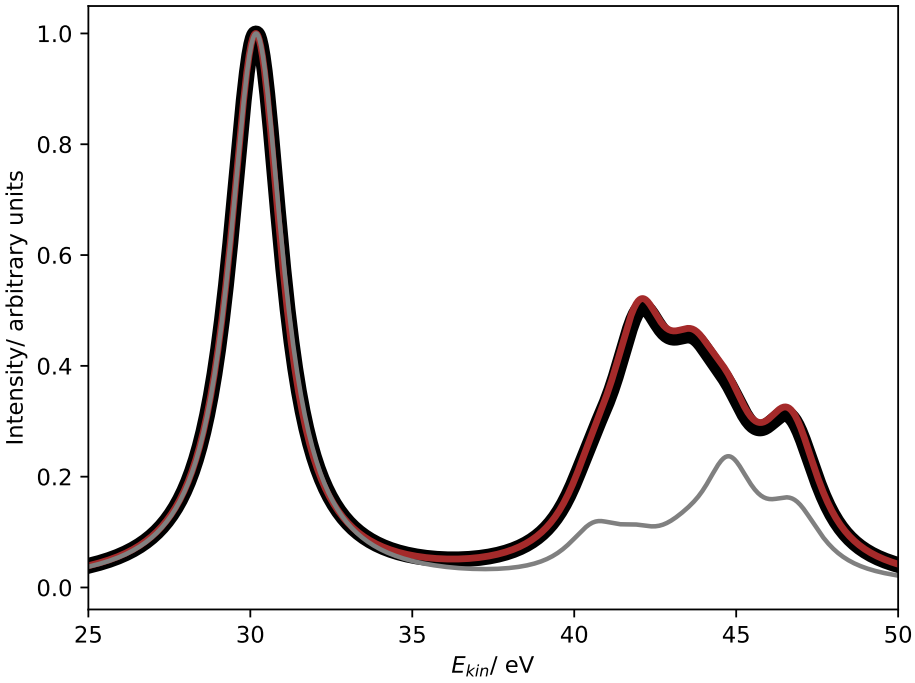

Figure 3: $L_1L_{2,3}M$ Coster-Kronig spectrum of hydrogen sulfide. Partial decay widths were computed with CBF-EOM-CCSD and the aug-cc-pCVTZ(5sp) basis set augmented by 4 (gray), 6 (brown), and 8 (black) complex-scaled s, p, and d shells.

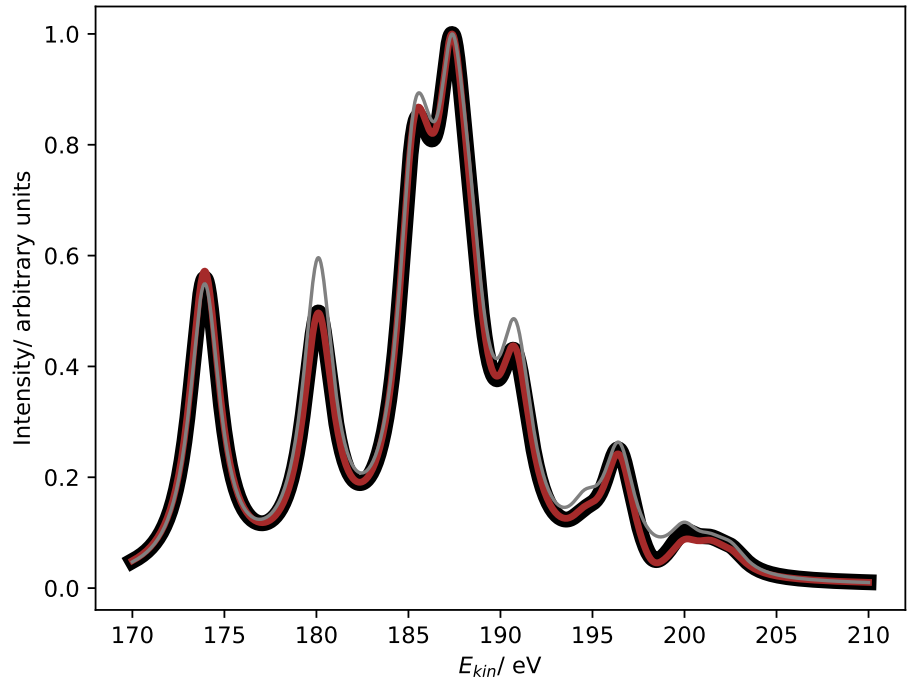

Figure 4: L_1MM Auger spectrum of hydrogen sulfide. Partial decay widths were computed with CBF-EOM-CCSD and the aug-cc-pCVTZ(5sp) basis set augmented by 4 (gray), 6 (brown), and 8 (black) complex-scaled s, p, and d shells.