SUPPLEMENTARY MATERIAL

Table S1. Results of ab initio calculations for Al_2Cl_6 and Al_2Br_6.

Table S2. Results of ab initio calculations for $AlCl_3$, $AlBr_3$ and AlI_3.

Table S3. Average molecular intensities, $sI_m(s)$, for Al_2Cl_6 at 150 °C. (All intensities in Tables S3-S7 are in the form: $sI_m(s) = k\Sigma A_i A_j r_{ij}^{-1} \cos(\eta_i - \eta_j) \exp(-l_{ij}^2 s^2/2) \sin s r_{ij}$ where $A_i = s^2 F_i$; F_i is the electron scattering amplitude).

Table S4. Average molecular intensities, $sI_m(s)$, for Al_2Br_6 at 167 °C.

Table S5. Average molecular intensities, $sI_m(s)$, for $AlCl_3$ at 400 °C.

Table S6. Average molecular intensities, $sI_m(s)$, for $AlBr_3$ at 330 °C.

Table S7. Average molecular intensities, $sI_m(s)$, for AlI_3 at 300 °C.

Table S1. Results of *Ab initio* Calculations for Al_2Cl_6 and Al_2Br_6[a]

	$r(Al\text{-}Cl_b)$	$r(Al_1\text{-}Cl_5)$	$r(Al_1\text{-}Cl_6)$	$\angle(Cl_tAlCl_t)$	$\angle(Cl_bAlCl_5)$	$\angle(Cl_bAlCl_6)$	$\angle(Cl_bAlCl_b)$	$\angle(AlCl_bAl)$	$E_h + 3241$
Φ[b]					Al_2Cl_6				
	HF/6-31G(d)								
0	2.289	2.083	2.083	121.76	110.29	110.29	89.13	90.87	-0.1812274
5	2.289	2.083	2.083	121.83	110.27	110.30	89.00	90.56	-0.1809760
10	2.290	2.083	2.083	121.87	110.38	110.33	88.55	89.68	-0.1801366
15	2.293	2.081	2.083	121.74	110.80	110.29	87.75	88.26	-0.1783924
20	2.299	2.079	2.084	121.25	111.85	110.00	86.54	86.35	-0.1750493
	HF/6-31G(d,p)								
0	2.289	2.083	2.083	121.76	110.29	110.29	89.13	90.87	-0.1812274
5	2.289	2.083	2.083	121.79	110.29	110.32	88.99	90.57	-0.1809763
10	2.290	2.083	2.083	121.82	110.39	110.36	88.55	89.68	-0.1801368
15	2.293	2.081	2.083	121.70	110.80	110.32	87.75	88.26	-0.1783924
20	2.299	2.079	2.084	121.20	111.86	110.02	86.55	86.35	-0.1750491
	HF/6-31+G(d)								
0	2.288	2.083	2.083	121.75	110.29	110.29	89.11	90.89	-0.1853243
5	2.288	2.083	2.083	121.78	110.29	110.33	88.97	90.59	-0.1850977
10	2.290	2.082	2.083	121.81	110.38	110.37	88.52	89.70	-0.1843181
15	2.293	2.081	2.083	121.70	110.79	110.33	87.73	88.28	-0.1826494
20	2.298	2.079	2.083	121.22	111.84	110.04	86.52	86.36	-0.1793860
	HF/6-311G(d)								
0	2.278	2.077	2.077	121.76	110.25	110.25	89.32	90.68	-0.3624824
5	2.278	2.077	2.077	121.78	110.25	110.28	89.18	90.38	-0.3622023
10	2.280	2.076	2.077	121.80	110.36	110.32	88.76	89.48	-0.3612750
15	2.283	2.075	2.077	121.68	110.77	110.27	88.00	88.03	-0.3593881
20	2.289	2.073	2.077	121.20	111.81	109.98	86.78	86.14	-0.3558512
	HF/6-311G(d,p)								
0	2.278	2.077	2.077	121.76	110.25	110.25	89.32	90.68	-0.3624824
5	2.278	2.077	2.077	121.77	110.25	110.29	89.18	90.38	-0.3622023
10	2.280	2.076	2.077	121.79	110.36	110.33	88.76	89.48	-0.3612750
15	2.283	2.075	2.077	121.69	110.76	110.29	87.94	88.08	-0.3593876
20	2.288	2.073	2.078	121.16	111.82	109.98	86.83	86.09	-0.3558517
	HF/6-311+G(d)								
0	2.282	2.079	2.079	121.84	110.23	110.23	89.28	90.72	-0.3748016
5	2.282	2.079	2.079	121.83	110.22	110.29	89.16	90.39	-0.3745515
10	2.284	2.079	2.079	121.87	110.29	110.36	88.71	89.52	-0.3737163
15	2.287	2.078	2.079	121.76	110.67	110.34	87.94	88.08	-0.3719774
20	2.292	2.076	2.080	121.23	111.74	110.04	86.77	86.15	-0.3686092

Continued

	MP2/6-31G(d)								
0	2.265	2.078	2.078	121.84	109.91	109.91	91.04	88.96	-1.0612557
5	2.266	2.078	2.078	121.91	109.88	109.96	90.85	88.72	-1.0611172
10	2.267	2.077	2.078	121.94	109.99	110.01	90.36	87.93	-1.0605964
15	2.270	2.076	2.078	121.78	110.51	109.95	89.40	86.72	-1.0593373
20	2.276	2.074	2.079	121.29	111.68	109.60	88.02	85.04	-1.0566801
	MP2/6-311G(d)								
0	2.256	2.070	2.070	122.42	109.70	109.70	91.16	88.85	-1.2934684
5	2.256	2.070	2.070	122.38	109.74	109.74	90.99	88.58	-1.2932769
10	2.258	2.069	2.070	122.40	109.88	109.76	90.54	87.75	-1.2926162
15	2.261	2.068	2.070	122.35	110.31	109.65	89.74	86.40	-1.2911911
20	2.266	2.067	2.071	121.76	111.39	109.40	88.52	84.60	-1.2883566
					Al_2Br_6				
	HF/6-311G(d)								E_h + 15918
0	2.454	2.246	2.246	120.72	110.20	110.20	91.42	88.58	-0.5285364
5	2.454	2.246	2.246	120.75	110.29	110.17	91.21	88.36	-0.5283579
10	2.456	2.245	2.246	120.78	110.42	110.19	90.77	87.53	-0.5277403
15	2.459	2.244	2.246	120.67	110.93	110.06	89.95	86.21	-0.5263916
20	2.464	2.241	2.247	120.19	112.08	109.67	88.74	84.41	-0.5236734

[a]Distances in Ångstrøms and angles in degrees. [b]Ring puckering angle.

Table S2. Results of *Ab Initio* Calculations for $AlCl_3$, $AlBr_3$, and AlI_3[a]

theory	*r*(Al-X)	energy/h
$AlCl_3$		
HF/6-31G(d)	2.077	-1620.5760867
HF/6-311G(d)	2.071	-1620.6668404
HF/6-311+G(d)	2.073	-1620.6719325
MP2/6-31G(d)	2.072	-1620.5760602
MP2/6-311G(d)	2.066	-1620.6668038
$AlBr_3$		
HF/6-311G(d)	2.235	-7959.2531757
AlI_3		
HF/LANL2DZ	2.534	-35.5326084
HF/HW(ECP)[b]	2.485	-275.5634803

[a]Distances in Ångstrøms, energies in hartrees. [b]HW(ECP) is HW(ECP)(d) basis set for I and 6-31G(d) for Al

Table S3. Average molecular intensities for Al_2Cl_6 at 150 °C.

1.AVE. 6-2-1 6-2-2 6-2-3

S	.00	.25	.50	.75
2.	.00	.77	-19.22	-52.54
3.	-65.38	-14.75	69.74	162.64
4.	235.19	183.07	-25.95	-248.16
5.	-333.87	-251.06	-65.04	117.77
6.	205.60	169.13	66.26	15.33
7.	57.88	118.60	66.69	-79.92
8.	-215.82	-268.16	-221.72	-77.17
9.	123.19	277.46	281.14	164.25
10.	15.34	-85.65	-113.07	-89.96
11.	-73.17	-78.89	-116.27	-115.97
12.	-35.02	104.05	215.75	224.76
13.	141.69	8.52	-108.25	-156.61
14.	-125.45	-53.95	-10.33	-3.01
15.	-20.03	-24.66	-2.48	56.16
16.	121.94	130.32		

2.AVE. 6-2-6 6-2-7 6-2-8

S	.00	.25	.50	.75
8.	.00	-278.44	-214.01	-65.79
9.	125.40	259.59	272.48	173.60
10.	35.02	-60.15	-86.75	-89.52
11.	-85.56	-105.98	-148.96	-143.06
12.	-43.09	102.22	208.66	230.41
13.	141.99	14.85	-105.57	-150.95
14.	-116.00	-32.53	21.79	29.95
15.	7.52	-20.76	-6.46	45.15
16.	106.73	128.03	88.46	-.65
17.	-90.23	-130.95	-137.98	-104.51
18.	-46.40	-7.72	19.95	32.85
19.	56.09	78.28	101.79	76.95
20.	28.12	-26.11	-82.19	-121.24
21.	-121.41	-79.93	-.07	62.45
22.	114.35	153.66	141.26	109.49
23.	30.21	-40.66	-103.09	-143.93
24.	-143.77	-92.16	-41.80	31.06
25.	90.94	122.81	100.32	80.35
26.	3.72	-62.09	-113.52	-137.39
27.	-139.99	-80.37	-21.05	62.02
28.	133.70	153.91	142.63	110.59
29.	34.34	-49.46	-91.67	-125.43
30.	-121.74	-81.57	-17.11	32.49
31.	69.88	88.21	83.31	81.50
32.	25.86	-45.56	-91.67	-81.54
33.	-79.75	-55.25	-4.92	40.70
34.	81.92	98.14	75.69	38.00
35.	-27.68	-24.40	-59.54	-75.75
36.	-72.27	-35.37	-28.96	23.69
37.	61.84	82.73	71.90	34.65
38.	-7.97			

Table S4. Average molecular intensities for Al_2Br_6 at 167 °C.

1.AVE. 5-19-1 5-19-2

S	.00	.25	.50	.75
2.	.00	12.56	-58.52	-103.00
3.	-61.21	76.74	238.83	314.61
4.	192.27	-166.10	-451.17	-439.58
5.	-137.03	196.48	333.51	246.77
6.	4.04	-125.22	1.12	239.02
7.	227.16	-78.21	-418.24	-526.69
8.	-344.52	71.79	491.32	606.96
9.	340.80	-47.99	-260.77	-248.94
10.	-112.81	-22.73	-75.92	-204.54
11.	-219.81	-9.18	316.32	429.21
12.	323.20	40.60	-218.53	-298.34
13.	-217.39	-49.73	62.88	6.80
14.	-31.79	-6.27	55.00	158.09
15.	183.12	121.72	-45.92	-137.72
16.	-169.42	-151.61		

2.AVE. 5-18-1 5-18-2 5-18-3

S	.00	.25	.50	.75
8.	.00	12.63	423.78	529.28
9.	255.89	-76.59	-238.21	-174.18
10.	-40.89	15.24	-39.80	-145.62
11.	-169.85	-64.97	226.30	282.92
12.	183.20	8.98	-175.75	-222.68
13.	-119.27	-10.78	20.67	17.00
14.	3.48	12.39	56.19	149.11
15.	214.36	150.32	6.06	-116.37
16.	-157.55	-136.69	-36.47	-5.98
17.	10.24	3.73	5.52	36.84
18.	41.61	52.72	14.41	-75.64
19.	-171.80	-150.05	-100.50	-1.54
20.	58.58	134.04	139.17	117.54
21.	103.28	7.06	-60.62	-89.16
22.	-114.50	-112.82	-50.50	55.47
23.	88.23	152.93	148.52	120.07
24.	15.98	-34.17	-93.59	-120.26
25.	-115.50	-40.96	8.21	47.84
26.	69.44	52.23	40.95	1.53
27.	-48.48	-91.28	-92.60	-106.17
28.	-71.57	-36.11	50.10	56.03
29.	80.11	20.55	91.31	38.85
30.	1.20	-44.52	-68.29	-14.88
31.	8.16	54.73	57.65	37.38
32.	62.47	39.62	-30.52	-103.52
33.	-25.23	-56.26	-1.97	-10.33
34.	64.90	58.76	93.83	-8.09
35.	-29.23	-82.50	-101.27	-81.55
36.	-83.07	-17.78	35.13	122.96
37.	61.25	99.49	59.32	-29.54
38.	-76.34			

Table S5. Average molecular intensities for $AlCl_3$ at 400 °C

1.AVE. 5-148-1 5-148-2

S	.00	.25	.50	.75
2.	.00	-3.24	-16.80	-34.68
3.	-41.26	-9.84	46.06	106.97
4.	134.74	87.91	-21.41	-117.20
5.	-153.49	-120.22	-46.34	22.83
6.	51.77	49.30	37.62	50.32
7.	86.70	105.51	61.66	-27.69
8.	-120.50	-169.59	-157.45	-82.62
9.	25.41	111.98	141.32	117.17
10.	73.96	29.70	-.71	-28.07
11.	-66.60	-106.02	-131.88	-116.84
12.	-54.94	45.28	125.37	164.44
13.	145.86	83.10	7.59	-56.30
14.	-95.77	-110.13	-111.30	-87.61
15.	-49.13	4.84	65.38	112.49
16.	121.32			

2.AVE. 5-149-1 5-149-2

S	.00	.25	.50	.75
8.	.00	-176.86	-157.29	-73.42
9.	28.86	106.14	139.48	128.02
10.	77.41	38.16	9.85	-27.33
11.	-72.19	-118.80	-147.00	-124.26
12.	-50.01	51.75	134.31	168.26
13.	143.10	76.89	-1.06	-60.60
14.	-97.78	-102.30	-91.53	-69.34
15.	-45.28	.34	56.80	98.42
16.	124.31	105.42	61.61	-9.95
17.	-75.27	-108.65	-120.20	-100.64
18.	-43.95	6.08	48.41	80.69
19.	104.32	96.02	65.97	23.31
20.	-29.21	-76.24	-95.32	-93.83
21.	-68.01	-17.49	31.00	72.61
22.	94.78	86.64	59.67	11.90
23.	-28.22	-68.84	-88.12	-85.01
24.	-68.71	-22.72	14.45	57.70
25.	78.03	80.80	62.87	23.41
26.	-12.92	-45.83	-58.71	-60.77
27.	-48.46	-18.64	10.37	33.68
28.	64.62	50.05	43.33	16.43
29.	-7.99	-33.25	-50.39	-44.21
30.	-44.97	-21.42	-.94	30.24
31.	36.29	44.65	38.06	29.56
32.	-10.51	-18.97	-41.83	-34.68
33.	-32.90	-17.83	10.84	4.74
34.	32.13	38.19	32.59	5.18
35.	-5.69	-12.72	-1.61	-19.15
36.	-30.16	-16.53	-6.73	-13.00
37.	22.00	31.70	29.82	8.98
38.	-7.49			

Table S6. Average molecular intensities for $AlBr_3$ at 330 °C

1.AVE. 5-138-1 5-138-2

S	.00	.25	.50	.75
2.	.00	-7.68	-28.42	-42.72
3.	-28.38	41.02	112.44	133.43
4.	71.55	-53.18	-153.42	-155.65
5.	-67.29	27.36	62.41	35.77
6.	-4.47	11.20	96.00	173.30
7.	141.46	-11.18	-201.50	-300.53
8.	-237.87	-49.26	144.39	230.19
9.	193.47	91.42	14.55	5.40
10.	7.02	-42.16	-139.26	-222.23
11.	-215.77	-82.68	114.26	258.96
12.	276.97	177.13	22.96	-94.71
13.	-147.41	-151.83	-133.73	-110.98
14.	-70.05	12.22	104.90	188.67
15.	205.79	139.54	17.87	-107.10
16.	-147.95			

2.AVE. 5-139-1 5-139-2

S	.00	.25	.50	.75
8.	.00	-58.54	134.31	214.44
9.	176.75	63.63	-1.37	12.72
10.	9.73	-23.19	-100.72	-195.37
11.	-188.76	-105.89	66.58	209.73
12.	260.28	184.57	56.86	-49.05
13.	-126.51	-147.37	-148.59	-114.39
14.	-62.91	-2.24	98.82	173.09
15.	199.64	123.67	35.62	-85.78
16.	-159.57	-173.51	-135.50	-81.66
17.	7.40	59.78	95.73	118.40
18.	96.78	62.14	-7.82	-71.19
19.	-96.01	-81.85	-42.97	2.15
20.	71.26	104.70	112.38	86.12
21.	56.57	-9.62	-47.57	-103.77
22.	-109.80	-87.31	-54.72	-2.29
23.	18.04	72.71	52.23	29.39
24.	2.25	-40.09	-74.95	-76.22
25.	-40.80	-19.07	26.70	47.61
26.	83.27	69.37	58.44	53.98
27.	15.80	-37.24	-50.09	-41.68
28.	-47.88	-1.18	13.30	25.34
29.	39.39	40.21	26.15	20.05
30.	-36.05	-41.42	-46.13	-34.08
31.	-25.96	-12.12	5.06	23.65
32.	-12.14	29.63	-3.91	2.51
33.	-1.68	-13.03	-19.48	-28.68
34.	26.95	30.05	19.40	31.38
35.	8.22	7.07	26.09	-32.73
36.	8.78	-16.30	-7.41	-30.36
37.	-15.23	13.12	-7.15	-10.44
38.	43.21			

Table S7. Average molecular intensities for AlI_3 at 300 °C

1.AVE. 5-129-1 5-129-11 5-129-12

S	.00	.25	.50	.75
2.	.00	-28.35	-51.30	-25.71
3.	54.44	146.80	125.45	-7.03
4.	-140.08	-173.61	-81.19	53.94
5.	86.29	8.82	-44.67	22.47
6.	150.84	202.27	60.60	-178.29
7.	-324.71	-238.45	3.75	209.84
8.	234.92	116.61	-12.72	-24.96
9.	11.43	11.29	-79.09	-195.09
10.	-188.28	-49.88	146.89	246.99
11.	192.94	41.17	-84.29	-122.91
12.	-94.93	-59.78	-58.57	-38.24
13.	17.57	90.52	141.85	116.37
14.	18.64			

2.AVE. 5-130-1 5-130-2

S	.00	.25	.50	.75
8.	.00	77.09	-7.56	-14.61
9.	14.48	-9.84	-71.47	-131.02
10.	-129.74	-14.94	143.17	194.06
11.	125.66	-2.25	-96.04	-112.12
12.	-65.00	-31.51	-23.79	-19.60
13.	10.52	52.46	79.89	72.54
14.	34.34	-35.55	-63.27	-53.66
15.	-21.46	6.82	33.89	45.04
16.	51.72	32.76	9.29	-30.19
17.	-52.56	-57.50	-69.20	-42.50
18.	-7.23	31.66	45.18	28.40
19.	33.23	15.35	-14.69	-13.12
20.	-16.75	-16.96	5.54	12.93
21.	33.13	38.97	15.54	7.14
22.	-10.87	-9.09	-13.35	-13.17
23.	-21.10	6.47	14.99	11.57
24.	8.18	-12.82	-20.45	-23.64
25.	-11.51	-12.09	-2.92	-12.75
26.	-2.80	-8.62	11.34	30.93
27.	3.19	2.59	14.39	-15.87
28.	-14.49	-32.64	9.48	27.55
29.	48.69	18.05	8.12	5.03
30.	-10.13	3.28	19.83	6.41
31.	2.01	-21.48	-6.92	-31.04
32.	-29.48	-42.39	-8.09	-1.59
33.	21.47	14.62	5.06	-15.87
34.	19.54	28.09	-13.69	-25.66
35.	3.67	25.29	32.46	8.73
36.	-3.28	-5.96	15.26	-13.04
37.	-30.96	-19.51	-15.88	.73
38.	36.30			