

Electronic Supplementary Information

for:

Assignment of the solid state spectra of the Group VI hexacarbonyls by inelastic neutron scattering spectroscopy

Stewart F. Parker^{*1,a)} and Upali A. Jayasooriya²⁾

¹ISIS Facility, STFC Rutherford Appleton Laboratory, Chilton, Didcot, Oxon OX11 0QX, UK,

²School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ, UK.

Table of contents	Page
Figure S1: Dispersion curves of Cr(CO) ₆ in the C≡O stretch region.	2
Figure S2: Dispersion curves of Mo(CO) ₆ in the C≡O stretch region.	2
Figure S3: Dispersion curves of Mo(CO) ₆ in the M–C stretch and M–C≡O deformation region.	3
Figure S4: Dispersion curves of Mo(CO) ₆ in the C–M–C bend and lattice mode region.	3
Figure S5: Dispersion curves of W(CO) ₆ in the C≡O stretch region.	4
Figure S6: Dispersion curves of W(CO) ₆ in the M–C stretch and M–C≡O deformation region.	4
Figure S7: Dispersion curves of W(CO) ₆ in the C–M–C bend and lattice mode region.	5
Table S1: CASTEP calculated transition energies for Cr(CO) ₆ and assignments.	6
Table S2: CASTEP calculated transition energies for Mo(CO) ₆ and assignments.	8
Table S3: CASTEP calculated transition energies for W(CO) ₆ and assignments.	11

^{*a)} Author to whom correspondence should be addressed.

Electronic mail: stewart.parker@stfc.ac.uk

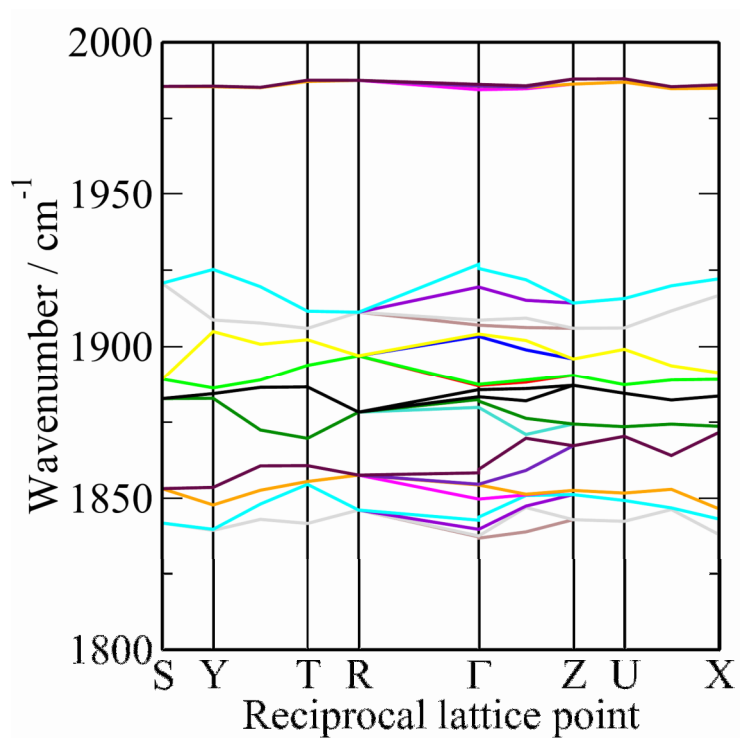


Figure S1: Dispersion curves of $\text{Cr}(\text{CO})_6$ in the $\text{C}\equiv\text{O}$ stretch region.

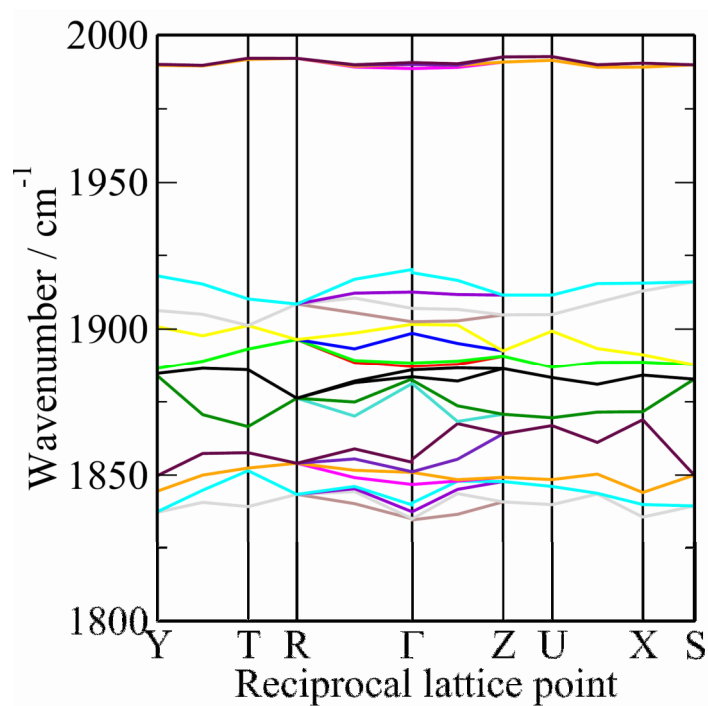


Figure S2: Dispersion curves of $\text{Mo}(\text{CO})_6$ in the $\text{C}\equiv\text{O}$ stretch region.

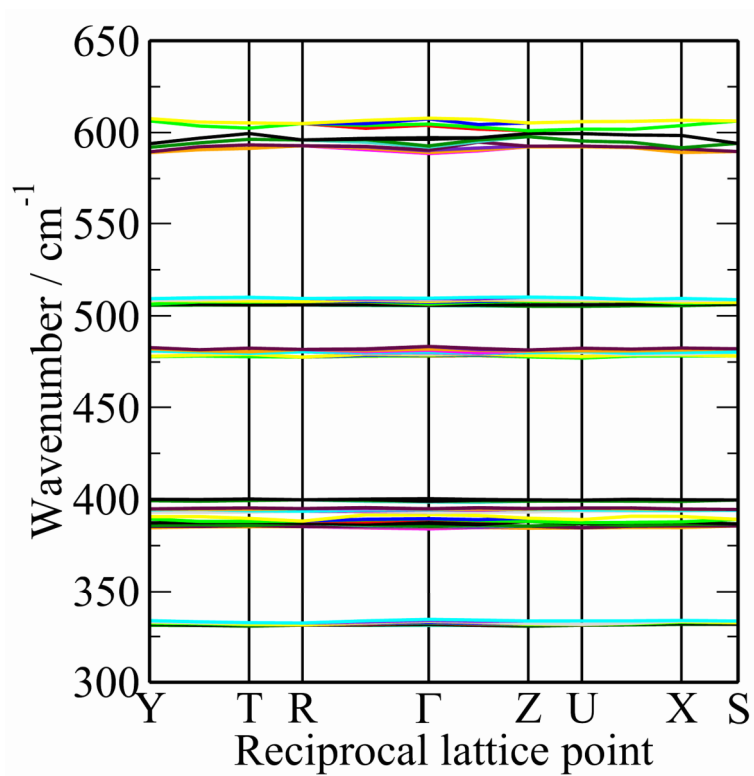


Figure S3: Dispersion curves of Mo(CO)₆ in the M-C stretch and M-C=O deformation region.

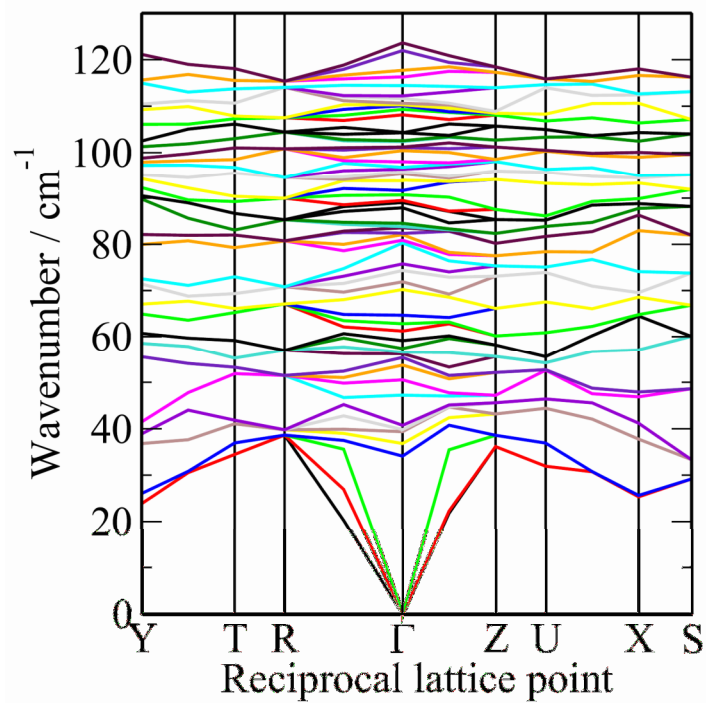


Figure S4: Dispersion curves of Mo(CO)₆ in the C-M-C bend and lattice mode region.

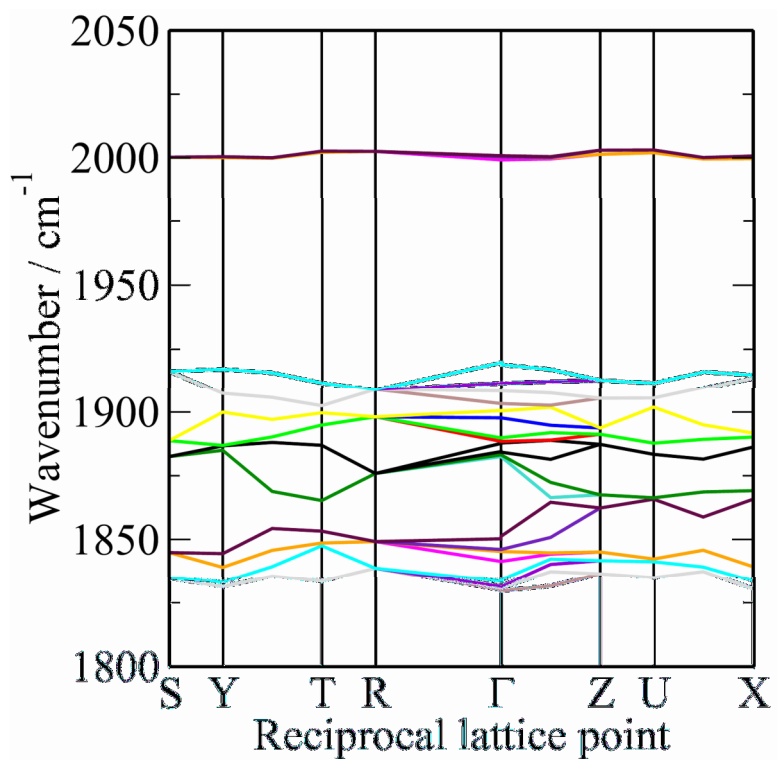


Figure S5: Dispersion curves of W(CO)₆ in the C=O stretch region.

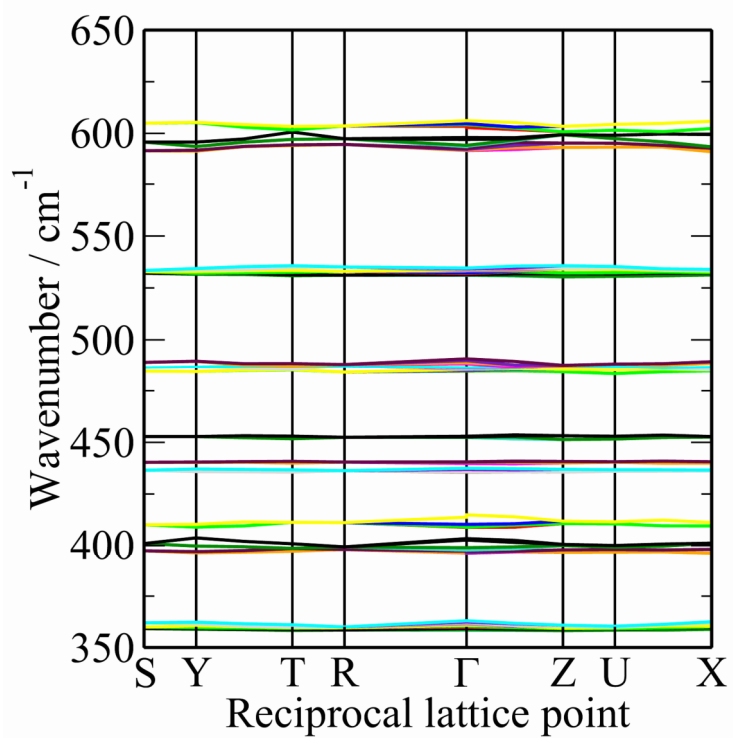


Figure S6: Dispersion curves of W(CO)₆ in the M-C stretch and M-C≡O deformation region.

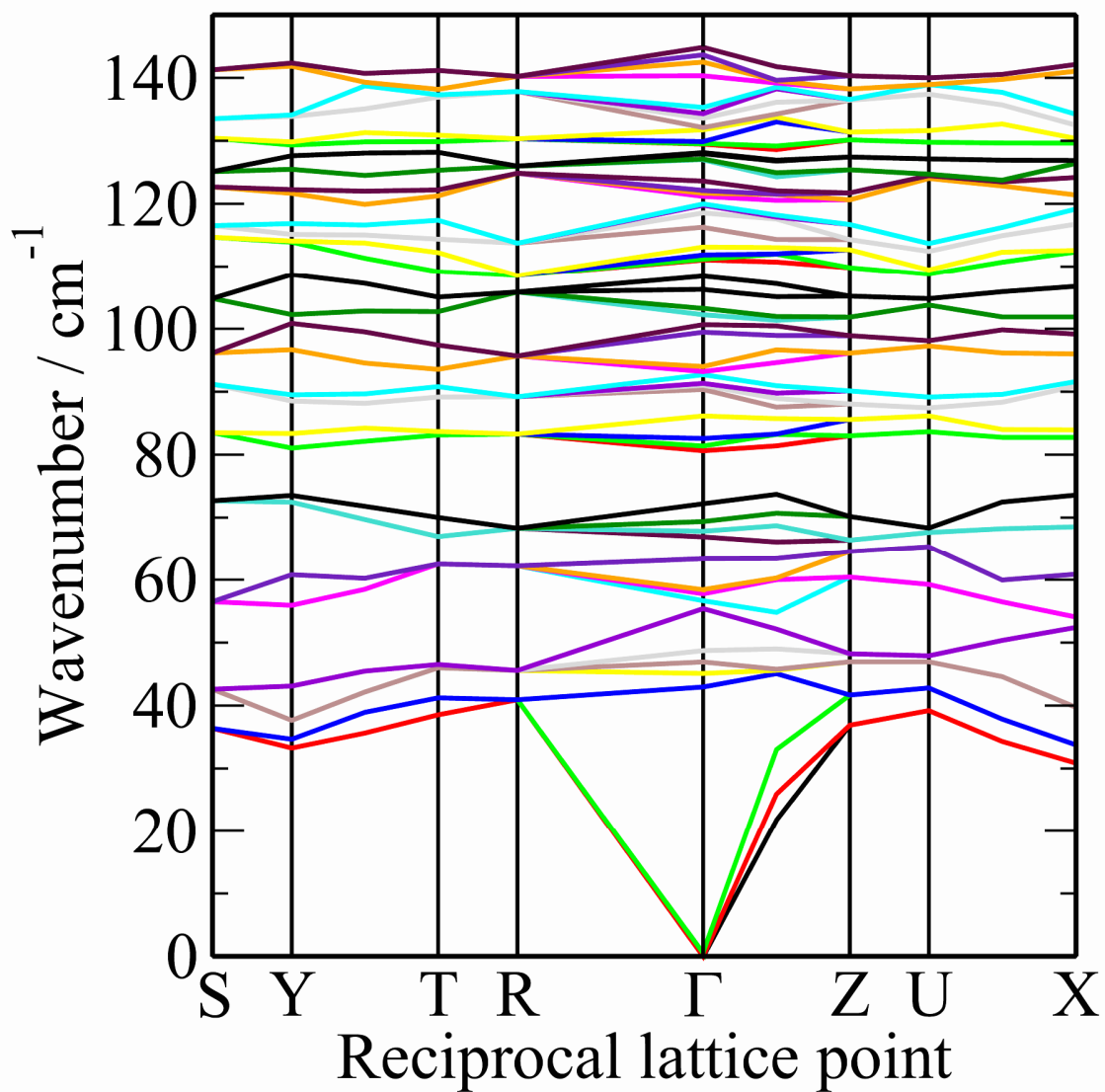


Figure S7: Dispersion curves of $W(CO)_6$ in the C-M-C bend and lattice mode region.

Table S1: CASTEP calculated transition energies for Cr(CO)6 and assignments.

Mode number	Transition energy (cm-1)	Infrared intensity ((D/A)**2/amu)	Raman intensity (A**4/amu)	Assignment	Pnma symmetry	Oh symmetry
1	0.00	0.00	0.00	Acoustic	B1u	
2	0.00	0.00	0.00	Acoustic	B3u	
3	0.00	0.00	0.00	Acoustic	B2u	
4	39.32	0.00	0.00	Translation	Au	
5	44.63	0.01	0.00	Libration	B2u	
6	44.91	0.00	0.88	Translation	Ag	
7	49.95	0.00	0.06	Translation	B2g	
8	52.03	0.00	0.00	Translation	B3u	
9	52.03	0.00	0.01	Translation	B3g	
10	54.76	0.00	0.21	Translation	Ag	
11	55.02	0.00	4.20	Libration	B3g	
12	56.84	0.00	0.00	Translation	B1g	
13	61.32	0.00	0.00	Libration	Au	
14	68.52	0.00	0.73	Libration	B1g	
15	69.08	0.00	0.00	Libration	B1u	
16	69.15	0.00	0.00	Libration	Au	
17	70.07	0.00	1.85	Libration	B3g	
18	70.80	0.00	5.56	Libration	Ag	
19	71.03	0.00	0.46	Translation	B2g	
20	75.74	0.00	0.00	Translation	B1u	
21	81.08	0.03	0.00	Libration	B3u	
22	81.23	0.00	0.18	Libration	B1g	
23	81.26	0.00	0.90	Libration	B2g	
24	81.53	0.04	0.00	Libration	B2u	
25	84.41	0.00	0.00	C-Cr-C bend	Au	T2u
26	86.40	0.00	0.00	C-Cr-C bend	B1u	T2u
27	88.71	0.00	0.00	C-Cr-C bend	B3u	T2u
28	88.79	0.00	2.76	C-Cr-C bend	B1g	T2u
29	91.71	0.08	0.00	C-Cr-C bend	B2u	T2u
30	93.17	0.00	0.90	C-Cr-C bend	B2g	T2u
31	93.96	0.00	85.10	C-Cr-C bend	Ag	T2u
32	95.19	0.00	9.84	C-Cr-C bend	B1g	T2u
33	95.37	0.00	6.20	C-Cr-C bend	B3g	T2u
34	98.01	0.00	0.00	C-Cr-C bend	Au	T2u
35	103.23	0.09	0.00	C-Cr-C bend	B1u	T1u
36	104.31	0.00	27.51	C-Cr-C bend	Ag	T1u
37	105.26	0.00	6.48	C-Cr-C bend	B2g	T2u
38	106.25	0.00	0.00	C-Cr-C bend	B2u	T2u
39	109.34	0.00	0.53	C-Cr-C bend	B3g	T1u
40	110.76	0.02	0.00	C-Cr-C bend	B3u	T1u
41	112.42	0.00	0.34	C-Cr-C bend	B1g	T1u
42	114.19	0.01	0.00	C-Cr-C bend	B2u	T1u
43	114.82	0.00	9.47	C-Cr-C bend	B3g	T1u
44	116.04	0.00	0.00	C-Cr-C bend	Au	T1u
45	116.57	0.11	0.00	C-Cr-C bend	B1u	T1u
46	116.97	0.00	37.67	C-Cr-C bend	Ag	T1u
47	117.65	0.16	0.00	C-Cr-C bend	B3u	T1u
48	118.42	0.00	0.59	C-Cr-C bend	B2g	T1u
49	119.52	0.00	0.00	C-Cr-C bend	Au	T2g
50	120.85	0.00	0.00	C-Cr-C bend	B1u	T2g
51	122.20	0.00	32.31	C-Cr-C bend	B1g	T2g
52	122.37	0.09	0.00	C-Cr-C bend	B2u	T2g
53	123.63	0.04	0.00	C-Cr-C bend	B3u	T2g
54	125.41	0.00	72.29	C-Cr-C bend	B3g	T2g
55	126.12	0.00	25.16	C-Cr-C bend	B2g	T2g
56	126.41	0.00	153.86	C-Cr-C bend	Ag	T2g
57	127.05	0.03	0.00	C-Cr-C bend	B1u	T2g
58	128.53	0.00	35.86	C-Cr-C bend	B2g	T2g
59	135.44	0.02	0.00	C-Cr-C bend	B3u	T2g
60	135.83	0.00	31.07	C-Cr-C bend	Ag	T2g
61	353.47	0.00	0.00	Cr-C≡O bend	Au	T1g
62	353.74	0.02	0.00	Cr-C≡O bend	B2u	T1g
63	354.12	0.00	0.06	Cr-C≡O bend	B3g	T1g
64	354.82	0.00	0.00	Cr-C≡O bend	Au	T1g
65	355.01	0.00	0.36	Cr-C≡O bend	B1g	T1g
66	355.03	0.00	0.00	Cr-C≡O bend	B2u	T1g
67	355.59	0.00	0.09	Cr-C≡O bend	B1g	T1g
68	355.96	0.00	0.05	Cr-C≡O bend	B3g	T1g
69	356.12	0.00	0.00	Cr-C≡O bend	B3u	T1g
70	356.76	0.00	0.92	Cr-C≡O bend	Ag	T1g
71	357.05	0.00	0.00	Cr-C≡O bend	B1u	T1g
72	357.73	0.00	0.01	Cr-C≡O bend	B2g	T1g
73	381.74	0.00	0.28	Cr-C stretch	B2g	A1g
74	382.08	0.00	0.00	Cr-C stretch	B3u	A1g
75	382.40	0.00	0.00	Cr-C stretch	B1u	A1g
76	384.21	0.00	875.07	Cr-C stretch	Ag	A1g
77	395.33	0.04	0.00	Cr-C stretch	B2u	Eg
78	395.70	0.00	48.88	Cr-C stretch	B1g	Eg
79	397.18	0.00	0.00	Cr-C stretch	Au	Eg
80	397.23	0.00	15.52	Cr-C stretch	B3g	Eg
81	398.07	0.00	42.86	Cr-C stretch	Ag	Eg
82	398.42	0.01	0.00	Cr-C stretch	B3u	Eg

83	399.08	0.01	0.00	Cr-C stretch	B1u	Eg
84	399.40	0.00	32.31	Cr-C stretch	B2g	Eg
85	453.18	0.00	0.00	Cr-C≡O bend	B1g	T1u
86	453.52	0.00	0.00	Cr-C≡O bend	Au	T1u
87	454.31	0.00	3.24	Cr-C≡O bend	B3g	T1u
88	454.41	0.00	1.32	Cr-C≡O bend	Ag	T1u
89	454.45	2.43	0.00	Cr-C≡O bend	B3u	T1u
90	455.24	0.00	0.96	Cr-C≡O bend	B2g	T1u
91	455.41	0.12	0.00	Cr-C≡O bend	B1u	T1u
92	456.48	3.06	0.00	Cr-C≡O bend	B2u	T1u
93	457.26	2.71	0.00	Cr-C≡O bend	B1u	T1u
94	457.45	0.00	0.02	Cr-C≡O bend	B2g	T1u
95	458.44	0.44	0.00	Cr-C≡O bend	B3u	T1u
96	458.91	0.00	0.44	Cr-C≡O bend	Ag	T1u
97	514.32	0.00	0.00	Cr-C≡O bend	Au	T2u
98	514.50	0.00	0.00	Cr-C≡O bend	B2u	T2u
99	514.77	0.00	0.01	Cr-C≡O bend	B3g	T2u
100	515.08	0.04	0.00	Cr-C≡O bend	B1u	T2u
101	515.18	0.00	0.02	Cr-C≡O bend	B1g	T2u
102	515.37	0.00	0.84	Cr-C≡O bend	B2g	T2u
103	515.64	0.00	0.00	Cr-C≡O bend	Au	T2u
104	516.56	0.00	0.00	Cr-C≡O bend	B3u	T2u
105	516.67	0.00	0.00	Cr-C≡O bend	B1g	T2u
106	517.01	0.00	1.34	Cr-C≡O bend	Ag	T2u
107	517.12	0.00	0.01	Cr-C≡O bend	B3g	T2u
108	517.63	0.05	0.00	Cr-C≡O bend	B2u	T2u
109	535.64	0.01	0.00	Cr-C≡O bend	B2u	T2g
110	535.65	0.00	15.03	Cr-C≡O bend	B1g	T2g
111	535.87	0.00	0.00	Cr-C≡O bend	Au	T2g
112	536.57	0.00	11.15	Cr-C≡O bend	B3g	T2g
113	536.89	0.02	0.00	Cr-C≡O bend	B1u	T2g
114	538.33	0.00	6.15	Cr-C≡O bend	B2g	T2g
115	538.39	0.00	0.00	Cr-C≡O bend	B3u	T2g
116	539.09	0.00	28.53	Cr-C≡O bend	Ag	T2g
117	540.57	0.00	19.89	Cr-C≡O bend	Ag	T2g
118	540.87	0.00	0.00	Cr-C≡O bend	B1u	T2g
119	541.93	0.00	0.18	Cr-C≡O bend	B2g	T2g
120	542.96	0.01	0.00	Cr-C≡O bend	B3u	T2g
121	665.12	0.00	0.19	Cr-C stretch	Ag	T1u
122	665.43	28.42	0.00	Cr-C stretch	B3u	T1u
123	665.80	39.60	0.00	Cr-C stretch	B1u	T1u
124	665.84	40.30	0.00	Cr-C stretch	B2u	T1u
125	666.71	0.00	0.93	Cr-C stretch	B2g	T1u
126	671.90	0.00	0.14	Cr-C stretch	Ag	T1u
127	672.01	10.72	0.00	Cr-C stretch	B3u	T1u
128	674.07	0.00	0.00	Cr-C stretch	Au	T1u
129	674.90	0.00	2.92	Cr-C stretch	B3g	T1u
130	689.07	0.13	0.00	Cr-C stretch	B1u	T1u
131	689.11	0.00	1.78	Cr-C stretch	B2g	T1u
132	691.65	0.00	0.00	Cr-C stretch	B1g	T1u
133	1836.74	236.08	0.00	C≡O stretch	B3u	Eg
134	1837.92	0.00	9.46	C≡O stretch	Ag	Eg
135	1839.30	0.00	5.02	C≡O stretch	B2g	Eg
136	1839.54	311.91	0.00	C≡O stretch	B1u	Eg
137	1842.44	320.55	0.00	C≡O stretch	B2u	Eg
138	1848.65	0.00	0.00	C≡O stretch	Au	Eg
139	1853.10	0.00	260.25	C≡O stretch	B3g	Eg
140	1853.38	0.00	41.85	C≡O stretch	Ag	T1u
141	1857.64	74.58	0.00	C≡O stretch	B3u	T1u
142	1877.85	0.00	2273.75	C≡O stretch	Ag	T1u
143	1881.13	0.00	3917.14	C≡O stretch	B1g	Eg
144	1881.35	2.75	0.00	C≡O stretch	B1u	T1u
145	1884.04	2.73	0.00	C≡O stretch	B2u	T1u
146	1884.11	0.00	3082.26	C≡O stretch	B2g	T1u
147	1885.19	0.80	0.00	C≡O stretch	B3u	T1u
148	1900.00	0.00	1310.79	C≡O stretch	B3g	T1u
149	1901.25	0.00	67.20	C≡O stretch	B2g	T1u
150	1903.17	0.04	0.00	C≡O stretch	B1u	T1u
151	1904.86	0.00	0.00	C≡O stretch	Au	T1u
152	1915.44	0.00	54.62	C≡O stretch	B1g	T1u
153	1980.73	0.00	2310.86	C≡O stretch	Ag	A1g
154	1981.68	0.08	0.00	C≡O stretch	B1u	A1g
155	1981.73	0.00	7.11	C≡O stretch	B2g	A1g
156	1982.17	0.04	0.00	C≡O stretch	B3u	A1g

Table S2: CASTEP calculated transition energies for Mo(CO)6 and assignments.

Mode number	Transition energy (cm-1)	Infrared intensity ((D/A)**2/amu)	Raman active?	Assignment	Pnma symmetry	Oh symmetry
1	0.00	0.00	N	Acoustic	B2u	
2	0.00	0.00	N	Acoustic	B1u	
3	0.00	0.00	N	Acoustic	B3u	
4	34.11	0.00	Y	Translation	Ag	
5	36.82	0.00	Y	Translation	Ag	
6	39.36	0.00	Y	Translation	B2g	
7	39.81	0.01	N	Translation	B3u	
8	40.74	0.00	Y	Translation	B3g	
9	47.22	0.01	N	Libration	B2u	
10	50.53	0.00	N	Translation	Au	
11	53.71	0.00	N	Libration	Au	
12	55.38	0.00	Y	Translation	B2g	
13	56.21	0.00	Y	Libration	B3g	
14	56.57	0.00	Y	Translation	B1g	
15	57.38	0.00	N	Translation	B1u	
16	59.13	0.00	Y	Libration	Ag	
17	61.21	0.00	N	Libration	Au	
18	62.81	0.00	N	Libration	B1u	
19	64.65	0.00	Y	Libration	B1g	
20	70.20	0.02	N	Libration	B3u	
21	71.89	0.00	Y	C-Mo-C bend	B2g	T2u
22	74.34	0.00	Y	C-Mo-C bend	B1g	T2u
23	75.77	0.00	Y	C-Mo-C bend	B3g	T2u
24	80.29	0.00	N	C-Mo-C bend	Au	T2u
25	80.88	0.00	N	Libration	B2u	
26	82.09	0.00	Y	Libration	B3g	
27	82.36	0.06	N	C-Mo-C bend	B2u	T2u
28	83.56	0.00	N	C-Mo-C bend	B3u	T2u
29	83.82	0.00	Y	Libration	B1g	
30	84.55	0.00	Y	C-Mo-C bend	Ag	T2u
31	87.90	0.00	Y	C-Mo-C bend	B1g	T2u
32	89.05	0.00	Y	Libration	B2g	
33	89.50	0.01	N	C-Mo-C bend	B2u	T2u
34	90.65	0.03	N	C-Mo-C bend	B1u	T2u
35	91.68	0.00	N	C-Mo-C bend	Au	T2u
36	93.58	0.09	N	C-Mo-C bend	B1u	T1u
37	95.30	0.03	N	C-Mo-C bend	B3u	T1u
38	95.83	0.00	Y	C-Mo-C bend	B1g	T1u
39	96.38	0.01	N	C-Mo-C bend	B1u	T1u
40	96.80	0.00	Y	C-Mo-C bend	B2g	T1u
41	98.00	0.00	N	C-Mo-C bend	Au	T1u
42	100.43	0.00	N	C-Mo-C bend	B2u	T1u
43	101.09	0.00	Y	C-Mo-C bend	Ag	T1u
44	101.20	0.00	Y	C-Mo-C bend	B3g	T2u
45	102.40	0.00	Y	C-Mo-C bend	Ag	T1u
46	102.58	0.00	Y	C-Mo-C bend	B2g	T1u
47	104.28	0.00	Y	C-Mo-C bend	B3g	T1u
48	104.29	0.11	N	C-Mo-C bend	B3u	T1u
49	108.12	0.01	N	C-Mo-C bend	B1u	T2g
50	109.31	0.01	N	C-Mo-C bend	B3u	T2g
51	110.11	0.00	Y	C-Mo-C bend	Ag	T2g
52	110.31	0.00	Y	C-Mo-C bend	B3g	T2g
53	110.63	0.00	Y	C-Mo-C bend	B2g	T2g
54	111.65	0.00	N	C-Mo-C bend	Au	T2g
55	112.22	0.00	Y	C-Mo-C bend	B1g	T2g
56	114.39	0.02	N	C-Mo-C bend	B1u	T2g
57	116.25	0.08	N	C-Mo-C bend	B2u	T2g
58	117.72	0.00	Y	C-Mo-C bend	B2g	T2g
59	121.97	0.00	Y	C-Mo-C bend	Ag	T2g
60	123.60	0.00	N	C-Mo-C bend	B3u	T2g
61	331.11	0.00	N	Mo-C≡O bend	Au	T1g
62	331.56	0.00	Y	Mo-C≡O bend	B3g	T1g
63	331.74	0.01	N	Mo-C≡O bend	B2u	T1g
64	332.23	0.00	N	Mo-C≡O bend	Au	T1g
65	332.34	0.02	N	Mo-C≡O bend	B2u	T1g
66	332.41	0.00	N	Mo-C≡O bend	B3u	T1g
67	332.65	0.00	Y	Mo-C≡O bend	B1g	T1g
68	333.27	0.00	Y	Mo-C≡O bend	Ag	T1g
69	333.45	0.00	Y	Mo-C≡O bend	B1g	T1g
70	333.70	0.00	N	Mo-C≡O bend	B1u	T1g

71	333.94	0.00	Y	Mo-C≡O bend	B3g	T1g
72	334.40	0.00	Y	Mo-C≡O bend	B2g	T1g
73	384.11	0.00	N	Mo-C≡O bend	Au	T1u
74	384.96	6.48	N	Mo-C≡O bend	B3u	T1u
75	385.20	0.00	Y	Mo-C≡O bend	Ag	T1u
76	385.42	0.00	Y	Mo-C≡O bend	B2g	T1u
77	385.59	0.00	Y	Mo-C≡O bend	B3g	T1u
78	385.60	6.90	N	Mo-C≡O bend	B2u	T1u
79	385.78	6.75	N	Mo-C≡O bend	B1u	T1u
80	387.11	0.00	Y	Mo-C≡O bend	Ag	T1u
81	387.54	0.12	N	Mo-C≡O bend	B3u	T1u
82	389.30	0.03	N	Mo-C≡O bend	B1u	T1u
83	389.48	0.00	Y	Mo-C≡O bend	B1g	T1u
84	389.62	0.00	Y	Mo-C≡O bend	B2g	T1u
85	393.05	0.17	N	Mo-C stretch	B2u	Eg
86	393.06	0.00	Y	Mo-C stretch	B1g	Eg
87	394.36	0.00	Y	Mo-C stretch	Ag	Eg
88	394.44	0.20	N	Mo-C stretch	B3u	Eg
89	394.79	0.00	Y	Mo-C stretch	B3g	Eg
90	394.80	0.00	N	Mo-C stretch	Au	Eg
91	394.87	0.05	N	Mo-C stretch	B1u	Eg
92	394.93	0.00	Y	Mo-C stretch	B2g	Eg
93	398.62	0.00	Y	Mo-C stretch	B2g	A1g
94	399.04	0.01	N	Mo-C stretch	B1u	A1g
95	399.07	0.00	N	Mo-C stretch	B3u	A1g
96	400.48	0.00	Y	Mo-C stretch	Ag	A1g
97	478.28	0.00	Y	Mo-C≡O bend	B1g	T2g
98	478.47	0.01	N	Mo-C≡O bend	B2u	T2g
99	478.77	0.02	N	Mo-C≡O bend	B1u	T2g
100	478.86	0.00	N	Mo-C≡O bend	Au	T2g
101	479.31	0.00	Y	Mo-C≡O bend	B3g	T2g
102	479.45	0.00	Y	Mo-C≡O bend	B2g	T2g
103	480.05	0.00	N	Mo-C≡O bend	B3u	T2g
104	480.33	0.00	Y	Mo-C≡O bend	Ag	T2g
105	481.33	0.00	Y	Mo-C≡O bend	Ag	T2g
106	482.01	0.00	N	Mo-C≡O bend	B1u	T2g
107	483.38	0.00	N	Mo-C≡O bend	B3u	T2g
108	483.47	0.00	Y	Mo-C≡O bend	B2g	T2g
109	505.50	0.00	N	Mo-C≡O bend	Au	T2u
110	505.65	0.03	N	Mo-C≡O bend	B1u	T2u
111	505.77	0.00	Y	Mo-C≡O bend	B3g	T2u
112	505.87	0.01	N	Mo-C≡O bend	B2u	T2u
113	506.22	0.00	Y	Mo-C≡O bend	B1g	T2u
114	506.36	0.00	Y	Mo-C≡O bend	B2g	T2u
115	507.40	0.00	N	Mo-C≡O bend	Au	T2u
116	507.79	0.00	N	Mo-C≡O bend	B3u	T2u
117	508.60	0.00	Y	Mo-C≡O bend	Ag	T2u
118	508.97	0.00	Y	Mo-C≡O bend	B1g	T2u
119	509.36	0.10	N	Mo-C≡O bend	B2u	T2u
120	509.53	0.00	Y	Mo-C≡O bend	B3g	T2u
121	588.55	20.82	N	Mo-C stretch	B3u	T1u
122	589.13	26.46	N	Mo-C stretch	B1u	T1u
123	589.16	0.00	Y	Mo-C stretch	Ag	T1u
124	590.37	26.86	N	Mo-C stretch	B2u	T1u
125	590.49	0.00	Y	Mo-C stretch	B2g	T1u
126	592.05	0.00	Y	Mo-C stretch	Ag	T1u
127	592.80	5.69	N	Mo-C stretch	B3u	T1u
128	596.32	0.00	N	Mo-C stretch	Au	T1u
129	597.22	0.00	Y	Mo-C stretch	B3g	T1u
130	604.62	0.00	Y	Mo-C stretch	B2g	T1u
131	604.62	0.27	N	Mo-C stretch	B1u	T1u
132	607.43	0.00	Y	Mo-C stretch	B1g	T1u
133	1834.74	255.29	N	C≡O stretch	B3u	Eg
134	1835.10	0.00	Y	C≡O stretch	Ag	Eg
135	1837.51	0.00	Y	C≡O stretch	B2g	Eg
136	1837.65	345.91	N	C≡O stretch	B1u	Eg
137	1840.51	357.65	N	C≡O stretch	B2u	Eg
138	1846.79	0.00	N	C≡O stretch	Au	Eg
139	1850.93	0.00	Y	C≡O stretch	Ag	T1u
140	1851.13	0.00	Y	C≡O stretch	B3g	Eg
141	1855.37	90.07	N	C≡O stretch	B3u	T1u
142	1881.21	0.00	Y	C≡O stretch	Ag	T1u
143	1883.44	3.69	N	C≡O stretch	B1u	T1u
144	1883.55	0.00	Y	C≡O stretch	B1g	Eg

145	1885.92	0.00	Y	C≡O stretch	B2g	T1u
146	1887.19	1.35	N	C≡O stretch	B2u	T1u
147	1888.45	0.30	N	C≡O stretch	B3u	T1u
148	1898.57	0.00	Y	C≡O stretch	B2g	T1u
149	1901.68	0.11	N	C≡O stretch	B1u	T1u
150	1902.49	0.00	Y	C≡O stretch	B3g	T1u
151	1907.04	0.00	N	C≡O stretch	Au	T1u
152	1912.58	0.00	Y	C≡O stretch	B1g	T1u
153	1988.63	0.00	Y	C≡O stretch	Ag	A1g
154	1990.00	0.00	Y	C≡O stretch	B2g	A1g
155	1990.01	0.08	N	C≡O stretch	B1u	A1g
156	1990.66	0.01	N	C≡O stretch	B3u	A1g

Table S3: CASTEP calculated transition energies for W(CO)6 and assignments.

Mode number	Transition energy (cm-1)	Infrared intensity ((D/A)**2/amu)	Raman active?	Assignment	Pnma symmetry	Oh symmetry
1	0.00	0.00	N	Acoustic	B1u	
2	0.00	0.00	N	Acoustic	B3u	
3	0.00	0.00	N	Acoustic	B2u	
4	42.95	0.00	Y	Translation	Ag	
5	45.10	0.00	Y	Translation	B3g	
6	46.92	0.00	Y	Translation	B2g	
7	48.74	0.00	N	Translation	Au	
8	55.40	0.00	Y	Translation	B1g	
9	56.64	0.00	Y	Translation	Ag	
10	57.74	0.00	N	Translation	B3u	
11	58.34	0.01	N	Translation	B1u	
12	63.35	0.00	Y	Translation	B2g	
13	66.91	0.00	N	Libration	Au	
14	67.83	0.00	N	Libration	B2u	
15	69.38	0.00	Y	Libration	B1g	
16	72.19	0.00	Y	Libration	B3g	
17	80.63	0.00	Y	Libration	Ag	
18	81.36	0.00	N	Libration	B1u	
19	82.58	0.00	N	Libration	Au	
20	86.14	0.00	Y	C-W-C bend	B1g	T2u
21	90.35	0.00	N	Libration	B2u	
22	91.02	0.01	N	Libration	B3u	
23	91.34	0.00	Y	Libration	B3g	
24	92.69	0.00	Y	C-W-C bend	B2g	T2u
25	93.20	0.01	N	C-W-C bend	B3u	T2u
26	94.00	0.00	Y	C-W-C bend	Ag	T2u
27	99.46	0.00	N	C-W-C bend	Au	T2u
28	100.66	0.00	Y	Libration	B2g	
29	102.22	0.00	Y	C-W-C bend	B3g	T2u
30	103.18	0.02	N	C-W-C bend	B1u	T2u
31	106.25	0.04	N	C-W-C bend	B2u	T2u
32	108.39	0.00	Y	Libration	B1g	
33	111.04	0.01	N	C-W-C bend	B1u	T1u
34	111.21	0.00	Y	C-W-C bend	B1g	T2u
35	111.84	0.00	N	C-W-C bend	Au	T2u
36	113.13	0.01	N	C-W-C bend	B3u	T1u
37	116.25	0.02	N	C-W-C bend	B2u	T2u
38	118.55	0.00	Y	C-W-C bend	B2g	T1u
39	119.77	0.00	Y	C-W-C bend	B3g	T2u
40	119.98	0.00	Y	C-W-C bend	Ag	T1u
41	121.16	0.00	N	C-W-C bend	B1u	T1u
42	121.68	0.00	Y	C-W-C bend	B2g	T1u
43	122.11	0.03	N	C-W-C bend	B2u	T1u
44	123.61	0.00	N	C-W-C bend	Au	T1u
45	126.97	0.10	N	C-W-C bend	B3u	T1u
46	127.11	0.00	Y	C-W-C bend	Ag	T1u
47	127.95	0.00	Y	C-W-C bend	B1g	T1u
48	128.13	0.00	Y	C-W-C bend	B3g	T1u
49	129.46	0.04	N	C-W-C bend	B1u	T2g
50	129.49	0.00	N	C-W-C bend	B3u	T2g
51	129.87	0.00	Y	C-W-C bend	B1g	T2g
52	131.75	0.00	Y	C-W-C bend	B2g	T2g
53	132.10	0.01	N	C-W-C bend	B2u	T2g
54	133.57	0.00	Y	C-W-C bend	B3g	T2g
55	134.29	0.00	N	C-W-C bend	Au	T2g
56	135.30	0.00	Y	C-W-C bend	Ag	T2g
57	140.32	0.00	N	C-W-C bend	B1u	T2g
58	142.49	0.00	Y	C-W-C bend	Ag	T2g
59	143.65	0.00	Y	C-W-C bend	B2g	T2g
60	144.85	0.01	N	C-W-C bend	B3u	T2g
61	358.42	0.00	N	W-C=O bend	B2u	T1g
62	358.63	0.00	N	W-C=O bend	Au	T1g
63	359.31	0.00	N	W-C=O bend	Au	T1g
64	359.44	0.00	Y	W-C=O bend	B3g	T1g
65	359.89	0.00	Y	W-C=O bend	B1g	T1g
66	360.23	0.22	N	W-C=O bend	B2u	T1g
67	360.57	0.00	Y	W-C=O bend	B3g	T1g
68	360.76	0.00	Y	W-C=O bend	B1g	T1g
69	361.39	0.01	N	W-C=O bend	B3u	T1g
70	362.09	0.00	Y	W-C=O bend	Ag	T1g
71	362.38	0.03	N	W-C=O bend	B1u	T1g
72	362.98	0.00	Y	W-C=O bend	B2g	T1g
73	396.31	8.84	N	W-C=O bend	B2u	T1u

74	396.45	0.00	N	W-C≡O bend	Au	T1u
75	396.50	6.95	N	W-C≡O bend	B3u	T1u
76	397.23	0.00	Y	W-C≡O bend	Ag	T1u
77	397.86	0.00	Y	W-C≡O bend	B3g	T1u
78	399.01	0.00	Y	W-C≡O bend	B2g	T1u
79	399.46	5.22	N	W-C≡O bend	B1u	T1u
80	403.39	0.00	Y	W-C≡O bend	B1g	T1u
81	408.85	0.00	Y	W-C≡O bend	Ag	T1u
82	408.97	1.86	N	W-C≡O bend	B3u	T1u
83	410.29	0.00	Y	W-C≡O bend	B2g	T1u
84	410.33	3.77	N	W-C≡O bend	B1u	T1u
85	435.55	0.08	N	W-C stretch	B2u	Eg
86	435.83	0.00	Y	W-C stretch	B1g	Eg
87	436.86	0.00	Y	W-C stretch	B3g	Eg
88	437.43	0.00	N	W-C stretch	Au	Eg
89	439.75	0.01	N	W-C stretch	B3u	Eg
90	440.32	0.00	Y	W-C stretch	B2g	Eg
91	440.38	0.03	N	W-C stretch	B1u	Eg
92	440.53	0.00	Y	W-C stretch	Ag	Eg
93	452.42	0.00	N	W-C stretch	B3u	A1g
94	452.48	0.00	Y	W-C stretch	B2g	A1g
95	452.63	0.00	N	W-C stretch	B1u	A1g
96	452.93	0.00	Y	W-C stretch	Ag	A1g
97	484.49	0.03	N	W-C≡O bend	B1u	T2g
98	484.59	0.00	Y	W-C≡O bend	B1g	T2g
99	484.85	0.00	N	W-C≡O bend	B2u	T2g
100	485.25	0.00	N	W-C≡O bend	Au	T2g
101	485.31	0.00	Y	W-C≡O bend	B3g	T2g
102	485.87	0.00	N	W-C≡O bend	B3u	T2g
103	486.27	0.00	Y	W-C≡O bend	Ag	T2g
104	486.46	0.00	Y	W-C≡O bend	B2g	T2g
105	488.43	0.00	Y	W-C≡O bend	Ag	T2g
106	489.02	0.00	N	W-C≡O bend	B1u	T2g
107	490.00	0.00	Y	W-C≡O bend	B2g	T2g
108	490.86	0.04	N	W-C≡O bend	B3u	T2g
109	531.10	0.00	N	W-C≡O bend	Au	T2u
110	531.23	0.07	N	W-C≡O bend	B1u	T2u
111	531.28	0.01	N	W-C≡O bend	B2u	T2u
112	531.85	0.00	Y	W-C≡O bend	B3g	T2u
113	531.91	0.00	Y	W-C≡O bend	B2g	T2u
114	532.28	0.00	N	W-C≡O bend	Au	T2u
115	532.37	0.00	Y	W-C≡O bend	B1g	T2u
116	533.31	0.00	Y	W-C≡O bend	B1g	T2u
117	533.35	0.00	N	W-C≡O bend	B3u	T2u
118	534.04	0.00	Y	W-C≡O bend	B3g	T2u
119	534.27	0.00	Y	W-C≡O bend	Ag	T2u
120	534.53	0.11	N	W-C≡O bend	B2u	T2u
121	591.02	20.36	N	W-C stretch	B1u	T1u
122	591.69	0.00	Y	W-C stretch	Ag	T1u
123	591.90	12.32	N	W-C stretch	B3u	T1u
124	592.32	20.79	N	W-C stretch	B2u	T1u
125	592.62	0.00	Y	W-C stretch	B2g	T1u
126	593.82	8.31	N	W-C stretch	B3u	T1u
127	594.21	0.00	Y	W-C stretch	Ag	T1u
128	597.03	0.00	N	W-C stretch	Au	T1u
129	598.00	0.00	Y	W-C stretch	B3g	T1u
130	604.19	0.00	Y	W-C stretch	B2g	T1u
131	604.30	0.31	N	W-C stretch	B1u	T1u
132	604.71	0.00	Y	W-C stretch	B1g	T1u
133	1829.65	287.60	N	C≡O stretch	B3u	Eg
134	1830.78	0.00	Y	C≡O stretch	Ag	Eg
135	1831.38	0.00	Y	C≡O stretch	B2g	Eg
136	1831.71	377.29	N	C≡O stretch	B1u	Eg
137	1834.00	381.75	N	C≡O stretch	B2u	Eg
138	1841.32	0.00	N	C≡O stretch	Au	Eg
139	1845.26	0.00	Y	C≡O stretch	Ag	T1u
140	1846.05	0.00	Y	C≡O stretch	B3g	Eg
141	1851.23	82.29	N	C≡O stretch	B3u	T1u
142	1882.51	0.00	Y	C≡O stretch	Ag	T1u
143	1883.22	0.00	Y	C≡O stretch	B1g	Eg
144	1884.86	1.78	N	C≡O stretch	B1u	T1u
145	1887.81	2.27	N	C≡O stretch	B2u	T1u
146	1888.45	0.00	Y	C≡O stretch	B2g	T1u
147	1889.86	0.58	N	C≡O stretch	B3u	T1u
148	1897.69	0.00	Y	C≡O stretch	B2g	T1u
149	1900.79	0.44	N	C≡O stretch	B1u	T1u
150	1903.32	0.00	Y	C≡O stretch	B3g	T1u

151	1908.42	0.00	N	C≡O stretch	Au	T1u
152	1911.75	0.00	Y	C≡O stretch	B1g	T1u
153	1999.27	0.00	Y	C≡O stretch	Ag	A1g
154	2000.40	0.11	N	C≡O stretch	B1u	A1g
155	2000.48	0.00	Y	C≡O stretch	B2g	A1g
156	2000.87	0.03	N	C≡O stretch	B3u	A1g