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# SECTION 7

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## SPECTROSCOPY

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## 7.1 X-RAY METHODS

An X-ray tube operating at a voltage  $V$  (in keV) emits a continuous X-ray spectrum, the minimum wavelength of which is given by  $\lambda_{\min} = 12.398/V$  with the wavelength expressed in angstroms. For expressing the wavelength in  $kX$  units, divide by the factor 1.00202. Tables 7.1 and 7.2 are based

**TABLE 7.1** Wavelengths of X-Ray Emission Spectra in Angstroms

Atomic No.	Element	$K\alpha_2$	$K\alpha_1$	$K\beta_1$	$L\alpha_1$	$L\beta_1$
3	Li	240				
4	Be	113				
5	B	67				
6	C	44				
7	N	31.60				
8	O	23.71				
9	F	18.31				
10	Ne	14.616		14.464		
11	Na	11.909		11.617	407.6	
12	Mg	9.889		9.558	251.0	
13	Al	8.3392	8.3367	7.981	169.8	
14	Si	7.1277	7.1253	6.7681	123	
15	P	6.1549		5.8038		
16	S	5.3747	5.3720	5.0317		
17	Cl	4.7305	4.7276	4.4031		
18	Ar	4.1946	4.1916	3.8848		
19	K	3.7446	3.7412	3.4538	42.7	
20	Ca	3.3616	3.3583	3.0896	36.32	35.95
21	Sc	3.0345	3.0311	2.7795	31.33	31.01
22	Ti	2.75207	2.7484	2.5138	27.39	27.02
23	V	2.5073	2.5035	2.2843	24.26	23.85
24	Cr	2.29351	2.28962	2.08480	21.67	21.28
25	Mn	2.1057	2.1018	1.9102	19.45	19.12
26	Fe	1.93991	1.93597	1.75653	17.567	17.255
27	Co	1.79278	1.78892	1.62075	15.968	15.667
28	Ni	1.66169	1.65784	1.50010	14.566	14.279
29	Cu	1.54433	1.54051	1.39217	13.330	13.053
30	Zn	1.4389	1.4351	1.2952	12.257	11.985
31	Ga	1.3439	1.3400	1.20784	11.290	11.023
32	Ge	1.2580	1.2540	1.1289	10.435	10.174
33	As	1.1798	1.1758	1.0573	9.671	9.414
34	Se	1.1088	1.1047	0.9921	8.990	8.736
35	Br	1.0438	1.0397	0.9327	8.375	8.125
36	Kr	0.9841	0.9801	0.8785	7.822	7.574
37	Rb	0.9296	0.9255	0.8286	7.3181	7.076
38	Sr	0.8794	0.8752	0.7829	6.8625	6.6237
39	Y	0.8330	0.8279	0.7407	6.4485	6.2117
40	Zr	0.7901	0.7859	0.7017	6.0702	5.8358
41	Nb	0.7504	0.7462	0.6657	5.7240	5.4921
42	Mo	0.713543	0.70926	0.632253	5.4063	5.1768
43	Tc	0.6793	0.6749	0.6014	5.1126	4.8782
44	Ru	0.6474	0.6430	0.5725	4.8455	4.6204
45	Rh	0.6176	0.6132	0.5456	4.5973	4.3739

**TABLE 7.1** Wavelengths of X-Ray Emission Spectra in Angstroms (*Continued*)

Atomic No.	Element	$K\alpha_2$	$K\alpha_1$	$K\beta_1$	$L\alpha_1$	$L\beta_1$
46	Pd	0.5898	0.5854	0.5205	4.3676	4.1460
47	Ag	0.563775	0.559363	0.49701	4.1541	3.9344
48	Cd	0.5394	0.5350	0.4751	3.9563	3.7381
49	In	0.5165	0.5121	0.4545	3.7719	3.5552
50	Sn	0.4950	0.4906	0.4352	3.5999	3.3848
51	Sb	0.4748	0.4703	0.4171	3.4392	3.2256
52	Te	0.4558	0.4513	0.4000	3.2891	3.0767
53	I	0.4378	0.4333	0.3839	3.1485	2.9373
54	Xe	0.4204	0.4160	0.3685	3.016	2.807
55	Cs	0.4048	0.4003	0.3543	2.9016	2.8920
56	Ba	0.3896	0.3851	0.3408	2.7752	2.5674
57	La	0.3753	0.3707	0.3280	2.6651	2.4583
58	Ce	0.3617	0.3571	0.3158	2.5612	2.3558
59	Pr	0.3487	0.3441	0.3042	2.4627	2.2584
60	Nd	0.3565	0.3318	0.2933	2.3701	2.1666
61	Pm	0.3249	0.3207	0.2821	2.282	2.0796
62	Sm	0.3137	0.3190	0.2731	2.1994	1.9976
63	Eu	0.3133	0.2985	0.2636	2.1206	1.9202
64	Gd	0.2932	0.2884	0.2544	2.0460	1.8462
65	Tb	0.2834	0.2788	0.2460	1.9755	1.7763
66	Dy	0.2743	0.2696	0.2376	1.9088	1.7100
67	Ho	0.2655	0.2608	0.2302	1.8447	1.6468
68	Er	0.2572	0.2525	0.2226	1.7843	1.5873
69	Tm	0.2491	0.2444	0.2153	1.7263	1.5299
70	Yb	0.2415	0.2368	0.2088	1.6719	1.4756
71	Lu	0.2341	0.2293	0.2021	1.6194	1.4235
72	Hf	0.2270	0.2222	0.1955	1.5696	1.3740
73	Ta	0.2203	0.2155	0.1901	1.5219	1.3270
74	W	0.213813	0.208992	0.184363	1.4764	1.2818
75	Re	0.2076	0.2028	0.1789	1.4329	1.2385
76	Os	0.2016	0.1968	0.1736	1.3911	1.1972
77	Ir	0.1959	0.1910	0.1685	1.3513	1.1578
78	Pt	0.1904	0.1855	0.1637	1.3130	1.1198
79	Au	0.1851	0.1802	0.1590	1.2764	1.0836
80	Hg	0.1799	0.1750	0.1544	1.2411	1.0486
81	Tl	0.1750	0.1701	0.1501	1.2074	1.0152
82	Pb	0.1703	0.1654	0.1460	1.1750	0.9822
83	Bi	0.1657	0.1608	0.1419	1.1439	0.9520
84	Po	0.1608	0.1559	0.1382	1.1138	0.9222
85	At	0.1570	0.1521	0.1343	1.0850	0.8936
86	Rn	0.1529	0.1479	0.1307	1.0572	0.8659
87	Fr	0.1489	0.1440	0.1272	1.030	0.840
88	Ra	0.1450	0.1401	0.1237	1.0047	0.8137
89	Ac	0.1414	0.1364	0.1205	0.9799	0.7890
90	Th	0.1378	0.1328	0.1174	0.9560	0.7652

**TABLE 7.1** Wavelengths of X-Ray Emission Spectra in Angstroms (*Continued*)

Atomic No.	Element	$K\alpha_2$	$K\alpha_1$	$K\beta_1$	$L\alpha_1$	$L\beta_1$
91	Pa	0.1344	0.1294	0.1143	0.9328	0.7422
92	U	0.1310	0.1259	0.1114	0.9105	0.7200
93	Np	0.1278	0.1226	0.1085	0.8893	0.6984
94	Pu	0.1246	0.1195	0.1058	0.8682	0.6777
95	Am	0.1215	0.1165	0.1031	0.8481	0.6576
96	Cm	0.1186	0.1135	0.1005	0.8287	0.6388
97	Bk	0.1157	0.1107	0.0980	0.8098	0.6203
98	Cf	0.1130	0.1079	0.0956	0.7917	0.6023
99	Es	0.1103	0.1052	0.0933	0.7740	0.5850
100	Fm	0.1077	0.1026	0.0910	0.7570	0.5682

**TABLE 7.2** Wavelengths of Absorption Edges in Angstroms

Atomic No.	Element	$K$	$L_I$	$L_{II}$	$L_{III}$
3	Li	226.5			
4	Be	110.68			
5	B	66.289			
6	C	43.68			
7	N	30.99			
8	O	23.32			
9	F	17.913			
10	Ne	14.183			
11	Na	11.478		400	
12	Mg	9.512	197.4	247.92	
13	Al	7.951	142.5	170	
14	Si	6.745	105.1	126.48	
15	P	5.787	81.0	96.84	
16	S	5.018	64.23	76.05	
17	Cl	4.397	52.08	61.37	62.93
18	Ar	3.871	43.19	50.39	50.60
19	K	3.436	36.35	42.02	42.17
20	Ca	3.070	31.07	35.20	35.49
21	Sc	2.757	26.83	30.16	30.53
22	Ti	2.497	23.39	26.83	27.37
23	V	2.269	20.52	23.70	24.26
24	Cr	2.07012	16.7	17.9	20.7
25	Mn	1.896	16.27	18.90	19.40
26	Fe	1.74334	14.60	17.17	17.53
27	Co	1.60811	13.34	15.53	15.93
28	Ni	1.48802	12.27	14.13	14.58
29	Cu	1.38043	11.27	13.01	13.29
30	Zn	1.283	10.33	11.86	12.13

**TABLE 7.2** Wavelengths of Absorption Edges in Angstroms (*Continued*)

Atomic No.	Element	$K$	$L_I$	$L_{II}$	$L_{III}$
31	Ga	1.195	9.54	10.61	11.15
32	Ge	1.116	8.73	9.97	10.23
33	As	1.044	8.108	9.124	9.367
34	Se	0.9800	7.505	8.417	8.646
35	Br	0.9199	6.925	7.752	7.989
36	Kr	0.8655	6.456	7.165	7.395
37	Rb	0.8155	5.997	6.643	6.863
38	Sr	0.7697	5.582	6.172	6.387
39	Y	0.7276	5.233	5.756	5.962
40	Zr	0.6888	4.867	5.378	5.583
41	Nb	0.6529	4.581	5.025	5.223
42	Mo	0.61977	4.299	4.719	4.912
43	Tc	0.5888	4.064	4.427	4.629
44	Ru	0.5605	3.841	4.179	4.369
45	Rh	0.5338	3.626	3.942	4.130
46	Pd	0.5092	3.428	3.724	3.908
47	Ag	0.48582	3.254	3.514	3.698
48	Cd	0.4641	3.084	3.326	3.504
49	In	0.4439	2.926	3.147	3.324
50	Sn	0.4247	2.778	2.982	3.156
51	Sb	0.4066	2.639	2.830	3.000
52	Te	0.3897	2.510	2.687	2.855
53	I	0.3738	2.390	2.553	2.719
54	Xe	0.3585	2.274	2.429	2.592
55	Cs	0.3447	2.167	2.314	2.474
56	Ba	0.3314	2.068	2.204	2.363
57	La	0.3184	1.973	2.103	2.258
58	Ce	0.3065	1.891	2.009	2.164
59	Pr	0.2952	1.811	1.924	2.077
60	Nd	0.2845	1.735	1.843	1.995
61	Pm	0.2743	1.668	1.766	1.918
62	Sm	0.2646	1.598	1.702	1.845
63	Eu	0.2555	1.536	1.626	1.775
64	Gd	0.2468	1.477	1.561	1.709
65	Tb	0.2384	1.421	1.501	1.649
66	Dy	0.2305	1.365	1.438	1.579
67	Ho	0.2229	1.319	1.390	1.535
68	Er	0.2157	1.269	1.339	1.483
69	Tm	0.2089	1.222	1.288	1.433
70	Yb	0.2022	1.181	1.243	1.386
71	Lu	0.1958	1.140	1.198	1.341
72	Hf	0.1898	1.099	1.154	1.297
73	Ta	0.1839	1.061	1.113	1.255

**TABLE 7.2** Wavelengths of Absorption Edges in Angstroms (*Continued*)

Atomic No.	Element	$K$	$L_I$	$L_{II}$	$L_{III}$
74	W	0.17837	1.025	1.074	1.215
75	Re	0.1731	0.9901	1.036	1.177
76	Os	0.1678	0.9557	1.001	1.140
77	Ir	0.1629	0.9243	0.9670	1.106
78	Pt	0.1582	0.8914	0.9348	1.072
79	Au	0.1534	0.8638	0.9028	1.040
80	Hg	0.1492	0.8353	0.8779	1.009
81	Tl	0.1447	0.8079	0.8436	0.9793
82	Pb	0.1408	0.7815	0.8155	0.9503
83	Bi	0.1371	0.7565	0.7891	0.9234
84	Po	0.1332	0.7322	0.7638	0.8970
85	At	0.1295	0.7092	0.7387	0.8720
86	Rn	0.1260	0.6868	0.7153	0.8479
87	Fr	0.1225	0.6654	0.6929	0.8248
88	Ra	0.1192	0.6446	0.6711	0.8027
89	Ac	0.1161	0.6248	0.6500	0.7813
90	Th	0.1129	0.6061	0.6301	0.7606
91	Pa	0.1101	0.5875	0.6106	0.7411
92	U	0.1068	0.5697	0.5919	0.7233
93	Np	0.1045	0.5531	0.5742	0.7042
94	Pu	0.1018	0.5366	0.5571	0.6867
95	Am	0.0992	0.5208	0.5404	0.6700
96	Cm	0.0967	0.5060	0.5246	0.6532
97	Bk	0.0943	0.4913	0.5093	0.6375
98	Cf	0.0920	0.4771	0.4945	0.6223
99	Es	0.0897	0.4636	0.4801	0.6076
100	Fm	0.0875	0.4506	0.4665	0.5935

on the  $K$  and  $L$  wavelength values as published by Y. Cauchois and H. Hulubei (*Tables de Constantes et Données Numériques, I. Longueurs d'Onde des Émissions X et des Discontinuités d'Absorption X*, Hermann, Paris, 1947) and by the International Union of Crystallography (*International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, England, 1962). Wavelength accuracy is only to about 1 in 25 000 except for the lines employed in X-ray diffraction work.

Use of energy-proportional detectors for X-rays creates a need for energy values of  $K$  and  $L$  absorption edges (Table 7.3) and emission series (Table 7.4). These values were obtained by a conversion to keV of tabulated experimental wavelength values and smoothed by a fit to Moseley's law. Although values are listed to 1 eV, chemical form may shift absorption edges and emission lines as much as 10 to 20 eV. S. Fine and C. F. Hendee [*Nuclonics*, **13**(3):36 (1955)] also give values for  $K\beta_2$ ,  $L\gamma_1$ , and  $L\beta_2$  lines.

The relative intensities of X-ray emission lines from targets varies for different elements. However, one can assume a ratio of  $K\alpha_1/K\alpha_2 = 2$  for the commonly used targets. The ratio of  $K\alpha_2/K\beta_1$  from these targets varies from 6 to 3.5. The intensities of  $K\beta_2$  radiations amount to about 1 percent

**TABLE 7.3** Critical X-Ray Absorption Energies in keV

Atomic No.	Element	$K$	$L_I$	$L_{II}$	$L_{III}$
1	H	0.0136			
2	He	0.0246			
3	Li	0.0547			
4	Be	0.112			
5	B	0.187			
6	C	0.284			
7	N	0.400			
8	O	0.532			
9	F	0.692			
10	Ne	0.874	0.048	0.022	
11	Na	1.08	0.055	0.034	
12	Mg	1.30	0.0628	0.0502	
13	Al	1.559	0.0870	0.0720	
14	Si	1.838	0.118	0.0977	
15	P	2.142	0.153	0.128	
16	S	2.469	0.193	0.163	0.162
17	Cl	2.822	0.238	0.202	0.201
18	Ar	3.200	0.287	0.246	0.244
19	K	3.606	0.341	0.295	0.292
20	Ca	4.038	0.399	0.350	0.346
21	Sc	4.496	0.462	0.411	0.407
22	Ti	4.966	0.530	0.462	0.456
23	V	5.467	0.604	0.523	0.515
24	Cr	5.988	0.679	0.584	0.574
25	Mn	6.542	0.762	0.656	0.644
26	Fe	7.113	0.849	0.722	0.709
27	Co	7.713	0.929	0.798	0.783
28	Ni	8.337	1.02	0.877	0.858
29	Cu	8.982	1.10	0.954	0.935
30	Zn	9.662	1.20	1.05	1.02
31	Ga	10.39	1.30	1.17	1.14
32	Ge	11.10	1.42	1.24	1.21
33	As	11.87	1.529	1.358	1.32
34	Se	12.65	1.66	1.472	1.431
35	Br	13.48	1.791	1.599	1.552
36	Kr	14.32	1.92	1.729	1.674
37	Rb	15.197	2.064	1.863	1.803
38	Sr	16.101	2.212	2.004	1.937
39	Y	17.053	2.387	2.171	2.096
40	Zr	17.998	2.533	2.308	2.224
41	Nb	18.986	2.700	2.467	2.372
42	Mo	20.003	2.869	2.630	2.525
43	Tc	21.050	3.045	2.796	2.680



**TABLE 7.3** Critical X-Ray Absorption Energies in keV (*Continued*)

Atomic No.	Element	$K$	$L_I$	$L_{II}$	$L_{III}$
44	Ru	22.117	3.227	2.968	2.839
45	Rh	23.210	3.404	3.139	2.995
46	Pd	24.356	3.614	3.338	3.181
47	Ag	25.535	3.828	3.547	3.375
48	Cd	26.712	4.019	3.731	3.541
49	In	27.929	4.226	3.929	3.732
50	Sn	29.182	4.445	4.139	3.911
51	Sb	30.497	4.708	4.391	4.137
52	Te	31.817	4.953	4.621	4.347
53	I	33.164	5.187	4.855	4.559
54	Xe	34.551	5.448	5.103	4.783
55	Cs	35.974	5.706	5.360	5.014
56	Ba	37.432	5.995	5.629	5.250
57	La	38.923	6.264	5.902	5.490
58	Ce	40.43	6.556	6.169	5.728
59	Pr	41.99	6.837	6.446	5.968
60	Nd	43.57	7.134	6.728	6.215
61	Pm	45.19	7.431	7.022	6.462
62	Sm	46.85	7.742	7.316	6.720
63	Eu	48.51	8.059	7.624	6.984
64	Gd	50.23	8.383	7.942	7.251
65	Tb	52.00	8.713	8.258	7.520
66	Dy	53.77	9.053	8.587	7.795
67	Ho	55.61	9.395	8.918	8.074
68	Er	57.47	9.754	9.270	8.362
69	Tm	59.38	10.12	9.622	8.656
70	Yb	61.31	10.49	9.985	8.949
71	Lu	63.32	10.87	10.35	9.248
72	Hf	65.37	11.28	10.75	9.567
73	Ta	67.46	11.68	11.14	9.883
74	W	69.51	12.09	11.54	10.20
75	Re	71.67	12.52	11.96	10.53
76	Os	73.87	12.97	12.38	10.86
77	Ir	76.11	13.41	12.82	11.21
78	Pt	78.35	13.865	13.26	11.55
79	Au	80.67	14.351	13.731	11.92
80	Hg	83.08	14.838	14.205	12.278
81	Tl	85.52	15.344	14.695	12.65
82	Pb	87.95	15.861	15.200	13.03
83	Bi	90.54	16.386	15.709	13.42
84	Po	93.16	16.925	16.233	13.81
85	At	95.73	17.481	16.777	14.21

**TABLE 7.3** Critical X-Ray Absorption Energies in keV (*Continued*)

Atomic No.	Element	$K$	$L_I$	$L_{II}$	$L_{III}$
86	Rn	98.45	18.054	17.331	14.61
87	Fa	101.1	18.628	17.893	15.02
88	Ra	103.9	19.228	18.473	15.44
89	Ac	107.7	19.829	19.071	15.86
90	Th	109.8	20.452	19.673	16.278
91	Pa	112.4	21.096	20.295	16.720
92	U	115.0	21.757	20.944	17.163
93	Np	118.2	22.411	21.585	17.606
94	Pu	121.2	23.117	22.250	18.062
95	Am	124.3	23.795	22.935	18.524
96	Cm	127.2	24.502	23.629	18.992
97	Bk	131.3	25.231	24.344	19.466
98	Cf	133.6	26.010	25.070	19.954
99	Es	138.1	26.729	25.824	20.422
100	Fm	141.5	27.503	26.584	20.912

**TABLE 7.4** X-Ray Emission Energies in keV

Atomic No.	Element	$K\beta_1$	$K\alpha_1$	$L\beta_1$	$L\alpha_1$
3	Li		0.052		
4	Be		0.110		
5	B		0.185		
6	C		0.282		
7	N		0.392		
8	O		0.523		
9	F		0.677		
10	Ne		0.851		
11	Na	1.067	1.041		
12	Mg	1.297	1.254		
13	Al	1.553	1.487		
14	Si	1.832	1.740		
15	P	2.136	2.015		
16	S	2.464	2.308		
17	Cl	2.815	2.622		
18	Ar	3.192	2.957		
19	K	3.589	3.313		
20	Ca	4.012	3.691	0.344	0.341
21	Sc	4.460	4.090	0.399	0.395
22	Ti	4.931	4.510	0.458	0.452
23	V	5.427	4.952	0.519	0.512

**TABLE 7.4** X-Ray Emission Energies in keV (*Continued*)

Atomic No.	Element	$K\beta_1$	$K\alpha_1$	$L\beta_1$	$L\alpha_1$
24	Cr	5.946	5.414	0.581	0.571
25	Mn	6.490	5.898	0.647	0.636
26	Fe	7.057	6.403	0.717	0.704
27	Co	7.649	6.930	0.790	0.775
28	Ni	8.264	7.477	0.866	0.849
29	Cu	8.904	8.047	0.948	0.928
30	Zn	9.571	8.638	1.032	1.009
31	Ga	10.263	9.251	1.122	1.096
32	Ge	10.981	9.885	1.216	1.186
33	As	11.725	10.543	1.317	1.282
34	Se	12.495	11.221	1.419	1.379
35	Br	13.290	11.923	1.526	1.480
36	Kr	14.112	12.649	1.638	1.587
37	Rb	14.960	13.394	1.752	1.694
38	Sr	15.834	14.164	1.872	1.806
39	Y	16.736	14.957	1.996	1.922
40	Zr	17.666	15.774	2.124	2.042
41	Nb	18.621	16.614	2.257	2.166
42	Mo	19.607	17.478	2.395	2.293
43	Tc	20.612	18.370	2.538	2.424
44	Ru	21.655	19.278	2.683	2.558
45	Rh	22.721	20.214	2.834	2.696
46	Pd	23.816	21.175	2.990	2.838
47	Ag	24.942	22.162	3.151	2.984
48	Cd	26.093	23.172	3.316	3.133
49	In	27.274	24.207	3.487	3.287
50	Sn	28.483	25.270	3.662	3.444
51	Sb	29.723	26.357	3.843	3.605
52	Te	30.993	27.471	4.029	3.769
53	I	32.292	28.610	4.220	3.937
54	Xe	33.644	29.779	4.422	4.111
55	Cs	34.984	30.970	4.620	4.286
56	Ba	36.376	32.191	4.828	4.467
57	La	37.799	33.440	5.043	4.651
58	Ce	39.255	34.717	5.262	4.840
59	Pr	40.746	36.023	5.489	5.034
60	Nd	42.269	37.359	5.722	5.230
61	Pm	43.811	38.726	5.956	5.431
62	Sm	45.400	40.124	6.206	5.636
63	Eu	47.027	41.529	6.456	5.846
64	Gd	48.718	42.983	6.714	6.059
65	Tb	50.391	44.470	6.979	6.275

**TABLE 7.4** X-Ray Emission Energies in keV (*Continued*)

Atomic No.	Element	$K\beta_1$	$K\alpha_1$	$L\beta_1$	$L\alpha_1$
66	Dy	52.178	45.985	7.249	6.495
67	Ho	53.934	47.528	7.528	6.720
68	Er	55.690	49.099	7.810	6.948
69	Tm	57.487	50.730	8.103	7.181
70	Yb	59.352	52.360	8.401	7.414
71	Lu	61.282	54.063	8.708	7.654
72	Hf	63.209	55.757	9.021	7.898
73	Ta	65.210	57.524	9.341	8.145
74	W	67.233	59.310	9.670	8.396
75	Re	69.298	61.131	10.008	8.651
76	Os	71.404	62.991	10.354	8.910
77	Ir	73.549	64.886	10.706	9.173
78	Pt	75.736	66.820	11.069	9.441
79	Au	77.968	68.794	11.439	9.711
80	Hg	80.258	70.821	11.823	9.987
81	Tl	82.558	72.860	12.210	10.266
82	Pb	84.922	74.957	12.611	10.549
83	Bi	87.335	77.097	13.021	10.836
84	Po	89.809	79.296	13.441	11.128
85	At	92.319	81.525	13.873	11.424
86	Rn	94.877	83.800	14.316	11.724
87	Fr	97.483	86.119	14.770	12.029
88	Ra	100.136	88.485	15.233	12.338
89	Ac	102.846	90.894	15.712	12.650
90	Th	105.592	93.334	16.200	12.966
91	Pa	108.408	95.851	16.700	13.291
92	U	111.289	98.428	17.218	13.613
93	Np	114.181	101.005	17.740	13.945
94	Pu	117.146	103.653	18.278	14.279
95	Am	120.163	106.351	18.829	14.618
96	Cm	123.235	109.098	19.393	14.961
97	Bk	126.362	111.896	19.971	15.309
98	Cf	129.544	114.745	20.562	15.661
99	Es	132.781	117.646	21.166	16.018
100	Fm	136.075	120.598	21.785	16.379

of that of the corresponding  $K\alpha_1$  radiation. In practical applications these ratios have to be corrected for differential absorption in the window of the tube and air path, the ratio of scattering factors for and differential absorption in the crystal, and for sensitivity characteristics of the detector. Generalizing, the intensities of radiations from the  $K$  and  $L$  series are as follows:

Emission line	$K\alpha_1$	$K\alpha_2$	$K\beta_1$	$K\beta_2$	$L\alpha_1$	$L\alpha_2$	$L\beta_1$	$L\beta_2$	$L\gamma_1$
Relative intensity	500	250	80–150	5	100	10	30	60	40

For angles at which the  $K\alpha_1$ ,  $K\alpha_2$  doublet is not resolved, a mean wavelength [ $K\bar{\alpha} = (2K\alpha_1 + K\alpha_2)/3$ ] can be used.

*Filters.* The  $K$  spectra of the light metals, often used as target material in the production of X-rays for diffraction studies, contain three strong lines,  $\alpha_1$ ,  $\alpha_2$  and  $\beta_1$ , of which the  $\alpha$  lines form a doublet with a narrow wavelength separation. The  $K\beta$  radiation can be eliminated by using a thin foil filter, usually of the element of next lower atomic number to that of the target element: the  $K\alpha$  lines are transmitted with a relatively small loss of intensity. Table 7.5, restricted to the  $K$  wavelengths of target elements in common use, lists the calculated thicknesses of  $\beta$  filters required to reduce the  $K\beta_1/K\alpha_1$  integrated intensity ratio to  $1/100$ .

*Interplanar Spacings.* Diffractometer alignment procedures require the use of a well-prepared polycrystalline specimen. Two standard samples found to be suitable are silicon and  $\alpha$ -quartz (including Novaculite). The  $2\theta$  values of several of the most intense reflections for these materials are listed in Table 7.6 (*Tables of Interplanar Spacings  $d$  vs. Diffraction Angle  $2\theta$  for Selected Targets*, Picker Nuclear, White Plains, N.Y., 1966). To convert to  $d$  for  $K\bar{\alpha}$  or to  $d$  for  $K\alpha_2$ , multiply the tabulated  $d$  value (Table 7.6) for  $K\alpha_1$  by the factor given below:

Element	$K\bar{\alpha}$	$K\alpha_2$
W	1.007 69	1.023 07
Ag	1.002 63	1.007 89
Mo	1.002 02	1.006 04
Cu	1.000 82	1.002 48
Ni	1.000 77	1.002 32
Co	1.000 72	1.002 16
Fe	1.000 67	1.002 04
Cr	1.000 57	1.001 70

*Analyzing Crystals.* The range of wavelengths usable with various analyzing crystals are governed by the  $d$  spacings of the crystal planes and by the geometric limits to which the goniometer can be rotated. The  $d$  value should be small enough to make the angle  $2\theta$  greater than approximately 10 or 15 deg, even at the shortest wavelength used: otherwise excessively long analyzing crystals would be needed to prevent the direct fluorescent beam from entering the detector. A small  $d$  value is also favorable for producing a large dispersion of the spectrum to give good separation of adjacent lines. On the other hand, a small  $d$  value imposes an upper limit to the range of wavelengths that can be analyzed. Actually the goniometer is limited mechanically to about 150 deg for a  $2\theta$  value. A final requirement is the reflection efficiency and minimization of higher-order reflections. Table 7.7 gives a list of crystals commonly used for X-ray spectroscopy.

**TABLE 7.5**  $\beta$  Filters for Common Target Elements

Target Element	$K\alpha$ , Å	Excitation Voltage, keV	$K\beta_1 K\alpha_1 = 1/100$			% Loss $K\alpha_1$
			Absorber	Thickness, mm	g/cm <sup>2</sup>	
Ag	0.560834	25.52	Pd	0.062	0.074	60
Mo	0.71069	20.00	Zr	0.081	0.053	57
Cu	1.54178	8.981	Ni	0.015	0.013	45
Ni	1.65912	8.331	Co	0.013	0.011	42
Co	1.79021	7.709	Fe	0.012	0.009	39
Fe	1.93728	7.111	Mn	0.011	0.008	38
			MnO <sub>2</sub>	0.026	0.013	45
Cr	2.29092	5.989	V	0.011	0.007	37
			V <sub>2</sub> O <sub>5</sub>	0.036	0.012	48
	$L\alpha_1$		$L\beta_1 L\alpha_1 = 1/100$			% Loss $L\alpha_1$
W	1.4763	10.200	Cu	0.035		77

**TABLE 7.6** Interplanar Spacings for  $K\alpha_1$  Radiation,  $d$  versus  $2\theta$ 

$\alpha$ -quartz (Including Novaculite)										
$hkl$ $d(\text{Å})$	100 4.260	101 3.343	110 2.458	102 2.282	200 2.128	112 1.817	202 1.672	211 1.541	203 1.375	301 1.372
W $K\alpha_1$ ; $2\theta$	2.81	3.58	4.87	5.25	5.63	6.59	7.17	7.78	8.72	8.74
Ag $K\alpha_1$ ; $2\theta$	7.53	9.60	13.07	14.08	15.10	17.71	19.26	20.91	23.47	23.52
Mo $K\alpha_1$ ; $2\theta$	9.55	12.18	16.59	17.88	19.19	22.51	24.49	26.61	29.89	29.96
Cu $K\alpha_1$ ; $2\theta$	20.83	26.64	36.52	39.45	42.44	50.16	54.86	59.98	68.14	68.31
Ni $K\alpha_1$ ; $2\theta$	22.44	28.71	39.42	42.60	45.85	54.28	59.44	65.08	74.15	74.34
Co $K\alpha_1$ ; $2\theta$	24.24	31.04	42.68	46.15	49.71	58.98	64.68	70.96	81.16	81.38
Fe $K\alpha_1$ ; $2\theta$	26.27	33.66	46.38	50.20	54.11	64.38	70.75	77.83	89.50	89.74
Cr $K\alpha_1$ ; $2\theta$	31.18	40.05	55.52	60.22	65.09	78.11	86.42	95.96	112.73	113.11
Silicon										
$hkl$ $d(\text{Å})$	111 3.1353	220 1.91997	311 1.63736	400 1.357630	331 1.24584	422 1.1085	511,333 1.0451	440 0.959986	531 0.917922	620 0.858637
W $K\alpha_1$ ; $2\theta$	3.82	6.24	7.32	8.83	9.62	10.82	11.48	12.50	13.07	13.98
Ag $K\alpha_1$ ; $2\theta$	10.24	16.75	19.67	23.78	25.95	29.23	31.04	33.88	35.48	38.02
Mo $K\alpha_1$ ; $2\theta$	12.99	21.29	25.02	30.28	33.08	37.32	39.67	43.36	45.45	48.79
Cu $K\alpha_1$ ; $2\theta$	28.44	47.30	56.12	69.13	76.38	88.03	94.96	106.71	114.10	127.55
Ni $K\alpha_1$ ; $2\theta$	30.66	51.16	60.83	75.26	83.42	96.80	104.96	119.42	129.12	149.76
Co $K\alpha_1$ ; $2\theta$	33.15	55.53	66.22	82.42	91.77	107.59	117.71	137.42	154.04	
Fe $K\alpha_1$ ; $2\theta$	35.97	60.55	72.48	90.96	101.97	121.67	135.70			
Cr $K\alpha_1$ ; $2\theta$	42.83	73.21	88.72	114.97	133.53					

**TABLE 7.7** Analyzing Crystals for X-Ray Spectroscopy

Crystal	Reflecting Plane	2d Spacing, Å	Reflectivity
Quartz	50 $\bar{5}\bar{2}$	1.624	Low
Aluminum	111	2.338	High
Topaz	303	2.712	Medium
Quartz	20 $\bar{2}\bar{3}$	2.750	Low
Lithium fluoride	220	2.848	High
Silicon	111	3.135	High
Quartz	112	3.636	Medium
Lithium fluoride	200	4.028	High
Sodium chloride	200	5.639	High
Calcium fluoride	111	6.32	High
Quartz	10 $\bar{1}\bar{1}$	6.686	High
Quartz	10 $\bar{1}\bar{0}$	8.50	Medium
Pentaerythritol (PET)	002	8.742	High
Ethylenediamine tartrate (EDT)	020	8.808	Medium
Ammonium dihydrogen phosphate (ADP)	110	10.648	Low
Gypsum	020	15.185	Medium
Mica	002	19.92	Low
Potassium hydrogen phthalate (KAP)	10 $\bar{1}\bar{1}$	26.4	Medium
Lead palmitate		45.6	
Strontium behenate		61.3	
Lead stearate		100.4	Medium

The long-wavelength analyzers are prepared by dipping an optical flat into the film of the metal fatty acid about 50 times to produce a layer 180 molecules in thickness.

Lithium fluoride is the optimum crystal for all wavelengths less than 3 Å. Pentaerythritol (PET) and potassium hydrogen phthalate (KAP) are usually the crystals of choice for wavelengths from 3 to 20 Å. Two crystals suppress even-ordered reflections: silicon (111) and calcium fluoride (111).

*Mass Absorption Coefficients.* Radiation traversing a layer of substance is diminished in intensity by a constant fraction per centimeter thickness  $x$  of material. The emergent radiant power  $P$ , in terms of incident radiant power  $P_0$ , is given by

$$P = P_0 \exp(-\mu x)$$

which defines the total linear absorption coefficient  $\mu$ . Since the reduction of intensity is determined by the quantity of matter traversed by the primary beam, the absorber thickness is best expressed on a mass basis, in g/cm<sup>2</sup>. The mass absorption coefficient  $\mu/\rho$ , expressed in units cm<sup>2</sup>/g, where  $\rho$  is the density of the material, is approximately independent of the physical state of the material and, to a good approximation, is additive with respect to the elements composing a substance.

Table 7.8 contains values of  $\mu/\rho$  for the common target elements employed in X-ray work. A more extensive set of mass absorption coefficients for  $K$ ,  $L$ , and  $M$  emission lines within the wavelength range from 0.7 to 12 Å is contained in Heinrich's paper in T. D. McKinley, K. F. J. Heinrich, and D. B. Wittry (eds.), *The Electron Microprobe*, Wiley, New York, 1966, pp. 351–377. This article should be consulted to ascertain the probable accuracy of the values and for a compilation of coefficients and exponents employed in the computations.

**TABLE 7.8** Mass Absorption Coefficients for  $K\alpha_1$  Lines and W  $L\alpha_1$  Line

Emitter wavelength, Å	Ag $K\alpha_1$ 0.559	Mo $K\alpha_1$ 0.709	Cu $K\alpha_1$ 1.541	Ni $K\alpha_1$ 1.658	Co $K\alpha_1$ 1.789	Fe $K\alpha_1$ 1.936	Cr $K\alpha_1$ 2.290	W $L\alpha_1$ 1.476
Absorber								
1 H	0.37	0.38	0.43	0.4	0.4	0.5	0.5	0.4
2 He	0.16	0.18	0.37	0.4	0.4	0.5	0.7	0.3
3 Li	0.18	0.22	0.50	0.6	0.7	0.9	1.5	0.4
4 Be	0.22	0.30	1.2	1.5	1.9	2.3	3.7	1.1
5 B	0.30	0.45	2.5	3.1	3.9	4.9	7.9	2.2
6 C	0.42	0.50	4.6	5.7	7.1	8.8	14.2	4.1
7 N	0.60	0.83	7.5	9.3	11.5	14.4	23.1	6.7
8 O	0.80	1.45	12.9	15.8	19.5	24.5	39.4	11.4
9 F	1.00	1.9	16.5	20.3	25.2	31.4	50.3	14.6
10 Ne	1.41	2.6	22.8	27.9	34.6	43.1	69.0	20.1
11 Na	1.75	3.5	30.3	37.2	45.9	57.2	91.4	26.8
12 Mg	2.27	4.6	39.5	48.4	59.8	74.6	119.1	34.9
13 Al	2.74	5.8	49.6	60.7	75.0	93.4	149.0	43.9
14 Si	3.44	7.3	61.4	75.2	92.8	115.5	183.8	54.4
15 P	4.20	8.8	74.7	91.4	112.9	140.5	223.6	66.2
16 S	5.15	10.6	89.2	109.2	134.7	167.4	266.1	79.1
17 Cl	5.86	12.4	104.8	128.2	158.1	196.6	312.4	92.8
18 Ar	6.40	14.5	121.4	148.5	183.0	227.3	360.7	107.6
19 K	8.0	16.7	139.8	171	211	262	415	124
20 Ca	9.7	18.9	158.6	194	239	296	469	141
21 Sc	10.5	21.8	180.5	221	272	337	534	160
22 Ti	11.8	25.3	203	247	304	378	597	180
23 V	13.3	27.7	228	278	342	424	77	202
24 Cr	15.7	31.0	254	311	382	474	88	226
25 Mn	17.4	34.5	282	344	423	63.5	101	250
26 Fe	19.9	38.1	311	380	57.6	71.4	113	276
27 Co	21.8	42.1	341	52.8	64.9	80.6	127	303
28 Ni	25.0	46.4	48.3	58.9	72.5	90.0	142	333
29 Cu	26.4	50.7	53.7	65.5	80.6	100.0	158	47.6
30 Zn	28.2	55.4	59.5	72.7	89.4	110.9	175	52.8
31 Ga	30.8	60.1	65.9	80.5	99.0	122.8	194	58.5
32 Ge	33.5	65.2	72.3	88.2	108.6	134.7	213	64.1
33 As	36.5	70.5	79.1	96.6	118.9	147	233	70.2
34 Se	38.5	76.0	86.1	105.1	129.4	161	254	76.4
35 Br	42.3	82.5	93.9	114.7	141.2	175	277	83.4
36 Kr	45.0	88.3	101.9	124.5	153.2	190	300	90.5
37 Rb	48	95	84	103	127	158	252	98
38 Sr	52	102	90	110	137	170	271	106



**TABLE 7.8** Mass Absorption Coefficients for  $K\alpha_1$  Lines and W  $L\alpha_1$  Line (*Continued*)

Emitter wavelength, Å	Ag $K\alpha_1$ 0.559	Mo $K\alpha_1$ 0.709	Cu $K\alpha_1$ 1.541	Ni $K\alpha_1$ 1.658	Co $K\alpha_1$ 1.789	Fe $K\alpha_1$ 1.936	Cr $K\alpha_1$ 2.290	W $L\alpha_1$ 1.476
Absorber								
39 Y	56	109	97	119	147	183	292	114
40 Zr	61	17	104	128	158	197	314	122
41 Nb	66	18	112	138	170	212	338	132
42 Mo	71	19	119	146	180	225	358	140
43 Tc	76	20	128	157	194	241	384	150
44 Ru	12	22	137	168	207	258	410	160
45 Rh	13	23	146	179	221	275	438	171
46 Pd	14	24	155	190	235	292	466	182
47 Ag	15	26	165	202	249	310	493	193
48 Cd	15	28	174	213	263	327	520	204
49 In	16	30	185	227	280	347	553	217
50 Sn	17	32	195	239	295	367	583	229
51 Sb	19	34	206	252	310	386	612	241
52 Te	19	36	216	265	326	405	644	253
53 I	21	37	230	281	346	431	684	269
54 Xe	22	39	239	293	361	448	710	280
55 Cs	24	42	332	404	495	612	822	295
56 Ba	25	44	349	425	522	645	622	311
57 La	26	46	365	444	545	673	647	325
58 Ce	28	48	383	466	571	603	216	341
59 Pr	29	51	401	487	597	453	229	356
60 Nd	31	54	420	510	534	473	241	373
61 Pm	32	56	440	535		164	254	392
62 Sm	33	59	456	473	417	173	268	406
63 Eu	35	61	$L_I$ 405	354	148	182	282	423
64 Gd	36	64	424	370	156	191	296	
65 Tb	38	67	$L_{II}$ 316	135	164	201	311	$\overline{393} L_I$
66 Dy	39	70	$L_{III}$ 329	141	172	211	327	$\overline{293} L_{II}$
67 Ho	41	72	123	148	181	222	343	304
68 Er	43	75	129	156	189	233	360	$\overline{316} L_{III}$
69 Tm	45	79	135	163	199	244	377	120
70 Yb	46	82	141	171	208	256	395	126
71 Lu	48	84	148	179	218	267	414	132
72 Hf	51	88	155	187	228	280	433	138
73 Ta	52	91	162	196	238	293	453	144
74 W	55	95	169	204	249	306	473	151
75 Re	57	98	176	213	260	319	494	157
76 Os	59	102	184	223	271	333	515	164
77 Ir	61	106	192	232	283	347	538	171
78 Pt	64	109	200	242	295	362	560	179

**TABLE 7.8** Mass Absorption Coefficients for  $K\alpha_1$  Lines and  $W L\alpha_1$  Line (*Continued*)

Emitter wavelength, Å	Ag $K\alpha_1$ 0.559	Mo $K\alpha_1$ 0.709	Cu $K\alpha_1$ 1.541	Ni $K\alpha_1$ 1.658	Co $K\alpha_1$ 1.789	Fe $K\alpha_1$ 1.936	Cr $K\alpha_1$ 2.290	W $L\alpha_1$ 1.476
Absorber								
79 Au	67	113	209	252	307	377	584	186
80 Hg	69	117	218	263	321	394	609	194
81 Tl	72	121	227	275	334	411	635	203
82 Pb	74	125	236	286	348	428	662	211
83 Bi	78	129	247	298	363	446	690	220
84 Po		131	258	311	380	466	721	230
85 At			269	325	397	487	753	240
86 Rn	85		281	340	414	509	787	251
87 Fr		89	294	356	433	532	823	262
88 Ra	91		307	372	453	556	861	274
89 Ac			322	389	474	582	900	287
90 Th	97		337	408	497	610	944	301
91 Pa			353	427	520	639	988	315
92 U	104		372	450	548	673	898	332
93 Np			392	474	578	709	945	350
94 Pu		54	418	505	615	755	835	373

## 7.2 ULTRAVIOLET-VISIBLE SPECTROSCOPY

Molecules with two or more isolated chromophores (absorbing groups) absorb light of nearly the same wavelength as does a molecule containing only a single chromophore of a particular type. The intensity of the absorption is proportional to the number of that type of chromophore present in the molecule. Representative chromophores are given in Table 7.9.

The solvent chosen must dissolve the sample, yet be relatively transparent in the spectral region of interest. In order to avoid poor resolution and difficulties in spectrum interpretation, a solvent should not be employed for measurements that are near the wavelength of or are shorter than the wavelength of its ultraviolet cutoff, that is, the wavelength at which absorbance for the solvent alone approaches one absorbance unit. Ultraviolet cutoffs for solvents commonly used are given in Table 7.10.

Appreciable interaction between chromophores does not occur unless they are linked directly to each other, or forced into close proximity as a result of molecular stereochemical configuration. Interposition of a single methylene group, or *meta* orientation about an aromatic ring, is sufficient to insulate chromophores almost completely from each other. Certain combinations of functional groups afford chromophoric systems which give rise to characteristic absorption bands.

Sets of empirical rules, often referred to as Woodward's rules or the Woodward-Fieser rules, enable the absorption maxima of dienes (Table 7.11) and enones and dienones (Table 7.12) to be predicted. To the respective base values (absorption wavelength of parent compound) are added the increments for the structural features or substituent groups present. When necessary, a solvent correction is also applied (Table 7.13).

**TABLE 7.9** Electronic Absorption Bands for Representative Chromophores

Chromophore	System	$\lambda_{\max}$	$\epsilon_{\max}$
Acetylide	$-\text{C}\equiv\text{C}-$	175–180	6 000
Aldehyde	$-\text{CHO}$	210	strong
		280–300	11–18
Amine	$-\text{NH}_2$	195	2 800
Azido	$\text{>C}=\text{N}-$	190	5 000
Azo	$-\text{N}=\text{N}-$	285–400	3–25
Bromide	$-\text{Br}$	208	300
Carbonyl	$\text{>C}=\text{O}$	195	1 000
		270–285	18–30
Carboxyl	$-\text{COOH}$	200–210	50–70
Disulfide	$-\text{S}-\text{S}-$	194	5 500
		255	400
Ester	$-\text{COOR}$	205	50
Ether	$-\text{O}-$	185	1 000
Ethylene	$-\text{C}=\text{C}-$	190	8 000
Iodide	$-\text{I}$	260	400
Nitrate	$-\text{ONO}_2$	270 (shoulder)	12
Nitrile	$-\text{C}\equiv\text{N}$	160	—
Nitrite	$-\text{ONO}$	220–230	1 000–2 000
		300–400	10
Nitro	$-\text{NO}_2$	210	strong
Nitroso	$-\text{NO}$	302	100
Oxime	$-\text{NOH}$	190	5 000
Sulfone	$-\text{SO}_2-$	180	—
Sulfoxide	$\text{>S}=\text{O}$	210	1 500
Thiocarbonyl	$\text{>C}=\text{S}$	205	strong
Thioether	$-\text{S}-$	194	4 600
		215	1 600
Thiol	$-\text{SH}$	195	1 400
	$-(\text{C}=\text{C})_2-$ (acyclic)	210–230	21 000
	$-(\text{C}=\text{C})_3-$	260	35 000
	$-(\text{C}=\text{C})_4-$	300	52 000
	$-(\text{C}=\text{C})_5-$	330	118 000
	$-(\text{C}=\text{C})_2-$ (alicyclic)	230–260	3 000–8 000
	$\text{C}=\text{C}-\text{C}\equiv\text{C}$	219	6 500
	$\text{C}=\text{C}-\text{C}=\text{N}$	220	23 000
	$\text{C}=\text{C}-\text{C}=\text{O}$	210–250	10 000–20 000
		300–350	weak
	$\text{C}=\text{C}-\text{NO}_2$	229	9 500
Benzene		184	46 700
		204	6 900
		255	170
Diphenyl		246	20 000
Naphthalene		222	112 000
		275	5 600
		312	175
Anthracene		252	199 000
		375	7 900
Phenanthrene		251	66 000
		292	14 000
Naphthacene		272	180 000
		473	12 500

**TABLE 7.9** Electronic Absorption Bands for Representative Chromophores (*Continued*)

Chromophore	System	$\lambda_{\max}$	$\epsilon_{\max}$
Pentacene		310	300 000
		585	12 000
Pyridine		174	80 000
		195	6 000
		257	1 700
Quinoline		227	37 000
		270	3 600
		314	2 750
Isoquinoline		218	80 000
		266	4 000
		317	3 500

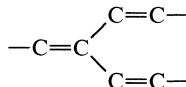
**TABLE 7.10** Ultraviolet Cutoffs of Spectrograde Solvents*Absorbance of 1.00 in a 10.0 mm cell vs. distilled water.*

Solvent	Wavelength, nm	Solvent	Wavelength, nm
Acetic acid	260	Hexadecane	200
Acetone	330	Hexane	210
Acetonitrile	190	Isobutyl alcohol	230
Benzene	280	Methanol	210
1-Butanol	210	2-Methoxyethanol	210
2-Butanol	260	Methylcyclohexane	210
Butyl acetate	254	Methylene chloride	235
Carbon disulfide	380	Methyl ethyl ketone	330
Carbon tetrachloride	265	Methyl isobutyl ketone	335
1-Chlorobutane	220	2-Methyl-1-propanol	230
Chloroform (stabilized with ethanol)	245	<i>N</i> -Methylpyrrolidone	285
Cyclohexane	210	Nitromethane	380
1,2-Dichloroethane	226	Pentane	210
Diethyl ether	218	Pentyl acetate	212
1,2-Dimethoxyethane	240	1-Propanol	210
<i>N,N</i> -Dimethylacetamide	268	2-Propanol	210
<i>N,N</i> -Dimethylformamide	270	Pyridine	330
Dimethylsulfoxide	265	Tetrachloroethylene	290
1,4-Dioxane	215	(stabilized with thymol)	
Ethanol	210	Tetrahydrofuran	220
2-Ethoxyethanol	210	Toluene	286
Ethyl acetate	255	1,1,2-Trichloro-1,2,2- trifluoroethane	231
Ethylene chloride	228	2,2,4-Trimethylpentane	215
Glycerol	207	<i>o</i> -Xylene	290
Heptane	197	Water	191

**TABLE 7.11** Absorption Wavelength of Dienes

Heteroannular and acyclic dienes usually display molar absorptivities in the 8000 to 20 000 range, whereas homoannular dienes are in the 5000 to 8000 range.

Poor correlations are obtained for cross-conjugated polyene systems such as



The correlations presented here are sometimes referred to as Woodward's rules or the Woodward-Fieser rules.

Base value for heteroannular or open chain diene, nm	214
Base value for homoannular diene, nm	253
Increment (in nm) for	
double bond extending conjugation	30
Alkyl substituent or ring residue	5
Exocyclic double bond	5
Polar groupings:	
-O-acyl	0
-O-alkyl	6
-S-alkyl	30
-Cl, -Br	5
-N (alkyl) <sub>2</sub>	60
Solvent correction (see Table 7.13)	—
Calculated wavelength =	total

Ring substitution on the benzene ring affords shifts to longer wavelengths (Table 7.14) and intensification of the spectrum. With electron-withdrawing substituents, practically no change in the maximum position is observed. The spectra of heteroaromatics are related to their isocyclic analogs, but only in the crudest way. As with benzene, the magnitude of substituent shifts can be estimated, but tautomeric possibilities may invalidate the empirical method.

When electronically complementary groups are situated *para* to each other in disubstituted benzenes, there is a more pronounced shift to a longer wavelength than would be expected from the additive effect due to the extension of the chromophore from the electron-donating group through the ring to the electron-withdrawing group. When the *para* groups are not complementary, or when the groups are situated *ortho* or *meta* to each other, disubstituted benzenes show a more or less additive effect of the two substituents on the wavelength maximum. Calculation of the principal band of selected substituted benzenes is illustrated in Table 7.15.

**TABLE 7.12** Absorption Wavelength of Enones and Dienones

$\text{O}=\text{C}-\overset{\alpha}{\text{C}}=\overset{\beta}{\text{C}}$ $\text{O}=\text{C}-\overset{\alpha}{\text{C}}=\overset{\beta}{\text{C}}-\overset{\gamma}{\text{C}}=\overset{\delta}{\text{C}}$	
Base values, nm	
Acyclic $\alpha,\beta$ -unsaturated ketones	215
Acyclic $\alpha,\beta$ -unsaturated aldehyde	210
Six-membered cyclic $\alpha,\beta$ -unsaturated ketones	215
Five-membered cyclic $\alpha,\beta$ -unsaturated ketones	214
$\alpha,\beta$ -Unsaturated carboxylic acids and esters	195
Increments (in nm) for	
Double bond extending conjugation:	
Heteroannular	30
Homoannular	69
Alkyl group or ring residue:	
$\alpha$	10
$\beta$	12
$\gamma, \delta$	18
Polar groups:	
—OH	
$\alpha$	35
$\beta$	30
$\gamma$	50
—O—CO—CH <sub>3</sub> and —O—CO—C <sub>6</sub> H <sub>5</sub> : $\alpha, \beta, \gamma, \delta$	6
—OCH <sub>3</sub>	
$\alpha$	35
$\beta$	30
$\gamma$	17
$\delta$	31
—S—alkyl, $\beta$	85
—Cl	
$\alpha$	15
$\beta$	12
—Br	
$\alpha$	25
$\beta$	30
—N(alkyl) <sub>2</sub> , $\beta$	95
Exocyclic double bond	5
Solvent correction (see Table 7.13)	—
Calculated wavelength =	total

**TABLE 7.13** Solvent Correction for Ultraviolet-Visible Spectroscopy

Solvent	Correction, nm
Chloroform	+ 1
Cyclohexane	
Diethyl ether	+ 11
1,4-Dioxane	+ 5
Ethanol	0
Hexane	+ 11
Methanol	0
Water	− 8

**TABLE 7.14** Primary Bands of Substituted Benzene and Heteroaromatics*In methanol.*

Base value: 203.5 nm.

Substituent	Wavelength shift, nm	Substituent	Wavelength shift, nm
—CH <sub>3</sub>	3.0	—COOH	25.5
—CH=CH <sub>2</sub>	44.5	—COO <sup>−</sup>	20.5
—C≡CH	44	—CN	20.5
—C <sub>6</sub> H <sub>5</sub>	48	—NH <sub>2</sub>	26.5
—F	0	—NH <sub>3</sub> <sup>+</sup>	− 0.5
—Cl	6.0	—N(CH <sub>3</sub> ) <sub>2</sub>	47.0
—Br	6.5	—NH—CO—CH <sub>3</sub>	38.5
—I	3.5	—NO <sub>2</sub>	57
—OH	7.0	—SH	32
—O <sup>−</sup>	31.5	—SO—C <sub>6</sub> H <sub>5</sub>	28
—OCH <sub>3</sub>	13.5	—SO <sub>2</sub> CH <sub>3</sub>	13
—OC <sub>6</sub> H <sub>5</sub>	51.5	—SO <sub>2</sub> NH <sub>2</sub>	14.0
—CHO	46.0	—CH=CH—C <sub>6</sub> H <sub>5</sub>	
—CO—CH <sub>3</sub>	42.0	<i>cis</i>	79
—CO—C <sub>6</sub> H <sub>5</sub>	48	<i>trans</i>	92.0
		—CH=CH—COOH, <i>trans</i>	69.5
Heteroaromatic	Base value, nm	Heteroaromatic	Base value, nm
Furan	200	Pyridine	257
Pyrazine	257	Pyrimidine	ca 235
Pyrazole	214	Pyrrole	209
Pyridazine	ca 240	Thiophene	231

**TABLE 7.15** Wavelength Calculation of the Principal Band of Substituted Benzene Derivatives*In ethanol.*

Base value of parent chromophore, nm	
$\text{C}_6\text{H}_5\text{COOH}$ or $\text{C}_6\text{H}_5\text{COO—alkyl}$	230
$\text{C}_6\text{H}_5\text{—CO—alkyl (or aryl)}$	246
$\text{C}_6\text{H}_5\text{CHO}$	250
Increment (in nm) for each substituent on phenyl ring	
—Alkyl or ring residue	
<i>o-</i> , <i>m-</i>	3
<i>p-</i>	10
—OH and —O— alkyl	
<i>o-</i> , <i>m-</i>	7
<i>p-</i>	25
—O <sup>−</sup>	
<i>o-</i>	11
<i>m-</i>	20
<i>p-</i>	78*
—Cl	
<i>o-</i> , <i>m-</i>	0
<i>p-</i>	10
—Br	
<i>o-</i> , <i>m-</i>	2
<i>p-</i>	15
—NH <sub>2</sub>	
<i>o-</i> , <i>m-</i>	13
<i>p-</i>	58
—NHCO—CH <sub>3</sub>	
<i>o-</i> , <i>m-</i>	20
<i>p-</i>	45
—NHCH <sub>3</sub>	
<i>p-</i>	73
—N(CH <sub>3</sub> ) <sub>2</sub>	
<i>o-</i> , <i>m-</i>	20
<i>p-</i>	85

\* Value may be decreased markedly by steric hindrance to coplanarity.



## 7.3 FLUORESCENCE

TABLE 7.16 Fluorescence Spectroscopy of Some Organic Compounds

Compound	Solvent	pH	Excitation wavelength, nm	Emission wavelength, nm
Acenaphthene	Pentane		291	341
Acridine	CF <sub>3</sub> COOH		358	475
Adenine	Water	1	280	375
Adenosine	Water	1	285	395
Adenosine triphosphate	Water	1	285	395
Adrenalin			295	335
<i>p</i> -Aminobenzoic acid	Water	8	295	345
Aminopterin	Water	7	280, 370	460
1-Aminopyrene	CF <sub>3</sub> COOH		330, 342	415
<i>p</i> -Aminosalicylic acid	Water	11	300	405
Amobarbital	Water	14	265	410
Anilines	Water	7	280, 291	344, 361
Anthracene	Pentane		420	430
Anthranilic acid	Water	7	300	405
Azaindoles	Water	10	290, 299	310, 347
Benz[ <i>c</i> ]acridine	CF <sub>3</sub> COOH		295, 380	480
Benz[ <i>a</i> ]anthracene	Pentane		284	382
1,2-Benzanthracene			280, 340	390, 410
Benzanthrone	CF <sub>3</sub> COOH		370, 420	550
Benzo[ <i>b</i> ]chrysene	Pentane		283	398
11- <i>H</i> -Benzo[ <i>a</i> ]fluorene	Pentane		317	340
Benzoic acid	70% H <sub>2</sub> SO <sub>4</sub>		285	385
3,4-Benzopyrene	Benzene		365	390, 480
Benzo[ <i>e</i> ]pyrene	Pentane		329	389
Benzoquinoline	CF <sub>3</sub> COOH		280	425
Benzoxanthane	Pentane		363	418
Bromolysergic acid diethyl amide	Water	1	315	460
Brucine	Water	7	305	500
Carbazole	<i>N,N</i> -Dimethyl formamide		291	359
Chlortetracycline			355	445
Chrysene	Pentane		250, 300, 310	260, 380
Cinchonine	Water	1	320	420
Coumarin	Ethanol		280	352
Dibenzo[ <i>a,c</i> ]anthracene	Pentane		280	381
Dibenzo[ <i>b,k</i> ]chrysene	Pentane		308	428
Dibenzo[ <i>a,e</i> ]pyrene	Pentane		370	401
3,4,8,9-Dibenzopyrene			370, 335, 390, 410	480, 510
5,12-Dihydronaphthacene	Pentane		282	340
1,4-Diphenylbutadiene	Pentane		328	370
Epinephrine	Water	7	295	335
Ethacridine	Water	2	370, 425	515
Fluoranthrene	Pentane		354	464
Fluorene	Pentane		300	321
Fluorescein	Water	7–11	490	515

**TABLE 7.16** Fluorescence Spectroscopy of Some Organic Compounds (*Continued*)

Compound	Solvent	pH	Excitation wavelength, nm	Emission wavelength, nm
Folic acid	Water	7	365	450
Gentisic acid	Water	7	315	440
Griseofulvin	Water	7	295, 335	450
Guanine	Water	1	285	365
Harmine	Water	1	300, 365	400
Hippuric acid	70% H <sub>2</sub> SO <sub>4</sub>		270	370
Homovanillic acid	Water	7	270	315
<i>m</i> -Hydroxybenzoic acid	Water	12	314	430
<i>p</i> -Hydroxycinnamic acid	Water	7	350	440
7-Hydroxycoumarin	Ethanol		325	441
5-Hydroxyindole	Water	1	290	355
5-Hydroxyindoleacetic acid	Water	7	300	355
3-Hydroxykynurenine	Water	11	365	460
<i>p</i> -Hydroxymandelic acid	Water	7	300	380
<i>p</i> -Hydroxyphenylacetic acid	Water	7	280	310
<i>p</i> -Hydroxyphenylpyruvic acid	Water	7	290	345
<i>p</i> -Hydroxyphenylserine	Water	1	290	320
5-Hydroxytryptophan	Water	7	295	340
Imipramine	Water	14	295	415
Indoleacetic acid	Water	8	285	360
Indoles	Water	7	269, 315	355
Indomethacin	Water	13	300	410
Kynurenic acid	Water	7	325	405
		11	325	440
Lysergic acid diethylamide	Water	1	325	445
Menadione	Ethanol		335	480
9-Methylanthracene	Pentane		382	410
3-Methylcholanthrene	Pentane		297	392
7-Methyldibenzopyrene	Pentane		460	467
2-Methylphenanthrene	Pentane		257	357
3-Methylphenanthrene	Pentane		292	368
1-Methylpyrene	Pentane		336	394
4-Methylpyrene	Pentane		338	386
Naphthacene			290, 310	480, 515
1-Naphthol	0.1 <i>M</i> NaOH 20% ethanol		365	480
2-Naphthol	0.1 <i>M</i> NaOH 20% ethanol		365	426
Oxytetracycline			390	520
Phenanthrene	Pentane		252	362
Phenylalanine	Water		215, 260	282
<i>o</i> -Phenylenepyrene	Pentane		360	506
Phenylephrine			270	305
Picene	Pentane		281	398
Procaine	Water	11	275	345
Pyrene	Pentane		330	382
Pyridoxal	Water	12	310	365
Quinacrine	Water	11	285	420
Quinidine	Water	1	350	450
Quinine	Water	1	250, 350	450
Reserpine	Water	1	300	375

**TABLE 7.16** Fluorescence Spectroscopy of Some Organic Compounds (*Continued*)

Compound	Solvent	pH	Excitation wavelength, nm	Emission wavelength, nm
Resorcinol	Water		265	315
Riboflavin	Water	7	270, 370, 445	520
Rutin	Water	1	430	520
Salicyclic acid	Water	11	310	435
Scoparone	Water	10	350, 365	430
Scopoletin	Water	10	365, 390	460
Serotonin	3 <i>M</i> HCl		295	550
Skatole	Water		290	370
Streptomycin	Water	13	366	445
<i>p</i> -Terphenyl	Pentane		284	338
Thiopental			315	530
Thymol	Water	7	265	300
Tocopherol	Hexane-ethanol		295	340
Tribenzo[ <i>a,e,i</i> ]pyrene	Pentane		384	448
Triphenylene	Pentane		288	357
Tryptamine	Water	7	290	360
Tryptophan	Water	11	285	365
Tyramine	Water	1	275	310
Tyrosine	Water	7	275	310
Uric acid	Water	1	325	370
Vitamin A	1-Butanol		340	490
Vitamin B <sub>12</sub>	Water	7	275	305
Warfarin	Methanol		290, 342	385
Xanthine	Water	1	315	435
2,6-Xylenol			275	305
3,4-Xylenol			280	310
Yohimbine	Water	1	270	360
Zoxazolamine	Water	11	280	320

**TABLE 7.17** Fluorescence Quantum Yield Values

Compound	Solvent	$Q_F$ value vs. $Q_F$ standard
$Q_F$ standard		
9-Aminoacridine	Water	0.99
Anthracene	Ethanol	0.30
POPOP*	Toluene	0.85
Quinine sulfate dihydrate	1N $H_2SO_4$	0.55
Secondary standards		
Acridine orange hydrochloride	Ethanol	0.54 Quinine sulfate 0.58 Anthracene
1,8-ANS† (free acid)	Ethanol	0.38 Anthracene 0.39 POPOP
1,8-ANS (magnesium salt)	Ethanol	0.29 Anthracene 0.31 POPOP
Fluorescein	0.1N NaOH	0.91 Quinine sulfate 0.94 POPOP
Fluorescein, ethyl ester	0.1N NaOH	0.99 Quinine sulfate 0.99 POPOP
Rhodamine B	Ethanol	0.69 Quinine sulfate 0.70 Anthracene
2,6-TNS‡ (potassium salt)	Ethanol	0.48 Anthracene 0.51 POPOP

\* POPOP *p*-bis[2-(5-phenyloxazolyl)]benzene.

† ANS, anilino-8-naphthalene sulfonic acid.

‡ TNS, 2-*p*-toluidinylnaphthalene-6-sulfonate.

#### 7.4 FLAME ATOMIC EMISSION, FLAME ATOMIC ABSORPTION, ELECTROTHERMAL (FURNACE) ATOMIC ABSORPTION, ARGON INDUCTION COUPLED PLASMA, AND PLASMA ATOMIC FLUORESCENCE

The tables of atomic emission and atomic absorption lines are presented in two parts. In Table 7.18 the data are arranged in alphabetic order by name of the element, whereas in Table 7.19 the sensitive lines of the elements are arranged in order of decreasing wavelengths. For additional lines and their relative intensities consult W. F. Meggers, C. H. Corliss, and B. F. Scribner, *Tables of Spectral-Line Intensities, Part I*, National Bureau of Standards Monograph 32, U.S. Government Printing Office, Washington, D.C., 1961.

The detection limits in the table correspond generally to the concentration of an element required to give a net signal equal to three times the standard deviation of the noise (background) in accordance with IUPAC recommendations. Detection limits can be confusing when steady-state techniques such as flame atomic emission or absorption, and plasma atomic emission or fluorescence, which

**TABLE 7.18** Detection Limits in ng/mL

The detection limits in the table correspond generally to the concentration of analyte required to give a net signal equal to three times the standard deviation of the background in accordance with IUPAC recommendations.

Element	Wavelength, nm	Flame emission	Flame atomic absorption	Electrothermal atomic absorption	Argon ICP	Plasma atomic fluorescence
Aluminum	308.22		40		10	
	309.28		20	0.05	11	4
	394.40	3.6	45		36	
	396.15	7.5	30	0.01	20	5
Antimony	206.83				50	
	217.58		30		50	
	231.15	70			30	10
	259.81	200		0.08		0.1
Arsenic	189.04		160		35	
	193.76		120	1	50	
	197.20		240			
	228.81	455				
	234.90	250				10
Barium	455.36	3			0.9	
	493.41	4			1	
	553.55	1.5	9	0.04		2
Beryllium	234.86		1	0.05	0.4	
	313.04		2	0.003	1	
	313.11	100			1	0.2
Bismuth	223.06		18	0.35	30	
	227.66			2		
	306.77	60		0.5	30	2
Boron	182.59				8	
	249.77		700	15	3	60
(as BO <sub>2</sub> )	518.0	50				
(as BO <sub>2</sub> )	547.6	50				
Bromine	154.07				50	
Cadmium	214.44				1.0	
	226.50				0.6	
	228.80	6	1	0.008	228	
	326.11	3	0.5	0.014		0.001
Calcium	315.89				20	
	393.37				0.6	
	396.85				1.2	
	422.67	1.5	1	0.3		0.08
Carbon	193.09				44	
	247.86				1000	
Cerium	413.38				30	
	418.66				30	
	569.92	150				
Cesium	852.11	0.02	8	0.04		
	894.35	0.04	130			
Chlorine	134.72				50	
Chromium	267.72				3	
	283.58				20	
	284.98				30	
	357.87	6	2	0.05		0.4
	359.35	7				

**TABLE 7.18** Detection Limits in ng/mL (*Continued*)

Element	Wavelength, nm	Flame emission	Flame atomic absorption	Electrothermal atomic absorption	Argon ICP	Plasma atomic fluorescence
Chromium	360.53	13				
( <i>cont.</i> )	425.44	3	6		66	
	427.48	4				
	428.97	5				
Cobalt	228.62				3	
	238.89				28	
	240.73	5	8	0.01	7	0.4
	345.35	30				
Copper	324.75	1.5	1	0.01	2	0.2
	327.40	3	2	0.02	4	
Dysprosium	353.17				3	
	340.78				6	
	404.60	30	50			300
	418.68		60			
	421.17		60			
Erbium	323.06				15	
	349.81				10	
	400.80	30	40	0.3		500
	408.77		40			
Europium	381.97				2	
	412.97				3	
	459.40	0.45	20	0.5		20
Gadolinium	335.05				10	
	368.41		4000			
	440.19	72	1000	8		800
Gallium	287.42		70			
	294.36		20		30	
	404.30	5	50			
	417.21	3	30	1	40	0.9
Germanium	209.43				50	
	219.87				100	
	265.12	400	40	7.5		50
Gold	242.80		10	0.5	5	
	267.60	500	8	0.5	10	0.3
Hafnium	263.87				10	
	277.34				10	
	307.29		2000			
Holmium	339.90				3	
	345.60				8	
	405.39	15	40	0.7		100
	410.38		30			
Indium	230.61				40	
	303.94	100	7	0.01		
	325.61	22	8			
	410.18	14	20			
	451.13	0.7	22		2	0.2
Iodine	178.38				20	
	183.0			3		
Iridium	208.88	400	500	0.5		
	212.68				20	
	224.27				20	

**TABLE 7.18** Detection Limits in ng/mL (*Continued*)

Element	Wavelength, nm	Flame emission	Flame atomic absorption	Electrothermal atomic absorption	Argon ICP	Plasma atomic fluorescence
Iron	238.20				4	
	248.33		3	0.01		
	259.94				3	
	302.06	18	5			
	371.99	15	10			0.3
	385.99	12	21			
Lanthanum	379.48				15	
	392.76		8000			
	408.67				2	
	550.13	20				
	579.13	5	2000	0.5		
	441.82	100				
(as LaO)	560.25	300				
Lead	217.10		20	0.4		
	220.35				20	
	283.31	60	10	1		5
	368.35	30				
	405.78	20				
Lithium	460.29	0.06	30		50	
	610.36	0.001				
	670.78	0.003	0.3	1.5	5	0.4
Lutetium	261.54				1	
	307.76				6	
Magnesium	279.08				30	
	279.55				1.5	
	285.21	4.5	0.1	0.018	3.6	0.4
Manganese	256.37				2.7	
	257.61				0.5	
	259.37		60		3	
	260.57				6	
	279.48	1	1	0.05		0.4
	293.30				24	
	294.92				24	
Mercury	403.08	1.5	30			
	194.23				30	
	253.65	150	0.001	6	50	5
Molybdenum	202.03				5	
	203.84				8	
	281.62				1.2	
	313.26	220	30	0.06		12
Neodymium	390.30	75	50			
	292.45	200				
	401.23				10	
	430.36				30	
Nickel	492.45	150	600			2000
	231.60				6	
	232.00	8	4	0.5	10	
	341.48	15	2			
Niobium	352.45	8	2			2
	316.34				20	
	405.89	250	1000			1000

**TABLE 7.18** Detection Limits in ng/mL (*Continued*)

Element	Wavelength, nm	Flame emission	Flame atomic absorption	Electrothermal atomic absorption	Argon ICP	Plasma atomic fluorescence
Osmium	225.58				20	
	228.23				40	
	263.71	2000	80			
	290.91		110			
Palladium	244.8	20	20	0.5		40
	340.46	25	80		40	
	363.47	50			60	
Phosphorus	178.28				50	
	213.62				50	
(as HPO)	524.9	100				
Platinum	214.42				20	
	265.95	2000	100	0.2	40	300
Potassium	404.41	1.3	100			
	404.72	2.6				
	766.49	0.15	1	0.004	200	0.6
	769.90	0.3	2			
Praseodymium	390.84				20	
	414.31				30	
	493.97	300				1000
Rhenium	197.31				8	
	345.19	690				
	346.05	200	200	10		
	346.47	275				
Rhodium	343.49	10	2	0.1	20	100
	369.24	20			30	
Rubidium	780.02	0.0065	0.3		500	3
	794.76	0.013				
Ruthenium	240.27				50	
	349.89	80	70	10	150	500
Samarium	442.43				10	
	476.03	30	500		100	
Scandium	255.24				21	
	357.24				1	
	361.38				1.5	
	391.18	21	20	6	120	10
	402.04	30				
	402.34	30				
Selenium	196.03		90	2.5	6	10
Silicon	251.61		80	0.5	10	50
	283.16				15	
Silver	328.07	2	0.9	0.001	4.5	0.1
	338.29	4			3	
Sodium	330.23	125		0.7	15	
	330.30	250				
Strontium	589.00	0.01	0.2	0.004	20	0.2
	589.59	0.02				
	407.78				1	
	421.55				0.5	
	460.73	0.1	2	0.01		0.3
Sulfur (as S <sub>2</sub> )	180.73		10		70	
	394.0	1600				



**TABLE 7.18** Detection Limits in ng/mL (*Continued*)

Element	Wavelength, nm	Flame emission	Flame atomic absorption	Electrothermal atomic absorption	Argon ICP	Plasma atomic fluorescence
Tantalum	240.06				20	
	271.47		800			
Tellurium	214.27	150	15	0.5		2
	238.58				60	
Terbium	350.92				10	
	384.87				40	
	431.89	150	600			500
Thallium	190.86				50	
	276.78		9	0.15		
	351.92				150	
	377.57	3		0.5		4
	535.0	1.5				
Thorium	283.73				30	
	401.91				30	
Thulium	313.13				3	
	371.79	4	10			100
	384.80				7	
Tin	189.99				15	
	224.60		110	1	30	
	284.00	100	200			10
	286.33		160	1.5		
Titanium	334.19	400				
	334.94				6	
	337.28				8	
	364.27	210	60	2.5		30
	365.35	180				
	399.86	150				
Tungsten	207.91				30	
	209.48				50	
	400.87	450	1000			2000
Uranium	358.49	100		30		
	385.96				70	
	409.01				140	
Vanadium	292.40				7.8	
	310.23				10	
	318.34	18				
	318.54	25	50	1		30
	437.92	15				
Ytterbium	328.94				1	
	369.42				2	
	398.80	0.45	5	0.1		10
Yttrium	360.07				3	
	362.09	40	50	10		50
	371.03				1	
	410.24	30	50			
Zinc	202.55				4	
	213.86	1000	0.8	0.005	2	0.0003
Zirconium	339.20				5	
	343.82				7	
	349.62				45	
	360.12	1000	350			

**TABLE 7.19** Sensitive Lines of the Elements

In this table the sensitive lines of the elements are arranged in order of decreasing wavelengths. A Roman numeral II following an element designation indicates a line classified as being emitted by the singly ionized atom. In the column headed Sensitivity, the most sensitive line of the non-ionized atom is indicated by U1, and other lines by U2, U3, and so on, in order of decreasing sensitivity. For the singly ionized atom the corresponding designations are V1, V2, V3, and so on.

Wavelength, nm	Element	Sensitivity	Wavelength, nm	Element	Sensitivity
894.35	Cs	U2	492.45	Nd	U1
852.11	Cs	U1	488.91	Re	U4
819.48	Na	U4	487.25	Sr	U3
818.33	Na	U3	483.21	Sr	U2
811.53	Ar	U2	482.59	Ra	U1
794.76	Rb	U2	481.95	Cl II	V4
780.02	Rb	U1	481.67	Br II	V3
769.90	K	U2	481.05	Zn	U3
766.49	K	U1	481.01	Cl II	V3
750.04	Ar	U4	479.45	Cl II	V2
706.72	Ar	U3	478.55	Br II	V2
696.53	Ar	U3	476.03	Sm	U1
690.24	F	U3	470.09	Br II	V1
685.60	F	U2	467.12	Xe	U2
670.78	Li	U1	462.43	Xe	U3
656.28	H	U2	460.73	Sr	U1
649.69	Ba II	V4	460.29	Li	U4
624.99	La	U3	459.40	Eu	U1
614.17	Ba II	V3	459.32	Cs	U4
610.36	Li	U2	455.54	Cs	U3
593.06	La	U4	455.40	Ba II	V1
589.59	Na	U2	451.13	In	U1
589.00	Na	U1	450.10	Xe	U4
587.76	He	U3	445.48	Ca	U2
587.09	Kr	U2	442.43	Sm II	V4
579.13	La	U1	440.85	V	U4
569.92	Ce	U1	440.19	Gd	U1
567.96	N II	V2	439.00	V	U3
567.60	N II	V4	437.49	Y II	V4
566.66	N II	V3	437.92	V	U1
557.02	Kr	U3	435.84	Hg	U3
553.55	Ba	U1	431.89	Tb	U1
550.13	La	U2	430.36	Nd II	V2
546.55	Ag	U4	430.21	W	U1
546.07	Hg	U2	429.67	Sm	U1
545.52	La	U3	428.97	Cr	U3
535.84	Hg	U3	427.48	Cr	U2
535.05	Tl	U1	425.43	Cr	U1
521.82	Cu	U3	422.67	Ca	U1
520.91	Ag	U3	421.56	Rb	U4
520.84	Cr	U8	421.55	Sr II	V1
520.60	Cr	U7	421.17	Dy	U2
515.32	Cu	U4	420.19	Rb	U3
498.18	Ti	U1	418.68	Dy	U2
496.23	Sr	U2	418.66	Ce II	V1
493.97	Pr	U1	417.21	Ga	U1
493.41	Ba II	V2	414.31	Pr II	V2

**TABLE 7.19** Sensitive Lines of the Elements (*Continued*)

Wavelength, nm	Element	Sensitivity	Wavelength, nm	Element	Sensitivity
414.29	Y	U4	386.41	Mo	U2
413.38	Ce II	V1	385.99	Fe	U2
413.07	Ba II	V5	385.96	U II	V1
412.97	Eu II	V2	384.87	Tb II	V2
412.83	Y	U3	384.80	Tm II	V2
412.38	Nb	U4	383.83	Mg	U2
412.32	La II	V4	383.82	Mo	U2
411.00	N	U2	382.23	Mg	U3
410.38	Ho	U1	382.94	Mg	U4
410.24	Y	U1	381.97	Eu II	V1
410.18	In	U2	379.94	Ru	U3
410.09	Nb	U3	379.63	Mo	U1
409.99	N	U3	379.48	La II	V2
409.01	U II	V2	379.08	La II	V3
408.77	Er	U1	377.57	Tl	U3
408.67	La II	V1	377.43	Y II	V3
407.97	Nb	U2	374.83	Fe	U4
407.77	Sr II	V2	373.49	Fe	U2
407.74	Y	U2	372.80	Ru	U1
407.74	La II	V2	371.99	Fe	U1
407.43	W	U2	371.79	Tm	U1
405.89	Nb	U1	371.03	Y II	V1
405.78	Pb	U1	369.42	Yb II	V2
405.39	Ho	U2	369.24	Rh	U2
404.72	K	U4	368.41	Gd	U2
404.66	Hg	U5	368.35	Pb	U2
404.60	Dy	U1	365.48	Hg	U4
404.41	K	U3	365.35	Ti	U2
403.45	Mn	U3	365.01	Hg	U3
403.31	Mn	U2	364.28	Sc II	V3
403.30	Ga	U2	364.27	Sn	U3
403.08	Mn	U1	363.47	Pd	U2
402.37	Sc	U3	363.07	Sc II	V2
402.04	Sc	U3	362.09	Y	U2
401.91	Th II	V1	361.38	Sc II	V1
401.23	Nd II	V1	360.96	Pd	U2
400.87	W	U1	360.12	Zr	U1
400.80	Er	U1	360.07	Y II	V2
399.86	Cr	U1	360.05	Cr	U6
399.86	Ti	U1	359.62	Ru	U3
398.80	Yb	U1	359.34	Cr	U5
396.85	Ca II	V2	359.26	Sm II	V1
396.15	Al	U1	358.49	U	V1
394.91	La II	V2	357.87	Cr	U4
394.40	Al	U2	357.25	Zr II	V4
393.37	Ca II	V1	357.24	Sc II	V1
391.18	Sc	U1	356.83	Sn II	V1
390.84	Pr II	V1	355.31	Pd	U3
390.75	Sc	U2	354.77	Zr	U3
390.30	Mo	U1	353.17	Dy II	V1
389.18	Ba	V4	352.98	Co	U3
388.86	He	U2	352.94	Tl	U4
388.63	Fe	U5	352.69	Co	U4

**TABLE 7.19** Sensitive Lines of the Elements (*Continued*)

Wavelength, nm	Element	Sensitivity	Wavelength, nm	Element	Sensitivity
352.45	Ni	U2	324.75	Cu	U1
351.96	Zr	U3	324.27	Pd	U4
351.92	Tl	U2	323.45	Cr	V3
351.69	Pd	U3	323.26	Li	U3
351.36	Ir	U2	323.06	Er II	V2
350.92	Tb II	V1	322.08	Ir	U1
350.63	Co	U3	318.54	V	U3
350.23	Co	U2	318.40	V	U2
349.89	Ru	U2	317.93	Ca II	V3
349.62	Zr II	V3	316.34	Nb II	V1
349.41	Er II	V1	315.89	Ca II	V4
348.11	Pd	U5	313.26	Mo	U2
347.40	Ni	U3	313.13	Tm II	V1
346.47	Re	U2	313.11	Be	U1
346.05	Re	U1	313.04	Be	U2
345.60	Ho II	V2	311.84	V II	V4
345.58	Co	U5	311.07	V II	V3
345.19	Re	U3	310.23	V II	V2
345.14	B II	V2	309.42	Nb II	V1
344.36	Co	U2	309.31	V II	V1
344.06	Fe	U2	309.27	Al	U3
343.82	Zr II	V2	308.22	Al	U4
343.67	Ru	U2	307.76	Lu II	V2
343.49	Rh	U1	307.29	Hf	U1
342.83	Ru	U4	306.77	Bi	U3
342.12	Pd	U3	306.47	Pt	U1
341.48	Ni	U3	303.94	In	U4
341.23	Co	U4	303.90	Ge	U2
340.78	Dy II	V2	303.41	Sn	U3
340.51	Co	U2	302.06	Fe	U3
340.46	Pd	U2	300.91	Sn	U4
339.90	Ho II	V1	294.91	Mn II	V4
339.20	Zr II	V1	294.44	W	U5
338.29	Ag	U2	294.36	Ga	U3
337.28	Ti II	V3	294.02	Ta	U3
336.12	Ti II	V2	293.30	Mn II	V4
335.05	Gd II	V1	292.98	Pt	U3
334.94	Ti II	V1	292.45	Nd	U2
334.50	Zn	U2	292.40	V II	V1
334.19	Ti	U4	290.91	Os	U2
332.11	Be	U3	289.80	Bi	U2
331.12	Ta	U3	289.10	Mo II	V4
330.03	Na	U6	288.16	Si	U1
330.26	Zn	U3	287.42	Ga	U4
330.23	Na	U5	287.15	Mo II	V3
328.94	Yb II	V1	286.33	Sn	U2
328.23	Zn	U5	286.04	As	U2
328.07	Ag	U1	285.21	Mg	U1
327.40	Cu	U2	284.82	Mo II	V2
326.95	Ge	U3	284.00	Sn	U1
326.23	Sn	U3	283.73	Th II	V1
326.11	Cd	U1	283.58	Cr II	V2
325.61	In	U3	283.31	Pb	U3

**TABLE 7.19** Sensitive Lines of the Elements (*Continued*)

Wavelength, nm	Element	Sensitivity	Wavelength, nm	Element	Sensitivity
283.16	Si II	V1	239.56	Fe II	V2
283.03	Pt	U3	238.89	Co II	V2
281.62	Al II	V2	238.58	Te	U2
281.61	Mo II	V1	238.32	Te	U3
280.27	Mg II	V2	238.20	Fe II	V1
280.20	Pb	U4	234.90	As	U4
279.83	Mn	U3	234.86	Be	U1
279.55	Mg II	V1	232.00	Ni	U2
279.48	Mn	U3	231.60	Ni II	V1
279.08	Mg II	V2	231.15	Sb	U1
278.02	As	U1	230.61	In II	V1
277.34	Hf II	V1	228.81	As	U5
276.78	Tl	U4	228.80	Cd	U2
272.44	W	U4	228.71	Ni II	V1
271.90	Fe	U5	228.62	Co II	V1
271.47	Ta	U1	228.23	Os II	V2
270.65	Sn	U4	227.66	Bi	U3
267.72	Cr II	V1	227.02	Ni II	V2
267.60	Au	U2	226.50	Cd II	V2
266.92	Al II	V1	226.45	Ni II	V3
265.95	Pt	U1	225.58	Os II	V1
265.12	Ge	U1	225.39	Ni II	V4
265.05	Ba	U2	224.70	Cu II	V3
264.75	Ta	U2	224.64	Ag II	V3
263.87	Hf II	V1	224.60	Sn	U1
263.71	Os	U1	224.27	Ir II	V1
260.57	Mn II	V3	223.06	Bi	U1
259.94	Fe II	V1	220.35	Pb II	V1
259.81	Sb	U2	219.87	Ge II	V2
259.37	Mn	U2	219.23	Cu II	V2
257.61	Mn II	V1	217.58	Sb	U2
256.37	Mn II	V2	217.00	Pb II	V1
255.33	P	U3	214.44	Cd II	V1
255.24	Sc II	V3	214.42	Pt II	V1
253.65	Hg	U1	214.27	Te	U1
253.57	P	U1	213.86	Zn	U1
252.85	Si	U2	213.62	P	U1
252.29	Fe	U3	213.60	Cu II	V1
251.61	Si	U3	212.68	Ir II	V1
250.69	Si	U4	209.48	W II	V2
250.20	Zn II	V4	209.43	Ge II	V1
249.77	B	U1	208.88	Ir	U1
249.68	B	U2	207.91	W II	V1
248.33	Fe	U3	207.48	Se	U4
247.86	C	U2	206.83	Sb	U1
245.65	As	U4	206.28	Se	U3
243.78	Ag II	V2	206.19	Zn II	V2
242.80	Au	U1	203.99	Se	U1
241.05	Fe II	V4	203.84	Mo II	V3
240.73	Co	U1	202.55	Zn II	V1
240.49	Fe	V3	202.03	Mo II	V2
240.27	Ru	V1	197.31	Re II	V1
240.06	Ta II	V1	197.20	As	U3

**TABLE 7.19** Sensitive Lines of the Elements (*Continued*)

Wavelength, nm	Element	Sensitivity	Wavelength, nm	Element	Sensitivity
196.03	Se	U2	183.00	I	U2
194.23	Hg II	V1	182.59	B II	V2
193.76	As	U1	180.73	S	U1
193.09	C	U1	178.38	I	U1
190.86	Tl II	V1	178.28	P	U1
189.99	Sn II	V1	154.07	Br II	V4
189.04	As	U2	134.72	Cl II	V1

are steady-state techniques, are compared with the electrothermal or furnace technique which uses the entire sample and detects an absolute amount of the analyte element. To compare the several methods on the basis of concentration, the furnace detection limits assume a 20- $\mu\text{L}$  sample.

Data for the several flame methods assume an acetylene–nitrous oxide flame residing on a 5- or 10-cm slot burner. The sample is nebulized into a spray chamber placed immediately ahead of the burner. Detection limits are quite dependent on instrument and operating variables, particularly the detector, the fuel and oxidant gases, the slit width, and the method used for background correction and data smoothing.

### 7.4.1 Some Common Spectroscopic Relationships

**7.4.1.1 Electromagnetic Radiation.** Electromagnetic radiation travels in straight lines in a uniform medium, has a velocity of  $299\,792\,500\text{ m}\cdot\text{s}^{-1}$  in a vacuum, and possesses properties of both a wave motion and a particle (photon). *Wavelength*  $\lambda$  is the distance from crest to crest; *frequency*  $\nu$  is the number of waves passing a fixed point in a unit length of time. Wavelength and frequency are related by the relation

$$c = \lambda\nu$$

where  $c$  is the velocity of light (in a vacuum). In any material medium the speed of propagation is smaller than this and is given by the product  $nc$ , where  $n$  is the refractive index of the medium.

Radiation is absorbed or emitted only in discrete packets called photons and quanta:

$$E = h\nu$$

where  $E$  is the energy of the quantum and  $h$  is Planck's constant.

The relation between energy and mass is given by the *Einstein equation*:

$$\Delta E = \Delta mc^2$$

where  $\Delta E$  is the energy release and  $\Delta m$  is the loss of mass. Strictly, the mass of a particle depends on its velocity, but here the masses are equated to their rest masses (at zero velocity).

The *Wien displacement law* states that the wavelength of maximum emission,  $\lambda_m$ , of a blackbody varies inversely with absolute temperature; the product  $\lambda_m T$  remains constant. When  $\lambda_m$  is expressed in micrometers, the law becomes

$$\lambda_m T = 2898$$

In terms of  $\sigma_m$ , the wavenumber of maximum emission:

$$\sigma_m = 3.48T$$

Another useful version is  $h\nu_m = 5kT$ , where  $k$  is the Boltzmann constant.

*Stefan's law* states that the total energy  $J$  radiated by a blackbody per unit time and area (power per unit area) varies as the fourth power of the absolute temperature:

$$J = aT^{-4}$$

where  $a$  is a constant whose value is  $5.67 \times 10^{-8} \text{ W} \cdot \text{m}^{-2} \cdot \text{K}^{-4}$ .

The relationship between the voltage of an X-ray tube (or other energy source), in volts, and the wavelength is given by the *Duane-Hunt equation*:

$$\lambda = \frac{hc}{eV} = \frac{12\,398}{V}$$

where the wavelength is expressed in angstrom units.

**7.4.1.2 Laws of Photometry.** The time rate at which energy is transported in a beam of radiant energy is denoted by the symbol  $P_0$  for the incident beam, and by  $P$  for the quantity remaining unabsorbed after passage through a sample or container. The ratio of radiant power transmitted by the sample to the radiant power incident on the sample is the *transmittance*  $T$ :

$$T = \frac{P}{P_0}$$

The logarithm (base 10) of the reciprocal of the transmittance is the *absorbance*  $A$ :

$$A = -\log T = \log \left( \frac{1}{T} \right)$$

When a beam of monochromatic light, previously rendered plane parallel, enters an absorbing medium at right angles to the plane-parallel surfaces of the medium, the rate of decrease in radiant power with the length of light path (cuvette interior)  $b$ , or with the concentration of absorbing material  $C$  (in grams per liter) will follow the exponential progression, often referred to as *Beer's law*:

$$T = 10^{-abC} \quad \text{or} \quad A = abC$$

where  $a$  is the absorptivity of the component of interest in the solution. When  $C$  is expressed in moles per liter,

$$T = 10^{-\epsilon bC} \quad \text{or} \quad A = \epsilon bC$$

where  $\epsilon$  is the molar absorptivity.

The total fluorescence (or phosphorescence) intensity is proportional to the quanta of light absorbed,  $P_0 - P$ , and to the efficiency  $\phi$ , which is the ratio of quanta absorbed to quanta emitted:

$$F = (P_0 - P)\phi = P_0\phi(1 - e^{-\epsilon bC})$$

When the terms  $\epsilon bC$  is not greater than 0.05 (or 0.01 in phosphorescence),

$$F = k\phi P_0\epsilon bC$$

where the term  $k$  has been introduced to handle instrumental artifacts and the geometry factor because fluorescence (and phosphorescence) is emitted in all directions but is viewed only through a limited aperture.

The thickness of a transparent film or the path length of infrared absorption cells  $b$ , in centimeters, is given by

$$b = \frac{1}{2n_D} \left( \frac{n}{\bar{\nu}_1 - \bar{\nu}_2} \right)$$

where  $n$  is the number of fringes (peaks or troughs) between two wavenumbers  $\bar{\nu}_1$  and  $\bar{\nu}_2$ , and  $n_D$  is the refractive index of the sample material (unity for the air path of an empty cuvette). If measurements are made in wavelength, as micrometers, the expression is

$$b = \frac{1}{2n_D} \left( \frac{n\lambda_1\lambda_2}{\lambda_2 - \lambda_1} \right)$$

**7.4.1.3 Grating Equation.** The light incident on each groove is diffracted or spread out over a range of angles, and in certain directions reinforcement or constructive interference occurs, as stated in the grating formula:

$$m\lambda = b(\sin i \pm \sin r)$$

where  $b$  is the distance between adjacent grooves,  $i$  is the angle of incidence,  $r$  is the angle of reflection (both angles relative to the grating normal), and  $m$  is the order number. A positive sign applies where incoming and emergent beams are on the same side of the grating normal.

The *blaze wavelength* is that wavelength for which the angle of reflectance from the groove face and the angle of reflection (usually the angle of incidence) from the grating are identical.

The *Bragg equation*

$$m\lambda = 2d \sin \theta$$

states the condition for reinforcement of reflection from a crystal lattice, where  $d$  is the distance between each set of atomic planes and  $\theta$  is the angle of reflection.

**7.4.1.4 Ionization of Metals in a Plasma.** A loss in spectrochemical sensitivity results when a free metal atom is split into a positive ion and an electron:



The degree of ionization,  $\alpha_i$ , is defined as

$$\alpha_i = \frac{[M^+]}{[M^+] + [M]}$$

At equilibrium, when the ionization and recombination rates are balanced, the ionization constant  $K_i$  (in atm) is given by

$$K_i = \frac{[M^+][e^-]}{[M]} = \left( \frac{\alpha_i^2}{1 - \alpha_i^2} \right) p_{\Sigma M}$$

where  $p_{\Sigma M}$  (in atm) is the total atom concentration of metal in all forms in the plasma.



The ionization constant can be calculated from the *Saha equation*:

$$\log K_i = -5040 \frac{E_i}{T} + \frac{5}{2} \log T - 6.49 + \log \frac{g_{M^+} g_{e^-}}{g_M}$$

where  $E_i$  is the ionization potential of the metal in eV (Table 4.2),  $T$  is the absolute temperature of the plasma (in kelvins), and the  $g$  terms are the statistical weights of the ionized atom, the electron, and the neutral atom. For the alkali metals the final term is zero; for the alkaline earth metals, it is 0.6.

To suppress the ionization of a metal, another easily ionized metal (denoted a *deionizer* or *radiation buffer*) is added to the sample. To ensure that ionization is suppressed for the test element, the product  $(K_i)_M p_M$  of the deionizer must exceed the similar product for the test element one hundred-fold (for 1 percent residual ionization of the test element).

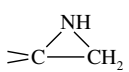
## 7.5 INFRARED SPECTROSCOPY

**TABLE 7.20** Absorption Frequencies of Single Bonds to Hydrogen

Abbreviations Used in the Table		
m, moderately strong	var, of variable strength	
m–s, moderate to strong	w, weak	
s, strong	w–m, weak to moderately strong	

Group	Band, cm <sup>-1</sup>	Remarks
Saturated C—H		
<div><div><div>H</div><div>—C—H</div><div>H</div></div></div>	<div>2975–2950 (s)</div> <div>2885–2865 (w)</div> <div>1450–1260 (m)</div>	<div>Two or three bands usually; asymmetrical and symmetrical CH stretching, respectively. In presence of double bond adjacent to CH<sub>3</sub> group symmetrical band splits into two.</div> <div>Sensitive to adjacent negative substituents</div>
<div><div><div>H</div><div>—C—</div><div>H</div></div><div>acyclic</div></div>	<div>ca 2930 (s)</div> <div>2870–2840 (w)</div> <div>1480–1440 (m)</div> <div>ca 720 (w)</div>	<div>Frequency increased in strained systems.</div> <div>Symmetrical band splits into two bands when double bond adjacent.</div> <div>Scissoring mode</div> <div>Rocking mode</div>
Alkane residues attached to carbon		
Cyclopropane	<div>ca 3050 (w)</div> <div>540–500</div> <div>470–460 (s)</div>	<div>CH stretching</div> <div>Aliphatic cyclopropanes</div>
Cyclobutanes	580–490 (s)	Alkyl derivatives: 550–530 cm <sup>-1</sup>
Cyclopentanes	595–490 (s)	Alkyl derivatives: 585–530 cm <sup>-1</sup>

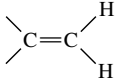
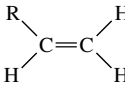
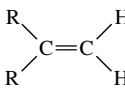
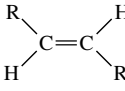
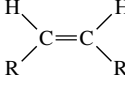
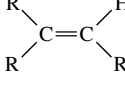
**TABLE 7.20** Absorption Frequencies of Single Bonds to Hydrogen (*Continued*)

Group	Band, cm <sup>-1</sup>	Remarks
Alkane residues attached to carbon ( <i>continued</i> )		
$\text{>C(CH}_3)_2$	ca 1380 (m) 1175–1165 (m) 1150–1130 (m)	A roughly symmetrical doublet If no H on central carbon, then one band at ca 1190 cm <sup>-1</sup>
$\text{—C(CH}_3)_3$	1395–1385 (m) 1365 (s)	Split into two bands
Aryl-CH <sub>3</sub> Aryl-C <sub>2</sub> H <sub>5</sub> Aryl-C <sub>3</sub> H <sub>7</sub> (or C <sub>4</sub> H <sub>9</sub> )	390–260 (m) 565–540 (m-s) 585–565 (m)	Two bands
$\text{—(CH}_2)_n\text{—}$ $n = 1$ $n = 2$ $n = 3$ $n \geq 4$	785–770 (w-m) 745–735 (w-m) 735–725 (w-m) 725–720 (w-m)	Rocking vibrations
Alkane residues attached to miscellaneous atoms		
Epoxide C—H 	ca 3050 (m-s) ca 3050 (m-s)	
$\text{—CH}_2\text{—halogen}$	ca 3050 (m-s) 1435–1385 (m) 1300–1240 (s)	Halogens except fluorine
$\text{—CHO}$	2900–2800 (w) 2775–2700 (w) 1420–1370 (m)	
$\text{—CO—CH}_3$	3100–2900 (w) 1450–1400 (s) 1360–1355 (s)	
$\text{—O—CH}_3$ ethers	2835–2810 (s) 1470–1430 (m-s) ca 1030 (w-m)	Two bands
$\text{—O—C(CH}_3)_3$	1200–1155 (s)	
$\text{—O—CH}_2\text{—O—}$	2790–2770 (m)	
$\text{—O—CH}_2\text{—}$ esters	1475–1460 (m-s) 1470–1435 (m-s)	Acyclic esters. Frequency increased ca 30 cm <sup>-1</sup> for cyclic and small ring systems.

**TABLE 7.20** Absorption Frequencies of Single Bonds to Hydrogen (*Continued*)

Group	Band, $\text{cm}^{-1}$	Remarks
Alkane residues attached to miscellaneous atoms ( <i>continued</i> )		
$-\text{O}-\text{CO}-\text{CH}_3$	1450–1400 (s) 1385–1365 (s) 1360–1355 (s)	Acetate esters The high intensity of these bands often dominates this region of the spectrum.
$-\text{CH}_2-\overset{\textstyle  }{\text{C}}=\text{C}\leq$	1445–1430 (m)	
$-\text{CH}_2-\text{SO}_2-$	ca 1250 (m)	
P—CH <sub>3</sub> Se—CH <sub>3</sub> B—CH <sub>3</sub> Si—CH <sub>3</sub> Sn—CH <sub>3</sub> Pb—CH <sub>3</sub> As—CH <sub>3</sub> Ge—CH <sub>3</sub> Sb—CH <sub>3</sub> Bi—CH <sub>3</sub> $-\text{CH}_2-(\text{Cd, Hg, Zn, Sn})$	1320–1280 (s) ca 1280 (m) 1460–1405 (m) 1320–1280 (m) 1265–1250 (m–s) 1200–1180 (m) 1170–1155 (m) 1265–1240 (m) 1240–1230 (m) 1215–1195 (m) 1165–1145 (m) 1430–1415 (m)	
N—CH <sub>3</sub> and N—CH <sub>2</sub> — N—CH <sub>2</sub> —CH <sub>2</sub> —N N—CH <sub>3</sub> Amine · HCl Amino acid · HCl Amides N—CH <sub>2</sub> — amides	2820–2780 (s) 1440–1390 (m) 1480–1450 (s) 1475–1395 (m) 1490–1480 (m) 1420–1405 (s) ca 1440 (m)	Ethylenediamine complexes Ethylenediamine complexes
S—CH <sub>3</sub>	2990–2955 (m–s) 2900–2865 (m–s) 1440–1415 (m) 1325–1290 (m) 1030–960 (m) 710–685 (w–m)	
S—CH <sub>2</sub> —	2950–2930 (m) 2880–2845 (m) 1440–1415 (m) 1270–1220 (s)	
$-\text{C}\equiv\text{CH}$	ca 3300 (s) 700–600	Sharp Bending
$\begin{array}{c} \diagup \quad \diagdown \\ \text{C}=\text{C} \quad \text{H} \\ \diagdown \quad \diagup \end{array}$	3040–3010 (m)	

**TABLE 7.20** Absorption Frequencies of Single Bonds to Hydrogen (*Continued*)

Group	Band, $\text{cm}^{-1}$	Remarks
Alkane residues attached to miscellaneous atoms ( <i>continued</i> )		
	3095–3075 (m) 2985–2970 (m)	CH stretching sometimes obscured by much stronger bands of saturated CH groups
	995–980 (s) 940–900 (s) ca 635 (s) 485–445 (m–s)	
	895–885 (s) 560–530 (s) 470–435 (m)	
	980–955 (s) 455–370 (m–s)	
	730–655 (m) 670–455 (s)	
	850–790 (m) 570–515 (s) 525–470 (s)	
—O—CH=CH <sub>2</sub>	965–960 (s) 945–940 (m) 820–810 (s)	
—S—CH=CH <sub>2</sub>	ca 965 (s) ca 860 (s)	
—CO—CH=CH <sub>2</sub> —CO—OCH=CH <sub>2</sub> —CO—C=CH <sub>2</sub> —CO—OC=CH <sub>2</sub> —O—CH=CH— <i>trans</i> —CO—CH=CH— <i>trans</i>	995–980 (s) 965–955 (m) 950–935 (s) 870–850 (s) ca 930 (s) 880–865 (s) 940–920 (s) ca 990 (s)	
Hydroxyl group O—H compounds		
Primary aliphatic alcohols	3640–3630 (s)  1350–1260 (s) 1085–1030 (s)	Only in very dilute solutions in nonpolar solvents OH bending Also broad band at 700–600 $\text{cm}^{-1}$

**TABLE 7.20** Absorption Frequencies of Single Bonds to Hydrogen (*Continued*)

Group	Band, $\text{cm}^{-1}$	Remarks
Hydroxyl group O—H compounds ( <i>continued</i> )		
Secondary aliphatic alcohols	3625–3620 (s)	See comments under primary aliphatic alcohols
	1350–1260 (s)	
	1125–1085 (s)	Also for $\alpha$ -unsaturated and cyclic tertiary aliphatic alcohols
Tertiary aliphatic alcohols	3620–3610 (s)	See comments under primary aliphatic alcohols
	1410–1310 (s)	
	1205–1125 (s)	
Aryl—OH	ca 3610 (s)	See comments under primary aliphatic alcohols
	1410–1310 (s)	
	1260–1180 (s)	Also for unsaturated secondary aliphatic alcohols
	1085–1030 (s)	
Carboxylic acids	3300–2500 (w–m) 995–915 (s)	Broad Broad diffuse band
Enol form of $\beta$ -diketones	2700–2500 (var)	Broad
Free oximes	3600–3570 (w–m)	Shoulder
Free hydroperoxides	3560–3530 (m)	
Peroxy acids	ca 3280 (m)	
Phosphorus acids	2700–2560 (m)	Broad
Water in solution	3710	When solution is damp
Intermolecular H bond		
Dimeric	3600–3500	Rather sharp. Absorptions arising from H bond with polar solvents also appear in this region.
Polymeric	3400–3200 (s)	Broad
Intramolecular H bond		
Polyvalent alcohols	3600–3500 (s)	Sharper than dimeric band above
Chelation	3200–2500	Broad and occasionally weak; the lower the frequency, the stronger the intramolecular bond
Water of crystallation (solid state spectra)	3600–3100 (w)	Usually a weak band at 1640–1615 $\text{cm}^{-1}$ also. Water in trace amounts in KBr disks shows a broad band at 3450 $\text{cm}^{-1}$ .

**TABLE 7.20** Absorption Frequencies of Single Bonds to Hydrogen (*Continued*)

Group	Band, cm <sup>-1</sup>	Remarks
Amine, imine, ammonium, and amide N—H		
Primary amines	3550–3300 (m)	Two bands in this range
Aliphatic	1650–1560 (m)	
	1090–1020 (w–m)	With $\alpha$ -carbon branching at 795 cm <sup>-1</sup> and strong
	850–810 (w–m)	Broad
	495–445 (m–s)	Broad
	ca 290 (s)	Also for secondary aryl amines
Aromatic	1350–1260 (s)	
	445–345	
Amino acids	3100–3030 (m)	Values for solid states; broad bands also (but not always) near 2500 and 200 cm <sup>-1</sup>
	2800–2400 (m)	Number of sharp bands; dilute solution
	1625–1560 (m)	
	1550–1550 (m)	
Amino salts	3550–3100 (m)	Values for solid state
	ca 3380	Dilute solutions
	ca 3280	
Secondary amines	3550–3400 (w)	Only one band, whereas primary amines show two bands
	1580–1490 (w)	Often too weak to be noticed
	1190–1170 (m)	
	1145–1130 (m)	
	455–405 (w–m)	
Salts	ca 2500	Sharp; broad values for solid state
	ca 2400	Sharp; broad values for solid state
	1620–1560 (m–s)	
Tertiary amines R <sub>1</sub> R <sub>2</sub> R <sub>3</sub> NH <sup>+</sup>	2700–2250	Group of relatively sharp bands; broad bands in solid state
Ammonium ion	3300–3030 (s) 1430–1390 (s)	Group of bands
Imines =N=H	3350–3310 (w) 3490 (s) 3490 (s)	Aliphatic Aryl Pyrroles, indoles; band sharp
Imine salts	2700–2330 (m–s) 2200–1800 (m)	Dilute solutions One or more bands; useful to distinguish from protonated tertiary amines
Primary amide —CONH <sub>2</sub>	ca 3500 (m) ca 3400 (m)	Lowered ca 150 cm <sup>-1</sup> in the solid state and on H bonding; often several bands 3200–3050 cm <sup>-1</sup>
Secondary amide —CONH—	3460–3400 (m) 3100–3070 (w)	Two bands; lowered on H bonding and in solid state. Only one band with lactams Extra band with bonded and solid-state samples

**TABLE 7.20** Absorption Frequencies of Single Bonds to Hydrogen (*Continued*)

Group	Band, $\text{cm}^{-1}$	Remarks
Miscellaneous R—H		
—S—H	2600–2550 (w)	Weaker than OH and less affected by H bonding
P—H	2440–2350 (m)	Sharp
$\begin{array}{c} \text{O} \\ \parallel \\ \text{P} \\ \diagdown \\ \text{OH} \end{array}$	2700–2560 (m)	Associated OH
R—D	100/137 times the corresponding RH frequency	Useful when assigning RH bands; deuteration leads to a known shift to lower frequency

**TABLE 7.21** Absorption Frequencies of Triple Bonds*Abbreviations Used in the Table*

m, moderately strong      var, of variable strength  
 m–s, moderate to strong      w–m, weak to moderately strong  
 s, strong

Group	Band, $\text{cm}^{-1}$	Remarks
Alkynes		
Terminal	3300 (s) 2140–2100 (w–m)* 1375–1225 (w–m) 695–575 (m–s)	CH stretching C $\equiv$ C stretching  Two bands if molecule has axial symmetry
Nonterminal	ca 630 (s) 2260–2150 (var)*	Alkyl monosubstituted Symmetrical or nearly symmetrical substitution makes the C $\equiv$ C stretching frequency inactive. When more than one C $\equiv$ C linkage is present, and sometimes when there is only one, there are frequently more absorption bands in this region than there are triple bonds to account for them.
R <sub>1</sub> —C $\equiv$ C—R <sub>2</sub>	540–465 (m)	The longer the chain, the lower the frequency
Aryl—C $\equiv$ C—	ca 550 (m) ca 350 (var)	
—C $\equiv$ C—halogen (Cl, Br, I)	185–160 (var)	

\* Conjugation with olefinic or acetylenic groups lowers the frequency and raises the intensity. Conjugation with carbonyl groups usually has little effect on the position of absorption.

**TABLE 7.21** Absorption Frequencies of Triple Bonds (*Continued*)

Group	Band, $\text{cm}^{-1}$	Remarks
Nitriles $\text{—C}\equiv\text{N}$	2260–2200 (var)	Stronger and toward the lower end of the range when conjugated; occasionally very weak or absent
Aliphatic	580–555 (m–s)	
	560–525 (m–s)	
Aromatic	390–350 (s)	
	580–540 (s)	
	430–380 (m)	
Isonitriles $\text{R—N}^+\equiv\text{C}^-$ or $\text{R—N}=\text{C:}$	2175–2150 (s) 2150–2115 (s) 1595	Very sensitive to changes in substituents Not found for nitriles
Cyanamides $\text{>N—C}\equiv\text{N} \rightleftharpoons \text{>N}^+ \text{—C}=\text{N}^-$	2225–2210 (s)	
Thiocyanates $\text{R—S—C}\equiv\text{N}$	2175–2140 (s) 404–400 (s) ca 600 (m–s)	Aryl thiocyanates at the upper end of the range, alkyl at the lower end Aliphatic derivatives
Nitrile <i>N</i> -oxides $\text{—C}\equiv\text{N}\rightarrow\text{O}$	2305–2285 (s) 1395–1365 (s)	Aryl derivatives
Diazonium salts $\text{R—N}^+\equiv\text{N}$	2300–2230 (m–s)	
Selenocyanates $\text{R—Se—C}\equiv\text{N}$	ca 2160 (m–s) 545–520 ca 390 ca 350	



**TABLE 7.22** Absorption Frequencies of Cumulated Double Bonds*Abbreviations Used in the Table*

m-s, moderate to strong      vs, very strong  
s, strong                              w, weak

Group	Band, $\text{cm}^{-1}$	Remarks
Carbon dioxide $\text{O}=\text{C}=\text{O}$	2349 (s)	Appears in many spectra as a result of inequalities in path length
Isocyanates $-\text{N}=\text{C}=\text{O}$	2275–2250 (vs)	Position unaffected by conjugation
Isoselenocyanates $-\text{N}=\text{C}=\text{Se}$	2200–2000 (s) 675–605	Broad; usually two bands
Azides $-\text{N}_3$ or $-\text{N}=\text{N}^+=\text{N}^-$	2140–2030 (s) 1340–1180 (w)	Not observed for ionic azides
$-\text{N}=\text{C}=\text{N}-$	2155–2130 (s)	Split into unsymmetrical doublet by conjugation with aryl groups: 2145–2125 (vs) and 2115–2105 (vs)
Isothiocyanates $-\text{N}=\text{C}=\text{S}$	2140–1990 (vs) 649–600 (m-s) 565–510 (m-s) 470–440 (m-s)	Broad; usually a doublet
Ketenes $>\text{C}=\text{C}=\text{O}$	ca 2150 (s)	
Ketenimines $\text{C}=\text{C}=\text{N}-$	2050–2000 (s)	
Allenes $>\text{C}=\text{C}=\text{C}<$	2000–1915 (m-s)	Two bands when terminal allene or when bonded to electron-attracting groups
Thionylamines $-\text{N}=\text{S}=\text{O}$	1300–1230 (s) 1180–1110 (s)	
Diazoalkanes $\text{R}_2\text{C}=\text{N}^+=\text{N}^-$ $-\text{CH}=\text{N}^+=\text{N}^-$	2030–2000 (s) 2050–2035 (s)	
Diazoketones $-\text{CO}-\text{CH}=\text{N}^+=\text{N}^-$	2100–2080 2075–2050	Monosubstituted Disubstituted

**TABLE 7.23** Absorption Frequencies of Carbonyl Bands*All bands quoted are strong.*

Groups	Band, cm <sup>-1</sup>	Remarks
<b>Acid anhydrides</b> —CO—O—CO—		
Saturated	1850–1800 1790–1740	Two bands usually separated by about 60 cm <sup>-1</sup> . The higher-frequency band is more intense in acyclic anhydrides, and the lower-frequency band is more intense in cyclic anhydrides.
Aryl and $\alpha,\beta$ -unsaturated	1830–1780 1790–1710	
Saturated five-ring	1870–1820 1800–1750	
All classes	1300–1050	
<b>Acid chlorides</b> —COCl		
Saturated	1815–1790	Acid fluorides higher, bromides and iodides lower
Aryl and $\alpha,\beta$ -unsaturated	1790–1750	
<b>Acid peroxide</b> CO—O—O—CO—		
Saturated	1820–1810 1800–1780	
Aryl and $\alpha,\beta$ -unsaturated	1805–1780 1785–1755	
<b>Esters and lactones</b> —CO—O—		
Saturated	1750–1735	
Aryl and $\alpha,\beta$ -unsaturated	1730–1715	
Aryl and vinyl esters C=C—O—CO—alkyl	1800–1750	
Esters with electronegative $\alpha$ substituents; e.g., >CCl—CO—O—	1770–1745	
$\alpha$ -Keto esters	1755–1740	The C=C stretching band also shifts to higher frequency.
Six-ring and larger lactones	Similar values to the corresponding open-chain esters	
Five-ring lactone	1780–1760	
$\alpha,\beta$ -Unsaturated five-ring lactone	1770–1740	
$\beta,\gamma$ -Unsaturated five-ring lactone, vinyl ester type	ca 1800	When $\alpha$ -CH is present, there are two bands, the relative intensity depending on the solvent.
Four-ring lactone	ca 1820	
$\beta$ -Keto ester in H bonding enol form	ca 1650	
All classes	1300–1050	Usually two strong bands due to CO stretching

**TABLE 7.23** Absorption Frequencies of Carbonyl Bands (*Continued*)

Groups	Band, $\text{cm}^{-1}$	Remarks
<b>Aldehydes —CHO</b>		
(See also Table 7.49 for C—H.) All values given below are lowered in liquid-film or solid-state spectra by about 10–20 $\text{cm}^{-1}$ . Vapor-phase spectra have values raised about 20 $\text{cm}^{-1}$ .		
Saturated	1740–1720	
Aryl	1715–1695	<i>o</i> -Hydroxy or amino groups shift this value to 1655–1625 $\text{cm}^{-1}$ because of intramolecular H bonding.
$\alpha,\beta$ -Unsaturated	1705–1680	
$\alpha,\beta,\gamma,\delta$ -Unsaturated	1680–1660	
$\beta$ -Ketoaldehyde in enol form	1670–1645	Lowering caused by chelate-type H bonding
<b>Ketones <math>\text{&gt;C=O}</math></b>		
All values given below are lowered in liquid-film or solid-state spectra by about 10–20 $\text{cm}^{-1}$ . Vapor-phase spectra have values raised about 20 $\text{cm}^{-1}$ .		
Saturated	1725–1705	
Aryl	1700–1680	
$\alpha,\beta$ -Unsaturated	1685–1665	
$\alpha,\beta,\alpha',\beta'$ -Unsaturated and diaryl	1670–1660	
Cyclopropyl	1705–1685	
Six-ring ketones and larger	Similar values to the corresponding open-chain ketones	
Five-ring ketones	1750–1740	$\alpha,\beta$ Unsaturation, $\alpha,\beta,\alpha',\beta'$ unsaturation, etc., have a similar effect on these values as on those of open-chain ketones.
Four-ring ketones	ca 1780	
$\alpha$ -Halo ketones	1745–1725	Affected by conformation; highest values are obtained when both halogens are in the same plane as the C=O.
$\alpha,\alpha'$ -Dihalo ketones	1765–1745	
1,2-Diketones, <i>syn-trans</i> -open chains	1730–1710	Antisymmetrical stretching frequency of both C=O's. The symmetrical stretching is inactive in the infrared but active in the Raman.
<i>syn-cis</i> -1,2-Diketones, six-ring	1760 and 1730	
<i>syn-cis</i> -1,2-Diketones, five-ring	1775 and 1760	

**TABLE 7.23** Absorption Frequencies of Carbonyl Bands (*Continued*)

Groups	Band, cm <sup>-1</sup>	Remarks
<b>Ketones</b> $\geq\text{C}=\text{O}$ ( <i>continued</i> )		
<i>o</i> -Amino-aryl or <i>o</i> -hydroxy-aryl ketones	1655–1635	Low because of intramolecular H bonding. Other substituents and steric hindrance affect the position of the band.
Quinones	1690–1660	C=C band is strong and is usually near 1600 cm <sup>-1</sup> .
Extended quinones	1655–1635	
Tropone	1650	Near 1600 cm <sup>-1</sup> when lowered by H bonding as in tropolones
<b>Carboxylic acids</b> $-\text{CO}_2\text{H}$		
All types	3000–2500	OH stretching; a characteristic group of small bands due to combination bands
Saturated	1725–1700	The monomer is near 1760 cm <sup>-1</sup> , but is rarely observed. Occasionally both bands, the free monomer, and the H-bonded dimer can be seen in solution spectra. Ether solvents give one band near 1730 cm <sup>-1</sup> .
$\alpha,\beta$ -Unsaturated	1715–1690	
Aryl	1700–1680	
$\alpha$ -Halo-	1740–1720	
<b>Carboxylate ions</b> $-\text{CO}_2^-$		
Most types	1610–1550	Antisymmetrical and symmetrical stretching, respectively
	1420–1300	
<b>Amides</b> $-\text{CO}-\text{N}<$		
(See also Table 7.49 for NH stretching and bending.)		
Primary $-\text{CONH}_2$		
In solution	ca 1690	Amide I; C=O stretching
Solid state	ca 1650	
In solution	ca 1600	Amide II: mostly NH bending
Solid state	ca 1640	Amide I is generally more intense than amide II. (In the solid state, amides I and II may overlap.)
Secondary $-\text{CONH}-$		
In solution	1700–1670	Amide I
Solid state	1680–1630	
In solution	1550–1510	Amide II; found in open-chain amides only
Solid state	1570–1515	Amide I is generally more intense than amide II.
Tertiary	1670–1630	Since H bonding is absent, solid and solution spectra are much the same.
Lactams		
Six-ring and larger rings	ca 1670	
Five-ring	ca 1700	Shifted to higher frequency when the N atom is in a bridged system
Four-ring	ca 1745	
$\text{R}-\text{CO}-\text{N}-\text{C}=\text{C}$		Shifted +15 cm <sup>-1</sup> by the additional double bond
$\text{C}=\text{C}-\text{CO}-\text{N}$		Shifted by up to +15 cm <sup>-1</sup> by the additional double bond. This is an unusual effect by $\alpha,\beta$ unsaturation. It is said to be due to the inductive effect of the C=C on the well-conjugated CO—N system, the usual conjugation effect being less important in such a system.

**TABLE 7.23** Absorption Frequencies of Carbonyl Bands (*Continued*)

Groups	Band, $\text{cm}^{-1}$	Remarks
<b>Imides</b> $\text{—CO—N—CO—}$		
Cyclic six-ring	ca 1710 and ca 1700	Shift of $+15 \text{ cm}^{-1}$ with $\alpha, \beta$ unsaturation
Cyclic five-ring	ca 1770 and ca 1700	
<b>Ureas</b> $\text{N—CO—N}$		
RNHCONHR	ca 1660	
Six-ring	ca 1640	
Five-ring	ca 1720	
<b>Urethanes</b> $\text{R—O—CO—N}$	1740–1690	Also shows amide II band when nonsubstituted on N
<b>Thioesters and Acids</b>		
$\text{RCO—S—R'}$		
RCOSH	ca 1720	$\alpha, \beta$ -Unsaturated or aryl acid or ester shifted about $-25 \text{ cm}^{-1}$
RCOS—alkyl	ca 1690	
RCOS—aryl	ca 1710	

### 7.5.1 Intensities of Carbonyl Bands

Acids generally absorb more strongly than esters, and esters more strongly than ketones or aldehydes. Amide absorption is usually similar in intensity to that of ketones but is subject to much greater variations.


### 7.5.2 Position of Carbonyl Absorption

The general trends of structural variation on the position of  $\text{C=O}$  stretching frequencies may be summarized as follows:

1. The more electronegative the group X in the system  $\text{R—CO—X—}$ , the higher is the frequency.
2.  $\alpha, \beta$  Unsaturation causes a lowering of frequency of 15 to  $40 \text{ cm}^{-1}$ , except in amides, where little shift is observed and that usually to higher frequency.
3. Further conjugation has relatively little effect.
4. Ring strain in cyclic compounds causes a relatively large shift to higher frequency. This phenomenon provides a remarkably reliable test of ring size, distinguishing clearly between four-, five-, and larger-membered-ring ketones, lactones, and lactams. Six-ring and larger ketones, lactones, and lactams show the normal frequency found for the open-chain compounds.
5. Hydrogen bonding to a carbonyl group causes a shift to lower frequency of 40 to  $60 \text{ cm}^{-1}$ . Acids, amides, enolized  $\beta$ -keto carbonyl systems, and *o*-hydroxyphenol and *o*-aminophenyl carbonyl compounds show this effect. All carbonyl compounds tend to give slightly lower values for the carbonyl stretching frequency in the solid state compared with the value for dilute solutions.
6. Where more than one of the structural influences on a particular carbonyl group is operating, the net effect is usually close to additive.

**TABLE 7.24** Absorption Frequencies of Other Double Bonds*Abbreviations Used in the Table*

m, moderately strong                      vs, very strong  
 m-s, moderate to strong                w, weak  
 var, of variable strength

Group	Band, $\text{cm}^{-1}$	Remarks
Alkenes $\text{>C=C<}$		
Nonconjugated	1680–1620 (w–m)	May be very weak if symmetrically substituted
Conjugated with aromatic ring	1640–1610 (m)	More intense than with unconjugated double bonds
Internal (ring)	3060–2995 (m)	Highest frequencies for smallest ring
Carbons: $n = 3$ $n = 4$ $n = 5$ $n \geq 6$	ca 1665 (w–m) ca 1565 (w–m) ca 1610 (w–m) 1370–1340 (s) 1650–1645 (w–m)	Characteristic
Exocyclic $\text{C}=\text{C}(\text{CH}_2)_n$ $n = 2$ $n = 3$ $n \geq 4$	1780–1730 (m) ca 1680 (m) 1655–1650 (m)	
Fulvene 	1645–1630 (m) 1370–1340 (s) 790–765 (s)	
Dienes, trienes, etc.	1650 (s) and 1600 (s)	Lower-frequency band usually more intense and may hide or overlap the higher-frequency band
$\alpha,\beta$ -Unsaturated carbonyl compounds	1640–1590 (m)	Usually much weaker than the $\text{C}=\text{O}$ band
Enol esters, enol ethers, and enamines	1700–1650 (s)	
Imines, oximes, and amidines $\text{>C=N-}$		
Imines and oximes Aliphatic $\alpha,\beta$ -Unsaturated and aromatic Conjugated cyclic systems	1690–1640 (w) 1650–1620 (m) 1660–1480 (var) 960–930 (s)	NO stretching of oximes
Imino ethers $\text{—O—C=N—}$	1690–1640 (var)	Usually a strong doublet

**TABLE 7.24** Absorption Frequencies of Other Double Bonds (*Continued*)

Group	Band, $\text{cm}^{-1}$	Remarks
Imines, oximes, and amidines $\text{>C=N-}$ ( <i>continued</i> )		
Imino thioethers $\text{—S—C=N=}$	1640–1605 (var)	
Imine oxides $\text{>C=N}^+\text{—O}^-$	1620–1550 (s)	
Amidines $\text{>N—C=N—}$	1685–1580 (var)	
Benzamidines Aryl—C=N—N	1630–1590	
Guanidine $\begin{array}{c} \text{>N—C=N—} \\   \\ \text{N} \end{array}$	1725–1625 (s)	
Azines $\text{>C=N—N=C<}$	1670–1600	
Hydrazoketones $\text{—CO—C=N—N}$	1600–1530 (vs)	
Azo compounds $\text{—N=N—}$		
Azo $\text{—N=N—}$ Aliphatic Aromatic <i>cis</i> <i>trans</i>	ca 1575 (var)  ca 1510 (w) 1440–1410 (w)	Very weak or inactive
Azoxy $\begin{array}{c} \text{—N}^+=\text{N—} \\   \\ \text{O}^- \end{array}$ Aliphatic Aromatic	1590–1495 (m–s) 1345–1285 (m–s) 1480–1450 (m–s) 1340–1315 (m–s)	
Azothio $\text{—N}^+=\text{N—S}^-$	1465–1445 (w) 1070–1055 (w)	
Nitro compounds $\text{N=O}$		
Nitro $\text{C—NO}_2$ Aliphatic	ca 1560 (s) 1385–1350 (s)	The two bands are due to asymmetrical and symmetrical stretching of the $\text{N=O}$ bond. Electron-withdrawing substituents adjacent to nitro group increase the frequency of the asymmetrical band and decrease that of the symmetrical frequency.

**TABLE 7.24** Absorption Frequencies of Other Double Bonds (*Continued*)

Group	Band, $\text{cm}^{-1}$	Remarks
Nitro compounds $\text{N}=\text{O}$ ( <i>continued</i> )		
Nitro $\text{C}-\text{NO}_2$ ( <i>continued</i> )		
Aromatic	1570–1485 (s) 1380–1320 (s)	See above remark; also bulky orthosubstituents shift band to higher frequencies. Strong H bonding shifts frequency to lower end of range. Strong and sometimes at ca 750 $\text{cm}^{-1}$
$\alpha,\beta$ -Unsaturated Nitroalkenes	865–835 (s) 580–520 (var) 1530–1510 (s) 1360–1335 (s)	
Nitrates $-\text{O}-\text{NO}_2$	1650–1625 (vs) 1285–1275 (vs) 870–855 (vs) 760–755 (w-m) 710–695 (w-m)	
Nitramines $>\text{N}-\text{NO}_2$	1630–1550 (s) 1300–1250 (s)	
Nitrates $-\text{O}-\text{N}=\text{O}$	1680–1610 (vs) 815–750 (s) 850–810 (s) 690–615 (s)	Two bands <i>Trans</i> form <i>Cis</i> form
Thionitrites $-\text{S}-\text{N}=\text{O}$	730–685 (m-s)	
Nitroso $\equiv\text{C}-\text{N}=\text{O}$	1600–1500 (s)	
$\text{N}=\text{N}=\text{O}$ Aliphatic Aromatic	1530–1495 (m-s) 1480–1450 (m-s) 1335–1315 (m-s)	
Nitrogen oxides $\text{N}\rightarrow\text{O}$ Pyridine Pyrazine	1320–1230 (m-s) 1190–1150 (m-s) 1380–1280 (m-s) 1040–990 (m-s) ca 850 (m)	Affected by ring substituents



**TABLE 7.25** Absorption Frequencies of Aromatic Bands*Abbreviations Used in the Table*

m, moderately strong      var, of variable strength  
 m-s, moderate to strong      w-m, weak to moderately strong  
 s, strong

Group	Band, $\text{cm}^{-1}$	Remarks
Aromatic rings	ca 1600 (m) ca 1580 (m) ca 1470 (m) ca 1510 (m)	Stronger when ring is further conjugated When substituent on ring is electron acceptor When substituent on ring is electron donor
Five adjacent H	900–860 (w-m) 770–730 (s) 720–680 (s) 625–605 (w-m) ca 550 (w-m)	Substituents: $\text{C}=\text{C}$ , $\text{C}\equiv\text{C}$ , $\text{C}\equiv\text{N}$
1,2-Substitution	770–735 (s) 555–495 (w-m) 470–415 (m-s)	
1,3-Substitution	810–750 (s) 560–505 (m) 460–415 (m-s)	490–460 $\text{cm}^{-1}$ when substituents are electron-accepting groups
1,4-Substitution	860–800 (s) 650–615 (w-m) 520–440 (m-s)	520–490 $\text{cm}^{-1}$ when substituents are electron-donating groups
1,2,3-Trisubstitution	800–760 (s) 720–685 (s) 570–535 (s) ca 485	
1,2,4-Trisubstitution	900–885 (m) 780–760 (s) 475–425 (m-s)	
1,3,5-Trisubstitution	950–925 (var) 865–810 (s) 730–680 (m-s) 535–495 (s) 470–450 (w-m)	
Pentasubstitution	900–860 (m-s) 580–535 (s)	
Hexasubstitution	415–385 (m-s)	

**TABLE 7.26** Absorption Frequencies of Miscellaneous Bands*Abbreviations Used in the Table*

m, moderately strong	vs, very strong
m-s, moderate to strong	w, weak
s, strong	w-m, weak to moderately strong
var, of variable strength	

Group	Band, cm <sup>-1</sup>	Remarks
Ethers		
Saturated aliphatic $\geq\text{C}-\text{O}-\text{C}\leq$	1150–1060 (vs)  1140–900 (s)	Two peaks may be observed for branched chain, usually 1140–1110 cm <sup>-1</sup> . Usually 930–900 cm <sup>-1</sup> ; may be absent for symmetric ethers
Alkyl-aryl $\begin{array}{c} \text{=C}-\text{O}-\text{C}\leq \\   \end{array}$	1270–1230 (vs) 1120–1020 (s)	$\text{=CO}$ stretching CO stretching
Vinyl	1225–1200 (s)	Usually about 1205 cm <sup>-1</sup>
Diaryl $\begin{array}{c} \text{=C}-\text{O}-\text{C=} \\   \quad   \end{array}$	1200–1120 (s) 1100–1050 (s)	
Cyclic	1270–1030 (s)	
Epoxides $\begin{array}{c} >\text{C}-\text{C}< \\ \diagup \quad \diagdown \\ \text{O} \end{array}$	1260–1240 (m-s) 880–805 (m) 950–860 (var) 865–785 (m) 770–750 (m)	Monosubstituted <i>Trans</i> form <i>Cis</i> form Trisubstituted
Ketals and acetals	1190–1140 (s) 1195–1125 (s) 1100–1000 (s) 1060–1035 (s)	Strongest band Sometimes obscured
Phthalanes	915–895 (s)	
Aromatic methylenedioxy	1265–1235 (s)	
Peroxides		
$-\text{O}-\text{O}-$	900–830 (w) 1150–1030 (m-s) ca 1000 (m)	Alkyl Aryl

**TABLE 7.26** Absorption Frequencies of Miscellaneous Bands (*Continued*)

Group	Band, $\text{cm}^{-1}$	Remarks
Sulfur compounds		
Thiols $\text{—S—H}$ $\text{—CO—SH}$ $\text{—CS—SH}$	2600–2450 (w) 840–830 (m) ca 860 (s)	Broad
Thiocarbonyl $\text{>C=S}$  $\text{>N—C=S}$ $\quad \quad  $ $\text{—S—C=S}$ $\quad \quad  $	1200–1050 (s)  1570–1395 1420–1260 1140–940 ca 580 (s)	Behaves generally in manner similar to carbonyl band
Sulfoxides $\text{>S=O}$	1075–1040 (vs)  730–690 (var) 395–360 (var)	Halogen or oxygen atom bonded to sulfur increases the frequency.
Sulfones $\text{>SO}_2$	1360–1290 (vs)  1170–1120 (vs) 610–545 (m–s) 525–495 (m–s)	Halogen or oxygen atom bonded to sulfur increases the frequency.
Sulfonamides $\text{—SO}_2\text{—N<}$	1380–1330 (vs) 1170–1140 (vs) 950–860 (m) 715–700 (w–m)	
Sulfonates $\text{—SO}_2\text{—O—}$	1420–1330 (s) 1200–1145 (s)	May appear as doublet
Thiosulfonates $\text{—SO}_2\text{—S—}$	ca 1340 (vs)	
Sulfates $\text{—O—SO}_2\text{—O—}$  Primary alkyl salts  Secondary alkyl salts	1415–1380 (s) 1200–1185 (s) 1315–1220 (s) 1140–1075 (m) 1270–1210 (vs) 1075–1050 (s)	Electronegative substituents increase frequencies. Strongly influenced by metal ion  Doublet; both bands strongly influenced by metal ion



**TABLE 7.26** Absorption Frequencies of Miscellaneous Bands (*Continued*)

Group	Band, $\text{cm}^{-1}$	Remarks
Phosphorus compounds ( <i>continued</i> )		
P=S	865–655 (m–s) 595–530 (var)	
$\begin{array}{c} \text{S} \\ \parallel \\ \text{P} \\ \diagup \\ \text{OH} \end{array}$	3100–3000 (w) 2360–2200 (w) 935–910 (s) 810–750 (m–s) 655585 (var)	PO stretching P=S stretching P=S stretching
Silicon compounds		
Si—H	2250–2100 (s) 985–800	SiH <sub>3</sub> has two bands.
Si—C	860–760	Accompanied by CH <sub>2</sub> rocking
Si—C $\equiv$	1280–1250 (s)	Sharp
Si—C <sub>2</sub> H <sub>5</sub>	1250–1220 (m) 1020–1000 (m) 970–945 (m)	
Si—Aryl	1125–1090 (vs)	Splits into two bands when two aryl groups are attached to one silicon atom, but has only one band when three aryl groups attached
$\equiv\text{Si—OH}$	870–820	OH deformation band
$\equiv\text{Si—O—Si}\equiv$	1100–1000	
$\equiv\text{Si—N—Si}\equiv$	940–870 (s)	
$\equiv\text{Si—Cl}$	550–470 (s) 250–150	
$\text{>SiCl}_2$	595–535 (s) 540–460 (m)	
$\text{—SiCl}_3$	625–570 (s) 535–450 (m)	
Boron compounds		
Boranes $\text{>BH}$ or $\text{—BH}_2$	2640–2450 (m–s) 2640–2570 (m–s) 2535–2485 (m–s) 2380–2315 (s) 2285–2265 (s) 2140–2080 (w–m) 2580–2450 (m)	Free H in BH Free H in BH <sub>2</sub> plus second band  In complexes; second band for BH <sub>2</sub>  Bridged H Borazoles and borazines

**TABLE 7.26** Absorption Frequencies of Miscellaneous Bands (*Continued*)

Group	Band, $\text{cm}^{-1}$	Remarks
Boron compounds ( <i>continued</i> )		
$\text{BH}_4^-$	2310–2195 (s)	Two bands
B—N	1550–1330 750–635	Borazines and borazoles
B—O	1390–1310 (s) 1280–1200	BO stretching Metal orthoborates
B—Cl B—Br	1090–890 (s)	Plus other bands at lower frequencies for $\text{BX}_2$ and $\text{BX}_3$
B—F	1500–840 (var)	Isotope splitting present
$\text{XBF}_2$	1500–1410 (s) 1300–1200 (s)	
$\text{X}_2\text{BF}$	1360–1300 (s)	
$\text{BF}_3$ complexes	1260–1125 (s) 1030–800 (s)	Band splitting may be added to isotopic splittings.
$\text{BF}_4^-$	ca 1030 (vs)	
Halogen compounds		
C—F Aliphatic, mono-F  Aliphatic, di-F Aliphatic, poly-F Aromatic	1110–1000 (vs) 780–680 (s) 1250–1050 (vs) 1360–1090 (vs) 1270–1100 (m) 680–520 (m–s) 420–375 (var) 340–240 (s)	Two bands Number of bands
— $\text{CF}_3$ Aliphatic   Aromatic	1350–1120 (vs) 780–680 (s) 680–590 (s) 600–540 (s) 555–505 (s) 1330–1310 (m–s) 600–580 (s)	
C—Cl Primary alkanes	730–720 (s) 685–680 (s) 660–650 (s)	

**TABLE 7.26** Absorption Frequencies of Miscellaneous Bands (*Continued*)

Group	Band, $\text{cm}^{-1}$	Remarks
Halogen compounds ( <i>continued</i> )		
C—Cl ( <i>continued</i> )		
Secondary alkanes	ca 760 (m) 675–655 (m–s) 615–605 (s)	
Tertiary alkanes	635–610 (m–s) 580–560 (m–s)	
Poly-Cl	800–700 (vs)	
Aryl:		
1,2-	1060–1035 (m)	
1,3-	1080–1075 (m)	
1,4-	1100–1090 (m)	
Chloroformates	ca 690 (s) 485–470 (s)	
Axial Cl	730–580 (s)	
Equatorial Cl	780–740 (s)	
C—Br		
Primary alkanes	645–635 (s) 565–555 (s) 440–430 (var)	
Secondary alkanes	620–605 (s) 590–575 (m–w) 540–530 (s)	
Tertiary alkanes	600–595 (m–s) 525–505 (s)	
Axial	690–550 (s)	
Equatorial	750–685 (s)	
Aryl:		
1,2-	1045–1025 (m)	
1,3-; 1,4-	1075–1065 (m)	
Other bands	400–260 (s) 325–175 (m–s) 290–225 (m–s)	
C—I		
Primary alkanes	600–585 (s) 515–500 (s)	
Secondary alkanes	ca 575 (s) 550–520 (s) 490–480 (s)	
Tertiary alkanes	580–560 (s) 510–485 (m) 485–465 (s)	
Aromatic	1060–1055 (m–s) 310–160 (s) 265–185	
Axial	ca 640 (s)	
Equatorial	ca 655 (s)	

**TABLE 7.26** Absorption Frequencies of Miscellaneous Bands (*Continued*)

Group	Band, $\text{cm}^{-1}$	Remarks
Inorganic ions		
Ammonium	3300–3030	Several bands, all strong
Cyanate	2220–2130 (s)	
Cyanide	2200–2000	
Carbonate	1450–1410	
Hydrogen sulfate	1190–1160 (s) 1180–1000 (s) 880–840 (m)	
Nitrate	1410–1350 (vs) 860–800 (m)	
Nitrite	1275–1230 (s) 835–800 (m)	Shoulder
Phosphate	1100–1000	
Sulfate	1130–1080 (s)	
Thiocyanate	ca 2050 (s)	

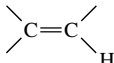
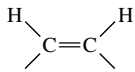
**TABLE 7.27** Absorption Frequencies in the Near Infrared

*Values in parentheses are molar absorptivity.*

Class	Band, $\text{cm}^{-1}$	Remarks
Acetylenes	9800–9430 6580–6400 (1.0)	Overtone of $\equiv\text{CH}$ stretching
Alcohols (nonhydrogen-bonded)	7140–7010 (2.0)	Overtone of OH stretching
Aldehydes Aliphatic  Aromatic  Formate	4640–4520 (0.5)  ca 8000 ca 4525 ca 4445 4775–4630 (1.0)	Combination of $\text{C}=\text{O}$ and CH stretchings



**TABLE 7.27** Absorption Frequencies in the Near Infrared (*Continued*)

Class	Band, $\text{cm}^{-1}$	Remarks
Alkanes $-\text{CH}_3$ $-\text{CH}_2-$ $\equiv\text{CH}$ Cyclopropane	9000–8350 (0.02) 5850–5660 (0.1) 4510–4280 (0.3) 9170–8475 (0.02) 5830–6640 (0.1) 4420–4070 (0.25) 8550–8130 7000–6800 5650–5560 6160–6060 4500–4400	All bands very weak
Alkenes  $>\text{C}=\text{CH}_2$ and $-\text{CH}=\text{CH}_2$  $-\text{O}-\text{CH}=\text{CH}_2$ $-\text{CO}-\text{CH}=\text{CH}_2$	6850–6370 (1.0) 7580–7300 (0.02) 6140–5980 (0.2) 4760–4700 (1.2) 4760–4660 (0.15) 6250–6040 (0.3) 7580–7410 (0.02) 6190–5990 (0.3) 4820–4750 (0.2–0.5)	<i>Trans</i> isomers have no unique bands.
Amides Primary Secondary	7400–6540 (0.7) 5160–5060 (3.0) 5040–4990 (0.5) 4960–4880 (0.5) 7330–7140 (0.5) 5050–4960 (0.4)	Two bands; overtone of NH stretch Second overtone of $\text{C}=\text{O}$ stretch; second overtone of NH deformation; combination of $\text{C}=\text{O}$ and NH Overtone of NH stretch Combination of NH stretch and NH bending
Amines, aliphatic Primary Secondary	9710–9350 6670–6450 (0.5) 5075–4900 (0.7) 9800–9350 6580–6410 (0.5)	Second overtone of NH stretch Two bands; overtone of NH stretch Two bands; combination of NH stretch and NH bending Second overtone of NH stretch Overtone of NH stretch
Amines, aromatic Primary Secondary	9950–9520 (0.4) 7040–6850 (0.2) 6760–6580 (1.4) 5140–5040 (1.5) 10 000–9710 6800–6580 (0.5)	

**TABLE 7.27** Absorption Frequencies in the Near Infrared (*Continued*)

Class	Band, $\text{cm}^{-1}$	Remarks
Aryl-H	7660–7330 (0.1) 6170–5880 (0.1)	Overtone of CH stretch
Carbonyl	5200–5100	
Carboxylic acids	7000–6800	
Epoxide (terminal)	6135–5960 (0.2) 4665–4520 (1.2)	Cyclopropane bands in same region
Glycols	7140–7040	
Hydroperoxides Aliphatic  Aromatic	6940–6750 (2.0) 4960–4880 (0.8) 7040–6760 (1.0) 4950–4850 (1.3)	Two bands
Imides	9900–9620 6540–6370	
Nitriles	5350–5200 (0.1)	
Oximes	7140–7050	
Phosphines	5350–5260 (0.2)	
Phenols Nonbonded  Intramolecularly bonded	7140–6800 (3.0) 5000–4950 7000–6700	
Thiols	5100–4950 (0.05)	

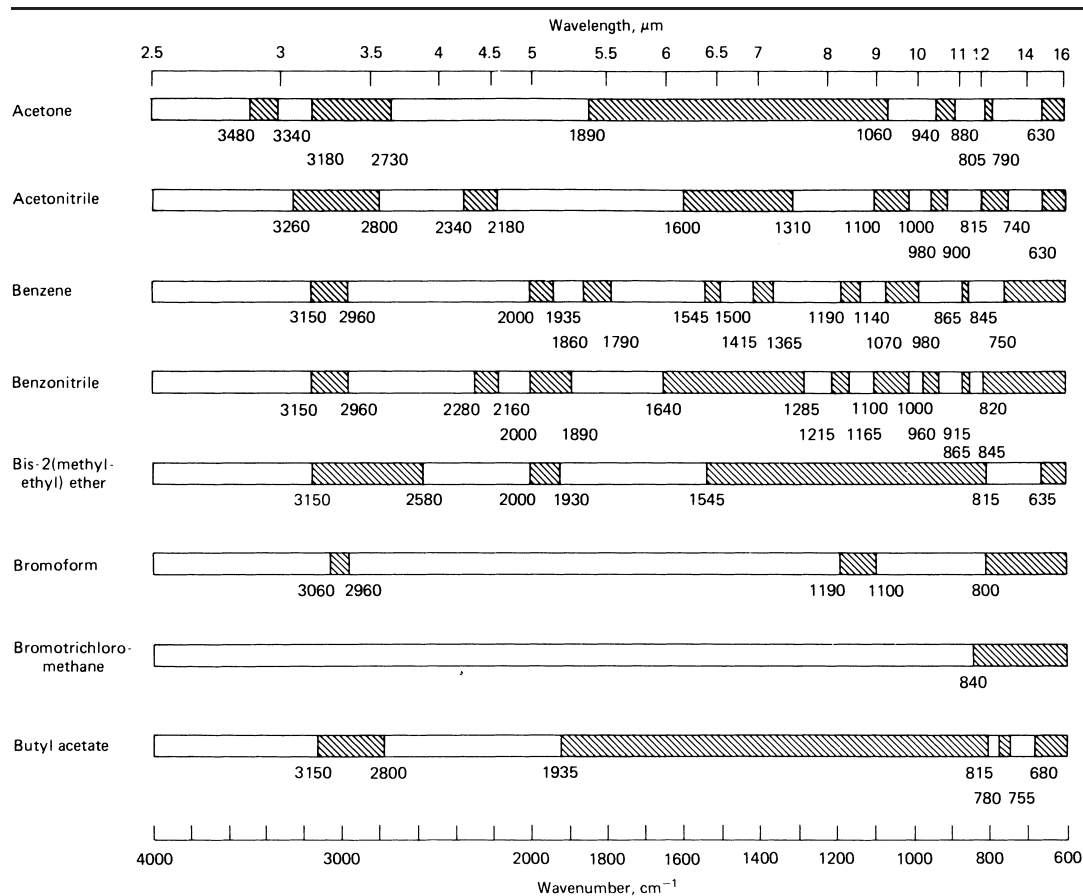
**TABLE 7.28** Infrared Transmitting Materials

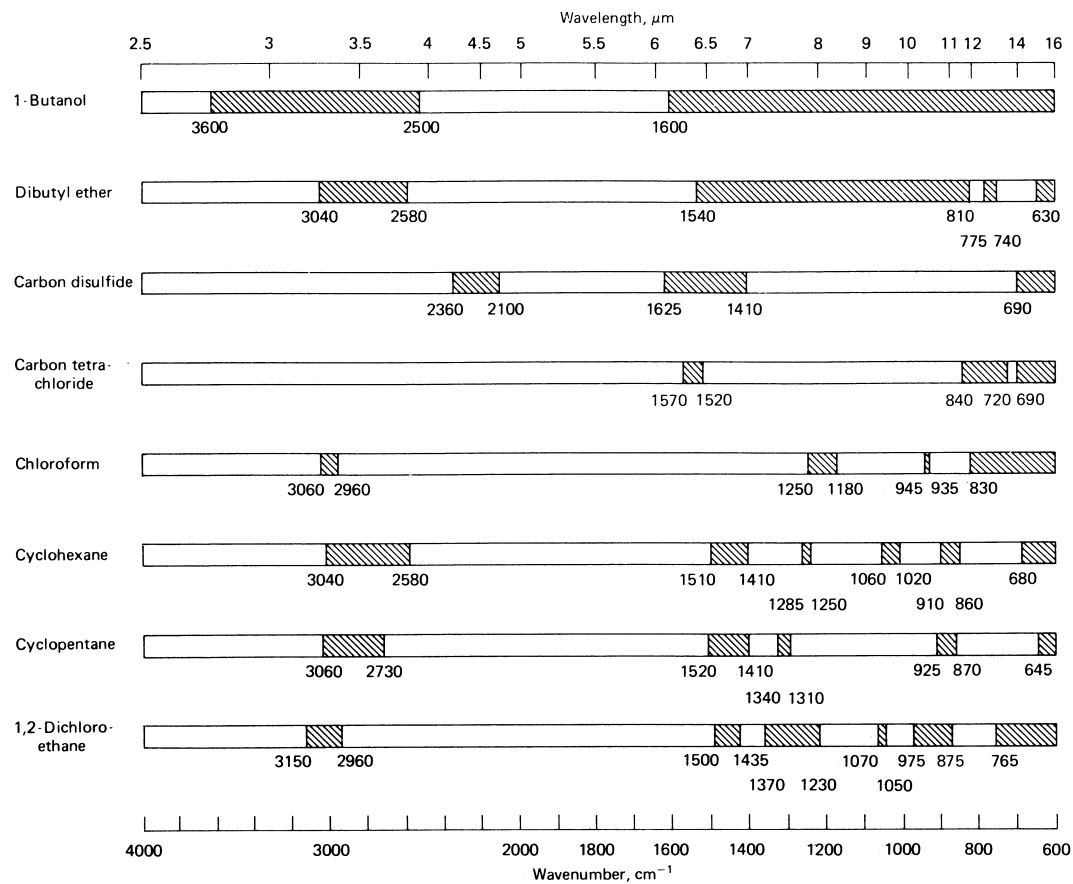
Material	Wavelength range, $\mu\text{m}$	Wavenumber range, $\text{cm}^{-1}$	Refractive index at $2\ \mu\text{m}$
NaCl, rock salt	0.25–17	40 000–590	1.52
KBr, potassium bromide	0.25–25	40 000–400	1.53
KCl, potassium chloride	0.30–20	33 000–500	1.5
AgCl, silver chloride*	0.40–23	25 000–435	2.0
AgBr, silver bromide*	0.50–35	20 000–286	2.2
CaF <sub>2</sub> , calcium fluoride (Irtran-3)	0.15–9	66 700–1 110	1.40
BaF <sub>2</sub> , barium fluoride	0.20–11.5	50 000–870	1.46
MgO, magnesium oxide (Irtran-5)	0.39–9.4	25 600–1 060	1.71
CsBr, cesium bromide	1–37	10 000–270	1.67
CsI, cesium iodide	1–50	10 000–200	1.74
TlBr-TlI, thallium bromide-iodide (KRS-5)*	0.50–35	20 000–286	2.37
ZnS, zinc sulfide (Irtran-2)	0.57–14.7	17 500–680	2.26
ZnSe, zinc selenide* (vacuum deposited) (Irtran-4)	1–18	10 000–556	2.45
CdTe, cadmium telluride (Irtran-6)	2–28	5 000–360	2.67
Al <sub>2</sub> O <sub>3</sub> , sapphire*	0.20–6.5	50 000–1538	1.76
SiO <sub>2</sub> , fused quartz	0.16–3.7	62 500–2 700	
Ge, germanium*	0.50–16.7	20 000–600	4.0
Si, silicon*	0.20–6.2	50 000–1 613	3.5
Polyethylene	16–300	625–33	1.54

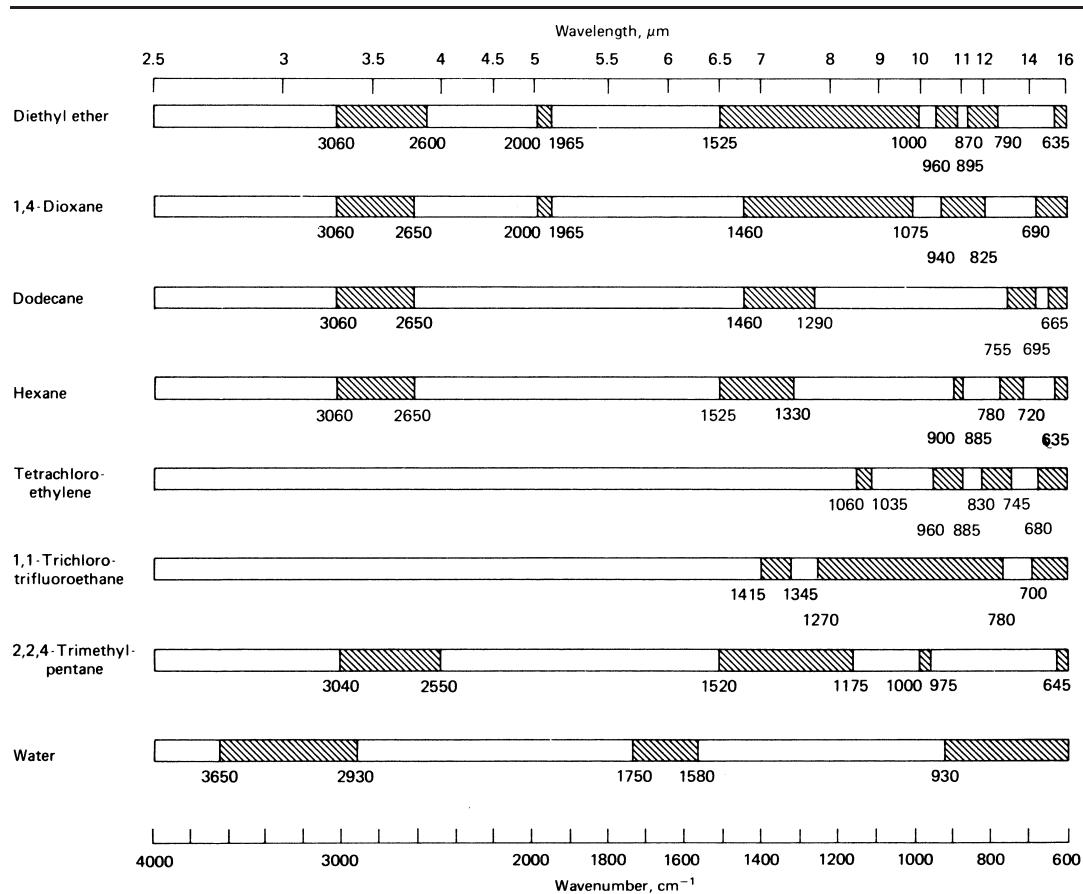
\* Useful for internal reflection work.

**TABLE 7.29** Infrared Transmission Characteristics of Selected Solvents

Transmission below 80%, obtained with a 0.10-mm cell path, is shown as shaded area.





**TABLE 7.29** Infrared Transmission Characteristics of Selected Solvents (*Continued*)

## 7.6 RAMAN SPECTROSCOPY

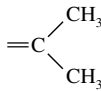
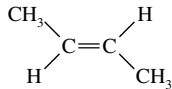
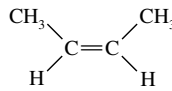
**TABLE 7.30** Raman Frequencies of Single Bonds to Hydrogen and Carbon

*Abbreviations Used in the Table*

m, moderately strong	vw, very weak
m-s, moderate to strong	w, weak
m-vs, moderate to very strong	w-m, weak to moderately strong
s, strong	w-vs, weak to very strong
vs, very strong	

Group	Band, $\text{cm}^{-1}$	Remarks
Saturated C—H and C—C		
—CH <sub>3</sub>	2969–2967 (s) 2884–2883 (s) ca 1205 (s) 1150–1135 1060–1056 975–835 (s) 280–220	In aryl compounds In unbranched alkyls In unbranched alkyls Terminal rocking of methyl group CH <sub>2</sub> —CH <sub>3</sub> torsion
—CH <sub>2</sub> —	2949–2912 (s) 2861–2849 (s) 1473–1443 (m-vs) 1305–1295 (s) 1140–1070 (m) 888–837 (w) 425–150 500–490	Intensity proportional to number of CH <sub>2</sub> groups Often two bands; see above  Substituent on aromatic ring
—CH(CH <sub>3</sub> ) <sub>2</sub>	1350–1330 (m) 835–750 (s)	If attached to C=C bond, 870– 800 $\text{cm}^{-1}$ . If attached to aryl ring, 740 $\text{cm}^{-1}$
—C(CH <sub>3</sub> ) <sub>3</sub>	1265–1240 (m) 1220–1200 (m) 760–685 (vs)	Not seen in <i>tert</i> -butyl bromide Not seen in <i>tert</i> -butyl bromide If attached to C=C or aromatic ring, 760–720 $\text{cm}^{-1}$
Internal tertiary carbon atom	855–805 (w) 455–410	
Internal quaternary carbon atom	710–680 (vs) 490–470	

**TABLE 7.30** Raman Frequencies of Single Bonds to Hydrogen and Carbon (*Continued*)

Group	Band, $\text{cm}^{-1}$	Remarks
Saturated C—H and C—C ( <i>continued</i> )		
Two adjacent tertiary carbon atoms	730–920 770–725	Often a band at $530\text{--}524\text{ cm}^{-1}$ indicates presence of adjacent tertiary and quaternary carbon atoms.
Dialkyl substitution at $\alpha$ -carbon atom	800–700 (m–s) 680–650 (vs) 605–550	
Cyclopropane	3101–3090 3038–3019 1210–1180 (s)	Shifts to $1200\text{ cm}^{-1}$ for monoalkyl or 1,2-dialkyl substitution and to $1320\text{ cm}^{-1}$ for <i>gem</i> -1,1-dialkyl substitution
Cyclobutane	1001–960 (vs)	Shifts to $933\text{ cm}^{-1}$ for monoalkyl, to $887\text{ cm}^{-1}$ for <i>cis</i> -1,3-dialkyl, and to $891\text{ cm}^{-1}$ plus $855\text{ cm}^{-1}$ (doublet) for <i>trans</i> -1,3,-dialkyl substitution
Cyclopentane	900–800 (s)	
Cyclohexane	825–815 (vs) 810–795 (vs)	Boat configuration Chair configuration
Cycloheptane	ca 733	
Cyclooctane	ca 703	
	1392–1377 450–400 (vw) 270–250 (m)	
	1380–1379 492–455 (vw) 220–200 (m)	
	1372–1368 970–952 (m) 592–545 (vw) 420–400 (m) 310–290 (m)	



**TABLE 7.30** Raman Frequencies of Single Bonds to Hydrogen and Carbon (*Continued*)

Group	Band, $\text{cm}^{-1}$	Remarks
Saturated C—H and C—C ( <i>continued</i> )		
$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{CH}_3 \quad \text{H} \end{array}$	1385–1375 522–488 (w)	
$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	1392–1386 690–678 (m–s) 510–485 (m) 424–388 (w)	
$\begin{array}{c} \equiv\text{C}-\text{C}-\text{C}\equiv \\ \parallel \\ \text{O} \end{array}$	1170–1100 (w–m) 600–580 (m–s)	
$\begin{array}{c} \equiv\text{C}-\text{C}- \\ \parallel \\ \text{O} \end{array}$	1120–1090 (m–vs)  600–510 (w–m)	Tertiary or quaternary carbon adjacent to carbonyl group lowers the frequency $300\text{ cm}^{-1}$ .
—CH <sub>2</sub> —CO—	1420–1410 (s)	
—CHO	2850–2810 (m) 2720–2695 (vs)	Often appears as a shoulder
Unsaturated C—H		
—C $\equiv$ C—H	3340–3270 (w–m)	Alkyl substituents at higher frequencies; unsaturated or aryl substituents at lower frequencies
$\begin{array}{c} \diagdown \quad \text{H} \\ \diagup \quad \diagdown \\ \text{C}=\text{C} \\ \diagdown \quad \diagup \end{array}$	3040–2995 (m)	
$\begin{array}{c} \diagdown \quad \text{H} \\ \diagup \quad \diagdown \\ \text{C}=\text{C} \\ \diagdown \quad \text{H} \end{array}$	3095–3050 (m) 2990–2983 (s)	Asymmetric =CH <sub>2</sub> stretch Symmetric =CH <sub>2</sub> stretch
$\begin{array}{c} \text{H} \quad \text{R} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{H} \end{array}$	1419–1415 (m) 1309–1288 (m)	Plus =CH and =CH stretching bands
$\begin{array}{c} \text{H} \quad \text{R}_1 \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{R}_2 \end{array}$	1413–1399 (m) 909–885 (m) 711–684 (w)	Plus =CH <sub>2</sub> stretching bands

**TABLE 7.30** Raman Frequencies of Single Bonds to Hydrogen and Carbon (*Continued*)

Group	Band, $\text{cm}^{-1}$	Remarks
Unsaturated C—H ( <i>continued</i> )		
$\begin{array}{c} \text{R}_1 \quad \text{R}_2 \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{H} \end{array}$	1270–1251 (m)	Plus =CH stretching band
$\begin{array}{c} \text{R}_1 \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{R}_2 \end{array}$	1314–1290 (m)	Plus =CH stretching band
$\begin{array}{c} \text{R}_1 \quad \text{R}_3 \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{R}_2 \quad \text{H} \end{array}$	1360–1322 (w) 830–800 (vw)	Plus =CH stretching band
Hydroxy O—H		
Free —OH Intermolecularly bonded Aromatic —OH	3650–3250 (w) 3400–3300 (w) ca 3160 (s)	
—OH	1460–1320 (w) 1276–1205 (w–m) 1260 (w–m)	Common to all OH substituents Primary Secondary
C—C—OH primary	1070–1050 (m–s) 1030–960 (m–s) 480–430 (w–m)	CCO stretching CCO deformation
C—C—OH Secondary  Tertiary	1135–1120 (m–s) 825–815 (vs) 500–490 (w–m) 1210–1200 (m–s) 755–730 (vs) 360–350 (w–m)	
—CO—O—H	1305–1270	CO stretching
N—H and C—N bonds		
Amine $\text{>N—H}$ Associated Nonbonded Salts  —NH <sub>2</sub>	3400–3250 (s) 3550–3250 (s) 2986–2974  1650–1590 (w–vs)	Primary amines show two bands.  Often obscured by intense CH stretching bands Bending

**TABLE 7.30** Raman Frequencies of Single Bonds to Hydrogen and Carbon (*Continued*)

Group	Band, $\text{cm}^{-1}$	Remarks
N—H and C—N Bonds ( <i>continued</i> )		
Amides		
Primary	3540–3500 (w) 3400–3380 (w) 1310–1250 (s)	Both bands lowered ca $150\text{ cm}^{-1}$ in solid state and H bonding Interaction of NH bending and CN stretching; lowered $50\text{ cm}^{-1}$ in nonbonded state
Secondary	1150–1095 (m) 3491–3404 (m–s)  1190–1130 (m) 931–865 (m–s) 430–395 (w–m)	Rocking of $\text{NH}_2$ Two bands; lowered in frequency on H bonding and in solid state
—CO—N	607–555 (m)	O=CN bending
$\begin{array}{c} \text{C} - \text{N} - \text{C} \\   \\ \text{C} \end{array}$	1070–1045 (m)	Stretching
$\equiv\text{C}-\text{N}<$		
Primary carbon	1090–1060 (m)	CN stretching
Secondary $\alpha$ carbon	1140–1035 (m)	Two bands but often obscured. Strong band at $800\text{ cm}^{-1}$
Tertiary $\alpha$ carbon	1240–1020 (m)	Two bands. Strong band also at $745\text{ cm}^{-1}$

**TABLE 7.31** Raman Frequencies of Triple Bonds*Abbreviations Used in the Table*

m, moderately strong      s-vs, strong to very strong  
 m-s, moderate to strong      vs, very strong  
 s, strong

Group	Band, cm <sup>-1</sup>	Remarks
R—C≡CH	2160–2100 (vs) 650–600 (m) 356–335 (s)	Monoalkyl substituted; C≡C stretch C≡CH deformation C≡C—C bending of monoalkyls
R <sub>1</sub> —C≡C—R <sub>2</sub>	2300–2190 (vs)	C≡C stretching of disubstituted alkyls; sometimes two bands
—C≡C—C≡C—	2264–2251 (vs)	
—C≡N	2260–2240 (vs) 2234–2200 (vs) 840–800 (s-vs) 385–350 (m-s) 200–160 (vs)	Unsaturated nonaryl substituents lower the frequency and enhance the intensity. Lowered ca 30 cm <sup>-1</sup> with aryl and conjugated aliphatics CCCN symmetrical stretching Aliphatic nitriles
H—C≡N	2094 (vs)	
Azides —N <sup>+</sup> ≡N <sup>-</sup>	2170–2080 (s) 1258–1206 (s)	Asymmetric NNN stretching Symmetric NNN stretching; HN <sub>3</sub> at 1300 cm <sup>-1</sup>
Diazonium salts R—N <sup>+</sup> ≡N <sup>-</sup>	2300–2240 (s)	
Isonitriles —N <sup>+</sup> ≡C <sup>-</sup>	2146–2134 2124–2109	Stretching of aliphatics Stretching of aromatics
Thiocyanates —S—C≡N	2260–2240 (vs) 650–600 (s)	Stretching of C≡N Stretching of SC

**TABLE 7.32** Raman Frequencies of Cumulated Double Bonds*Abbreviations Used in the Table*

s, strong                      vw, very weak  
 vs, very strong              w, weak

Group	Band, $\text{cm}^{-1}$	Remarks
Allenenes $\text{C}=\text{C}=\text{C}$	2000–1960 (s) 1080–1060 (vs) 356	Pseudo-asymmetric stretching Symmetric stretching $\text{C}=\text{C}=\text{C}$ bending
Carbodiimides (cyanamides) $-\text{N}=\text{C}=\text{N}-$	2140–2125 (s) 2150–2100 (vs) 1460 1150–1140 (vs)	Asymmetric stretching of aliphatics Asymmetric stretching of aromatics; two bands Symmetrical stretching of aliphatics Symmetric stretching of aryls
Cumulenes (trienes) $\text{C}=\text{C}=\text{C}=\text{C}$	2080–2030 (vs) 878	
Isocyanates $-\text{N}=\text{C}=\text{O}$	2300–2250 (vw) 1450–1400 (s)	Asymmetric stretching Symmetric stretching
Isothiocyanates $-\text{N}=\text{C}=\text{S}$	2220–2100 690–650	Two bands Alkyl derivatives
Ketenenes $\text{C}=\text{C}=\text{O}$	2060–2040 (vs) 1130 (s) 1374 (s) 1120 (s)	Pseudo-asymmetric stretching Pseudo-symmetric stretching Alkyl derivatives Aryl derivatives
Sulfinylamines $\text{R}-\text{N}=\text{S}=\text{O}$	1306–1214 (w) 1155–989 (s)	Asymmetric stretching Symmetric stretching

**TABLE 7.33** Raman Frequencies of Carbonyl Bands*Abbreviations Used in the Table*

m, moderately strong

s-vs, strong to very strong

m-s, moderate to strong

vs, very strong

s, strong

w, weak

Group	Band, $\text{cm}^{-1}$	Remarks
Acid anhydrides —CO—O—CO— Saturated  Conjugated, noncyclic	1850–1780 (m) 1771–1770 (m) 1775 1720	
Acid fluorides —CO—F Alkyl Aryl	1840–1835 1812–1800	
Acid chlorides —CO—Cl Alkyl Aryl	1810–1770 (s) 1774 1731	
Acid bromides —CO—Br Alkyl Aryl	1812–1788 1775–1754	
Acid iodides —CO—I Alkyl Aryl	ca 1806 ca 1752	
Lactones	1850–1730 (s)	
Esters Saturated  Aryl and $\alpha,\beta$ -unsaturated Diesters Oxalates Phthalates C $\equiv$ C—CO—O— Carbamates	1741–1725  1727–1714  1763–1761 1738–1728 1716–1708 1694–1688	Alkyl branching on carbon adjacent to C=O lowers frequency by 5–15 $\text{cm}^{-1}$ .
Aldehydes	1740–1720 (s-vs)	
Ketones Saturated Aryl Alicyclic $n = 4$ $n = 5$ $n \geq 6$	1725–1700 (vs) 1700–1650 (m)  1782 (m) 1744 (m) 1725–1699 (m)	

**TABLE 7.33** Raman Frequencies of Carbonyl Bands (*Continued*)

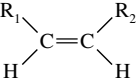
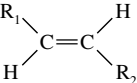
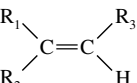
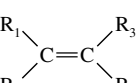
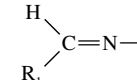
Group	Band, $\text{cm}^{-1}$	Remarks
Carboxylic acids		
Mono-	1686–1625 (s)	These $\alpha$ -substituents increase the frequency: F, Cl, Br, OH.
Poly-	1782–1645	Solid state; often two bands
Amino acids	1750–1710	In solution; very broad band
	1743–1729	
Carboxylate ions	1690–1550 (w)	
Amino acid anion	1440–1340 (vs)	Often masked by water deformation band near 1630 $\text{cm}^{-1}$
	1743–1729	
	1600–1570 (w)	
Amides (see also Table 7.30)		
Primary		
Associated	1686–1576 (m–s)	
Nonbonded	1650–1620 (m)	
Secondary	1715–1675 (m)	
Associated	1620–1585 (m)	
Nonbonded	1680–1630 (w)	Both <i>cis</i> and <i>trans</i> forms
Tertiary	1570–1510 (w)	<i>Trans</i> form
Lactams	1490–1440	<i>Cis</i> form
	1700–1650	Both <i>cis</i> and <i>trans</i> forms
	1550–1500	<i>Trans</i> form (no <i>cis</i> band)
	1670–1630 (m)	
	1750–1700 (m)	

**TABLE 7.34** Raman Frequencies of Other Double Bonds*Abbreviations Used in the Table*

m, moderately strong	vs, very strong
m–s, moderate to strong	w, weak
s, strong	s–vs, strong to very strong
w–m, weak to moderately strong	

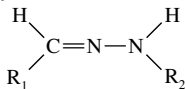
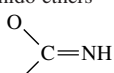
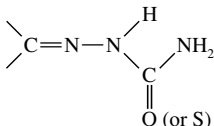
Group	Band, $\text{cm}^{-1}$	Remarks
Alkenes $\text{>C=C<}$		
$\text{>C=C<}$	1680–1576 (m–s)	General range
$\begin{array}{c} \text{H} \quad \text{R}_1 \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{H} \end{array}$	1648–1638 (vs)	C=C stretching
$\begin{array}{c} \text{H} \quad \text{R}_1 \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{R}_2 \end{array}$	ca 1650 (vs) 270–252 (w)	C=C stretching C=C–C skeletal deformation

**TABLE 7.34** Raman Frequencies of Other Double Bonds (*Continued*)

Group	Band, cm <sup>-1</sup>	Remarks		
Alkenes $\text{>C=C<}$ ( <i>continued</i> )				
	ca 1660 (vs) 970–952 (w)	C=C stretching Asymmetric CC stretching		
	1676–1665 (s)	C—C stretching		
	1678–1664 (vs) 522–488 (w)	C=C stretching C=C—C skeletal deformation		
	1680–1665 (s) 690–678 (m–s) 510–485 (m) 424–388 (w)	C=C stretching Symmetrical CC stretching Skeletal deformation Skeletal deformation		
Haloalkene	X = fluorine	X = chlorine	X = bromine	X-iodine
$\text{>C=C<}$ stretch of haloalkanes				
H <sub>2</sub> C=CHX HXC=CHX <i>cis</i> <i>trans</i> H <sub>2</sub> C=CX <sub>2</sub> X <sub>2</sub> C=CHX X <sub>2</sub> C=CX <sub>2</sub>	1654 1712 1694 1728 1792 1872	1603–1601 1590–1587 1578–1576 1616–1611 1589–1582 1577–1571	1596–1593 1587–1583 1582–1581 1593 1552 1547	1581 1543 1537   1465 (solid)
Group	Band, cm <sup>-1</sup>	Remarks		
$\text{>C=N—}$ bonds				
Aldimines (azomethines) 	1673–1639 1405–1400 (s)	Dialkyl substituents at higher frequency; diaryl substituents at lower end of range		
Aldoximes and Ketoximes $\text{>C=N—OH}$	1680–1617 (vs) 1335–1330 (w)			
Azines $\text{>C=N—N=C<}$	1625–1608 (s)			



**TABLE 7.34** Raman Frequencies of Other Double Bonds (*Continued*)

Group	Band, $\text{cm}^{-1}$	Remarks
$\text{>C=N—}$ bonds ( <i>continued</i> )		
Hydrazones 	1660–1610 (s–vs)	
Imido ethers 	1658–1648	NH stretching at 3360–3327 $\text{cm}^{-1}$
Semicarbazones and thio- semicarbazones 	1665–1642 (vs) 1620–1610 (vs)	Aliphatic. Thiosemicarbazones fall in lower end of range. Aromatic derivatives
Azo compounds $\text{—N=N—}$		
$\text{—N=N—}$	1580–1570 (vs) 1442–1380 (vs) 1060–1030 (vs)	Nonconjugated Conjugated to aromatic ring CN stretching in aryl compounds
Nitro compounds $\text{N=O}$		
Alkyl nitrites	1660–1620 (s)	$\text{N=O}$ stretching
Alkyl nitrates	1635–1622 (w–m) 1285–1260 (vs) 610–562 (m)	Asymmetric $\text{NO}_2$ stretching Symmetric $\text{NO}_2$ stretching $\text{NO}_2$ deformation
Nitroalkanes Primary  Secondary	1560–1548 (m–s) 1395–1370 (s)  915–898 (m–s) 894–873 (m–s) 618–609 (w) 640–615 (w) 494–472 (w–m)  1553–1547 (m) 1375–1360 (s) 908–868 (m) 863–847 (s) 625–613 (m) 560–516 (s)	Sensitive to substituents attached to $\text{CNO}_2$ group  Shoulder Broad; useful to distinguish from secondary nitroalkanes  Sharp band

**TABLE 7.34** Raman Frequencies of Other Double Bonds (*Continued*)

Group	Band, cm <sup>-1</sup>	Remarks
Nitro compounds N=O ( <i>continued</i> )		
Nitroalkanes ( <i>continued</i> ) Tertiary	1543–1533 (m) 1355–1345 (s)	
Nitrogen oxides $\geq \text{N}^+ \rightarrow \bar{\text{O}}$	1612–1602 (s) 1252 (m) 1049–1017 (s) 835 (s) 541 (w) 469 (w)	

**TABLE 7.35** Raman Frequencies of Aromatic Compounds*Abbreviations Used in the Table*

m, moderately strong	var, of variable strength
m–s, moderate to strong	vs, very strong
m–vs, moderate to very strong	w, weak
s, strong	w–m, weak to moderately strong
s–vs, strong to very strong	

Group	Band, cm <sup>-1</sup>	Remarks
Common features		
Aromatic compounds	3070–3020 (s) 1630–1570 (m–s)	CH stretching C—C stretching
Substitution patterns of the benzene ring		
Monosubstituted	1180–1170 (w–m) 1035–1015 (s) 1010–990 (vs)  630–605 (w)	Characteristic feature; found also with 1,3- and 1,3,5-substitutions
1,2-Disubstituted	1230–1215 (m) 1060–1020 (s) 740–715 (m)	Characteristic feature Lowered 60 cm <sup>-1</sup> for halogen substituents

**TABLE 7.35** Raman Frequencies of Aromatic Compounds (*Continued*)

Group	Band, cm <sup>-1</sup>	Remarks
Substitution patterns of the benzene ring ( <i>continued</i> )		
1,3-Disubstituted	1010–990 (vs) 750–640 (s)	Characteristic feature
1,4-Disubstituted	1230–1200 (s–vs) 1180–1150 (m) 830–750 (vs) 650–630 (m–w)	Lower frequency with Cl substituents
Isolated hydrogen	1379 (s–vs) 1290–1200 (s) 745–670 (m–vs) 580–480 (s)	Characteristic feature
1,2,3-Trisubstituted	1100–1050 (m) 670–500 (vs) 490–430 (w)	The lighter the mass of the substituent, the higher the frequency.
1,2,4-Trisubstituted	750–650 (vs) 580–540 (var) 500–450 (var)	Lighter mass at higher frequencies
1,3,5-Trisubstituted	1010–990 (vs)	
Completely substituted	1296 (s) 550 (vs) 450 (m) 361 (m)	
Other aromatic compounds		
Naphthalenes	1390–1370 1026–1012 767–762 535–512 519–512	Ring breathing $\alpha$ or $\beta$ substituents $\beta$ substituents $\alpha$ substituents $\beta$ substituents
Disubstituted naphthalenes	773–737 (s) 726–705 (s) 690–634 (s) 608 575–569 544–537	1,2-; 1,3-; 2,3-; 2,6-; 2,7- 1,3-; 1,4-(two bands); 1,6-; 1,7-(two bands) 1,2-; 1,4-(two bands); 1,5-; 1,8-(two bands) 1,3- 1,2-; 1,3-; 1,6- 1,2-; 1,7-; 1,8-
Anthracenes	1415–1385	Ring breathing

**TABLE 7.36** Raman Frequencies of Sulfur Compounds*Abbreviations Used in the Table*

m, moderately strong

s-vs, strong to very strong

m-s, moderate to strong

vs, very strong

s, strong

w-m, weak to moderately strong

Group	Band, cm <sup>-1</sup>	Remarks
—S—H	2590–2560 (s)	SH stretching for both aliphatic and aromatic
>C=S	1065–1050 (m) 735–690 (vs)	Solid state
>S=O In (RO <sub>2</sub> ) <sub>2</sub> SO In (R <sub>2</sub> N) <sub>2</sub> SO In R <sub>2</sub> SO SOF <sub>2</sub> SOCl <sub>2</sub> SOBr <sub>2</sub>	1209–1198 1108 1070–1010 (w-m) 1308 1233 1121	One or two bands Broad
—SO <sub>2</sub> —	1330–1260 (m-s) 1155–1110 (s) 610–540 (m) 512–485 (m)	Asymmetric SO <sub>2</sub> stretching Symmetric SO <sub>2</sub> stretching Scissoring mode of aryls Scissoring mode of alkyls
—SO <sub>2</sub> —N<	ca 1322 (m) 1163–1138 (s) 524–510 (s)	Asymmetric SO <sub>2</sub> stretching Symmetric SO <sub>2</sub> stretching Scissoring mode
—SO <sub>2</sub> —O	1363–1338 (w-m) 1192–1165 (vs) 589–517 (w-m)	SO <sub>2</sub> stretching. Aryl substituents occur at higher range. Scissoring (two bands). Aryl substituents occur at higher range of frequencies.
—SO <sub>2</sub> —S—	1334–1305 (m-s) 1128–1126 (s) 559–553 (m-s)	
X—SO <sub>2</sub> —X	1412–1361 (w-m) (F) (Cl) 1263–1168 (s) (F) (Cl) 596–531 (s)	
—O—SO <sub>2</sub> —O—	1388–1372 (s) 1196–1188 (vs)	
—O—C—S—    S	670–620 (vs) 480–450 (vs)	C=S stretching CS stretching
≡C—SH	920 (m) 850–820 (m)	C—SH deformation of aryls

**TABLE 7.36** Raman Frequencies of Sulfur Compounds (*Continued*)

Group	Band, cm <sup>-1</sup>	Remarks
$\equiv\text{C}-\text{S}-$	752 (vs), 731 (vs) 742–722 (m–s) 698 (w), 678 (s) 693–639 (s) 651–610 (s–vs) 589–585 (vs)	With vinyl group attached With CH <sub>3</sub> attached With allyl group attached Ethyl or longer alkyl chain Isopropyl group attached <i>tert</i> -Butyl group attached
$(\text{CH}_2)_n \text{S}$ $n = 2$ $n = 4$ $n = 5$	1112 688 659	
$\equiv\text{C}-(\text{S}-\text{S})_n-\text{C}\equiv$ Didi- <i>n</i> -alkyl disulfides Di- <i>tert</i> -butyl disulfide Trisulfides	715–620 (vs) 525–510 (vs) 576 (s) 543 (m) 510–480 (s)	Two bands; CS stretching Two bands; SS stretching CS stretching SS stretching SS stretching

**TABLE 7.37** Raman Frequencies of Ethers*Abbreviations Used in the Table*

m, moderately strong  
s, strong

var, of variable strength  
vs, very strong

Group	Band, cm <sup>-1</sup>	Remarks
$\equiv\text{C}-\text{O}-\text{C}\equiv$ Aliphatic	1200–1070 (m)  930–830 (s) 800–700 (s) 550–400	Asymmetrical COC stretching. Symmetrical substitution gives higher frequencies Symmetrical COC stretching Braching at $\alpha$ carbon gives higher frequencies.
Aromatic	1310–1210 (m) 1050–1010 (m)	
$\equiv\text{C}-\text{O}-\overset{\textstyle  }{\underset{\textstyle  }{\text{C}}}-\text{O}-\text{C}\equiv$	1145–1129 (m)  900–800 (vs) 537–370 (s) 396–295	
$\begin{array}{c} >\text{C} & \text{C}< \\ & \diagdown \quad \diagup \\ & \text{O} \end{array}$	1280–1240 (s)	Ring breathing
$-\text{O}-\text{O}-$	800–770 (var)	

**TABLE 7.37** Raman Frequencies of Ethers (*Continued*)

Group	Band, $\text{cm}^{-1}$	Remarks
$(\text{CH}_2)_n \text{O}$ $n = 3$ $n = 4$ $n = 5$	1040–1010 (s) 920–900 (s) 820–800 (s)	

**TABLE 7.38** Raman Frequencies of Halogen Compounds*Abbreviations Used in the Table*

m–s, moderate to strong      var, of variable strength  
 s, strong                              vs, very strong

Group	Band, $\text{cm}^{-1}$	Remarks
C—F	1400–870	Correlations of limited applicability because of vibrational coupling with stretching
C—Cl Primary Secondary Tertiary	350–290 (s) 660–650 (vs) 760–605 (s) 620–540 (var)	CClCl bending; general  May be one to four bands May be one to three bands
=C—Cl	844–564 438–396 381–170	
=CCl <sub>2</sub>	601–441 300–235	
C—Br	690–490 (s)  305–258 (m–s)	Often several bands; primary at higher range of frequencies. Tertiary has very strong band at ca 520 $\text{cm}^{-1}$ .
=C—Br	745–565 356–318 240–115	
=CBr <sub>2</sub>	467–265 185–145	
C—I	663–595 309 154–85	
=C—I	ca 180	Solid state
=CI <sub>2</sub>	ca 265 ca 105	Solid state Solid state

**TABLE 7.39** Raman Frequencies of Miscellaneous Compounds*Abbreviations Used in the Table*

m, moderately strong

vs, very strong

s, strong

vvs, very very strong

Group	Band, cm <sup>-1</sup>	Remarks
C—As	570–550 (vs) 240–220 (vs)	CAs stretching CAsC deformation
C—Pb	480–420 (s)	CPb stretching
C—Hg	570–510 (vvs)	CHg stretching
C—Si	1300–1200 (s)	CSi stretching
C—Sn	600–450 (s)	CSn stretching
P—H	2350–2240 (m)	PH stretching
Heterocyclic rings		
Trimethylene oxide	1029	2-Substituted
Trimethylene imine	1026	
Tetrahydrofuran	914	
Pyrrolidine	899	
1,3-Dioxolane	939	
1,4-Dioxane	834	
Piperidine	815	
Tetrahydropyran	818	
Morpholine	832	
Piperazine	836	
Furan	1515–1460 1140	
Pyrazole	1040–990	
Pyrrole	1420–1360 (vs) 1144	
Thiophene	1410 (s)	
	1365 (s)	
	1085 (vs)	
	1035 (s)	
	832 (vs)	
Pyridine	610 (s)	
	1030 (vs)	
	990 (vs)	

**TABLE 7.40** Principal Argon-Ion Laser Plasma Lines

Wavelength, nm	Wavenumber, $\text{cm}^{-1}$	Relative intensity	Shift relative to 488.0 nm, $\text{cm}^{-1}$	Shift relative to 514.5 nm, $\text{cm}^{-1}$
487.9860	20 486.67	5000	0	
488.9033	20 448.23	200	38.4	
490.4753	20 382.70	130	104.0	
493.3206	20 265.13	970	221.5	
496.5073	20 135.07	960	351.6	
497.2157	20 106.39	330	380.3	
500.9334	19 957.16	1500	529.5	
501.7160	19 926.03	620	560.6	
506.2036	19 749.39	1400	737.3	
514.1790	19 443.06	360	1043.6	
514.5319	19 429.73	1000	1056.9	0
516.5774	19 352.79	38	1133.9	76.9
517.6233	19 313.69	41	1173.0	116.0
521.6816	19 163.44	20	1323.2	266.3
528.6895	18 909.43	150	1577.2	520.3
539.7522	18 521.87	18	1964.8	907.9
545.4307	18 329.04	19	2157.6	1100.7
555.8703	17 984.81	30	2501.9	1444.9
560.6734	17 830.75	48	2655.9	1599.0
565.0705	17 692.00	29	2794.7	1737.7
565.4450	17 680.28	27	2806.4	1749.4
569.1650	17 564.73	27	2921.9	1865.0
577.2326	17 319.24	69	3167.4	2110.5
581.2746	17 198.80	49	3287.9	2230.9
598.5920	16 701.24	23	3785.4	2728.5
610.3546	16 379.38	91	4107.3	3050.4
611.4929	16 348.90	1750	4137.8	3080.8
612.3368	16 326.36	100	4160.3	3103.4
613.8660	16 285.69	97	4201.0	3144.0
617.2290	16 196.96	1400	4289.7	3232.8
624.3125	16 013.19	590	4473.5	3416.5
639.9215	15 622.60	160	4864.1	3807.1
641.6308	15 580.98	50	4905.7	3848.8



## 7.7 NUCLEAR MAGNETIC RESONANCE

**TABLE 7.41** Nuclear Properties of the Elements

In the following table the magnetic moment  $\mu$  is in multiples of the nuclear magneton  $\mu_N(eh/4\pi Mc)$  with diamagnetic correction. The spin  $I$  is in multiples of  $h/2\pi$ , and the electric quadrupole moment  $Q$  is in multiples of  $10^{-28}$  square meters. Nuclei with spin  $1/2$  have no quadrupole moment. Sensitivity is for equal numbers of nuclei at constant field. NMR frequency at any magnetic field is the entry for column 5 multiplied by the value of the magnetic field in kilogauss. For example, in a magnetic field of 23.490 kG, protons will process at  $4.2576 \times 23.490 \text{ kG} = 100.0 \text{ MHz}$ . Radionuclides are denoted with an asterisk.

The data were extracted from M. Lederer and V. S. Shirley, *Table of Isotopes*, 7th ed., Wiley-Interscience, New York, 1978; A. H. Wapstra and G. Audi, "The 1983 Atomic Mass Evaluation," *Nucl. Phys. A* **432**:1–54 (1985); V. S. Shirley, ed., *Table of Radioactive Isotopes*, 8th ed., Wiley-Interscience, New York, 1986; and P. Raghavan, "Table of Nuclear Moments," *At. Data Nucl. Data Tables*, **42**:189 (1989).

Nuclide	Natural abundance, %	Spin $I$	Sensitivity at constant field relative to $^1\text{H}$	NMR frequency for a 1-kG field, MHz	Magnetic moment $\mu/\mu_N$ , $\text{J} \cdot \text{T}^{-1}$	Electric quadrupole moment $Q$ , $10^{-28} \text{ m}^2$
$^1\text{n}$	*	$1/2$	0.321 39	2.916 39	−1.913 043	
$^1\text{H}$	99.985	$1/2$	1.000 00	4.257 64	2.792 847	
$^2\text{H}$	0.015	1	0.009 65	0.653 57	0.857 438	0.002 860
$^3\text{H}$	*	$1/2$	1.213 54	4.541 37	2.978 963	
$^3\text{He}$	0.0001	$1/2$	0.442 12	3.243 52	−2.127 624	
$^6\text{Li}$	7.5	1	0.008 50	0.626 60	0.822 047	0.000 82
$^7\text{Li}$	92.5	$3/2$	0.293 55	1.654 78	3.256 427	−0.040 1
$^9\text{Be}$	100	$3/2$	0.013 89	0.598 6	−1.177 9	0.052 88
$^{10}\text{B}$	19.9	3	0.019 85	0.457 51	1.800 645	0.084 59
$^{11}\text{B}$	80.1	$3/2$	0.165 22	1.366 26	2.688 649	0.040 59
$^{13}\text{C}$	1.10	$1/2$	0.015 91	1.070 81	0.702 412	
$^{14}\text{N}$	99.634	1	0.001 01	0.307 76	0.403 761	0.020 2
$^{15}\text{N}$	0.366	$1/2$	0.001 04	0.431 72	−0.283 189	
$^{17}\text{O}$	0.038	$5/2$	0.029 10	0.577 41	−1.893 80	−0.025 58
$^{19}\text{F}$	100	$1/2$	0.834 00	4.007 65	2.628 867	
$^{21}\text{Ne}$	0.27	$3/2$	0.002 46	0.336 30	−0.661 797	0.101 55
$^{22}\text{Na}$	*	3	0.018 1	0.443 4	1.745	
$^{23}\text{Na}$	100	$3/2$	0.092 70	1.126 86	2.217 522	0.108 9
$^{25}\text{Mg}$	10.00	$5/2$	0.002 68	0.260 82	−0.855 46	0.199 4
$^{27}\text{Al}$	100	$5/2$	0.206 89	1.110 28	3.641 504	0.140 3
$^{29}\text{Si}$	4.67	$1/2$	0.007 86	0.846 53	−0.555 29	
$^{31}\text{P}$	100	$1/2$	0.066 52	1.725 10	1.131 60	
$^{33}\text{S}$	0.75	$3/2$	0.002 27	0.327 16	0.643 821	−0.067 8
$^{35}\text{S}$	*	$3/2$	0.008 50	0.508	1.00	0.045
$^{35}\text{Cl}$	75.77	$3/2$	0.004 72	0.417 64	0.821 874	−0.081 65
$^{36}\text{Cl}$	*	2	0.012 1	0.489 3	1.283 8	−0.016 8
$^{37}\text{Cl}$	24.23	$3/2$	0.002 72	0.347 64	0.684 124	−0.064 35
$^{37}\text{Ar}$	*	$3/2$	0.012 76	0.581 8	1.145	
$^{39}\text{K}$	93.258	$3/2$	0.000 51	0.198 93	0.391 466	0.060 1
$^{40}\text{K}$	0.0117	4	0.005 23	0.247 37	−1.298 099	−0.074 9
$^{41}\text{K}$	6.730	$3/2$	0.000 084	0.109 19	0.214 870	0.073 3
$^{43}\text{Ca}$	0.135	$7/2$	0.006 42	0.286 88	−1.317 26	−0.0408
$^{45}\text{Sc}$	100	$7/2$	0.302 44	1.035 88	4.756 483	−0.22
$^{47}\text{Ti}$	7.3	$5/2$	0.002 10	0.240 40	−0.788 48	0.29
$^{49}\text{Ti}$	5.5	$7/2$	0.003 78	0.240 47	−1.104 17	0.24
$^{50}\text{V}$	0.250	6	0.055 71	0.425 04	3.345 689	0.21

**TABLE 7.41** Nuclear Properties of the Elements (*Continued*)

Nuclide	Natural abundance, %	Spin $I$	Sensitivity at constant field relative to $^1\text{H}$	NMR frequency for a 1-kG field, MHz	Magnetic moment $\mu/\mu_N$ , $\text{J} \cdot \text{T}^{-1}$	Electric quadrupole moment $Q$ , $10^{-28} \text{ m}^2$
$^{51}\text{V}$	99.750	$\frac{7}{2}$	0.383 60	1.121 30	5.148 706	−0.052
$^{53}\text{Cr}$	9.501	$\frac{3}{2}$	0.000 91	0.241 14	−0.474 54	−0.15
$^{55}\text{Mn}$	100	$\frac{5}{2}$	0.178 81	1.057 60	3.468 72	0.33
$^{57}\text{Fe}$	2.1	$\frac{1}{2}$	0.000 03	0.138 15	0.090 623	
$^{59}\text{Co}$	100	$\frac{7}{2}$	0.278 41	1.007 7	4.627	0.42
$^{61}\text{Ni}$	1.140	$\frac{3}{2}$	0.003 59	0.381 13	−0.750 02	0.162
$^{63}\text{Cu}$	69.17	$\frac{3}{2}$	0.093 42	1.129 79	2.223 29	−0.220
$^{65}\text{Cu}$	30.83	$\frac{3}{2}$	0.114 84	1.210 27	2.381 67	−0.204
$^{67}\text{Zn}$	4.1	$\frac{5}{2}$	0.002 87	0.266 93	0.875 479	0.150
$^{69}\text{Ga}$	60.108	$\frac{3}{2}$	0.069 71	1.024 75	2.016 59	0.170
$^{71}\text{Ga}$	39.892	$\frac{3}{2}$	0.143 00	1.302 04	2.562 27	0.100
$^{73}\text{Ge}$	7.73	$\frac{9}{2}$	0.001 41	0.148 97	−0.879 468	−0.173
$^{75}\text{As}$	100	$\frac{3}{2}$	0.025 36	0.731 48	1.439 475	0.314
$^{77}\text{Se}$	7.63	$\frac{1}{2}$	0.007 03	0.815 66	0.535 042	
$^{79}\text{Br}$	50.69	$\frac{3}{2}$	0.079 45	1.070 39	2.106 399	0.331
$^{81}\text{Br}$	49.31	$\frac{3}{2}$	0.099 51	1.153 81	2.270 562	0.276
$^{83}\text{Kr}$	11.5	$\frac{9}{2}$	0.001 90	0.164 42	−0.970 669	0.253
$^{85}\text{Rb}$	72.165	$\frac{5}{2}$	0.010 61	0.412 53	1.353 03	0.274
$^{87}\text{Rb}$	27.835	$\frac{3}{2}$	0.177 03	1.398 07	2.751 24	0.132
$^{87}\text{Sr}$	7.00	$\frac{9}{2}$	0.002 72	0.185 24	−1.093 603	0.335
$^{89}\text{Y}$	100	$\frac{1}{2}$	0.000 12	0.209 49	−0.137 415	
$^{91}\text{Zr}$	11.22	$\frac{5}{2}$	0.009 49	0.397 47	−1.303 62	−0.206
$^{93}\text{Nb}$	100	$\frac{9}{2}$	0.488 21	1.045 20	6.170 5	−0.32
$^{95}\text{Mo}$	15.92	$\frac{5}{2}$	0.003 27	0.278 74	−0.914 2	−0.022
$^{97}\text{Mo}$	9.55	$\frac{5}{2}$	0.003 49	0.284 62	−0.933 5	−0.255
$^{99}\text{Tc}$	*	$\frac{9}{2}$	0.381 74	0.963	5.684 7	−0.129
$^{99}\text{Ru}$	12.7	$\frac{5}{2}$	0.001 13	0.195 53	−0.641 3	0.079
$^{101}\text{Ru}$	17.0	$\frac{5}{2}$	0.001 59	0.219 2	−0.718 8	0.457
$^{103}\text{Rh}$	100	$\frac{1}{2}$	0.000 03	0.134 76	−0.088 40	
$^{105}\text{Pd}$	22.33	$\frac{5}{2}$	0.001 13	0.195 7	−0.642	0.660
$^{107}\text{Ag}$	51.839	$\frac{1}{2}$	0.000 066 9	0.173 30	−0.113 680	
$^{109}\text{Ag}$	48.161	$\frac{1}{2}$	0.000 101	0.199 24	−0.130 691	
$^{111}\text{Cd}$	12.80	$\frac{1}{2}$	0.009 66	0.906 89	−0.594 886	
$^{113}\text{Cd}$	12.22	$\frac{1}{2}$	0.011 06	0.948 68	−0.622 301	
$^{113}\text{In}$	4.3	$\frac{9}{2}$	0.351 21	0.936 52	5.528 9	0.799
$^{115}\text{In}$	95.7	$\frac{9}{2}$	0.353 48	0.938 54	5.540 8	0.81
$^{115}\text{Sn}$	0.34	$\frac{1}{2}$	0.035 61	1.400 74	−9.18 84	
$^{117}\text{Sn}$	7.68	$\frac{1}{2}$	0.046 05	1.526 06	−1.001 05	
$^{119}\text{Sn}$	8.59	$\frac{1}{2}$	0.052 73	1.596 56	−1.047 28	
$^{121}\text{Sb}$	57.36	$\frac{5}{2}$	0.163 02	1.025 49	3.363 4	−0.36
$^{123}\text{Sb}$	42.64	$\frac{7}{2}$	0.046 59	0.555 30	2.549 8	−0.49
$^{123}\text{Te}$	0.908	$\frac{1}{2}$	0.018 37	1.123 46	−0.736 948	
$^{125}\text{Te}$	7.139	$\frac{1}{2}$	0.032 20	1.354 51	−0.888 505	
$^{127}\text{I}$	100	$\frac{5}{2}$	0.095 40	0.857 76	2.813 327	−0.789
$^{129}\text{Xe}$	26.4	$\frac{1}{2}$	0.021 62	1.186 01	−0.777 976	
$^{131}\text{Xe}$	21.2	$\frac{3}{2}$	0.002 82	0.351 58	0.691 862	−0.12
$^{133}\text{Cs}$	100	$\frac{7}{2}$	0.048 38	0.562 32	2.582 025	−0.003 7
$^{135}\text{Ba}$	6.592	$\frac{3}{2}$	0.005 00	0.425 81	0.837 943	0.160
$^{137}\text{Ba}$	11.23	$\frac{3}{2}$	0.006 97	0.476 33	0.937 365	0.245
$^{138}\text{La}$	* 0.0902	5	0.094 04	0.566 14	3.713 646	0.45

**TABLE 7.41** Nuclear Properties of the Elements (*Continued*)

Nuclide	Natural abundance, %	Spin $I$	Sensitivity at constant field relative to $^1\text{H}$	NMR frequency for a 1-kG field, MHz	Magnetic moment $\mu/\mu_N$ , $\text{J} \cdot \text{T}^{-1}$	Electric quadrupole moment $Q$ , $10^{-28} \text{ m}^2$
$^{139}\text{La}$	99.9098	$\frac{7}{2}$	0.060 58	0.606 10	2.783 045	0.20
$^{137}\text{Ce}$	*	$\frac{3}{2}$	0.006 41	0.462	0.91	
$^{139}\text{Ce}$	*	$\frac{3}{2}$	0.006 41	0.462	0.91	
$^{141}\text{Ce}$	*	$\frac{7}{2}$	0.003 64	0.237	1.09	
$^{141}\text{Pr}$	100	$\frac{5}{2}$	0.334 83	1.303 55	4.275 4	−0.059
$^{143}\text{Nd}$	12.18	$\frac{7}{2}$	0.003 39	0.231 9	−1.065	−0.63
$^{145}\text{Nd}$	8.30	$\frac{7}{2}$	0.000 79	0.142 9	−0.656	−0.33
$^{143}\text{Pm}$	*	$\frac{5}{2}$	0.235 10	1.16	3.8	
$^{147}\text{Pm}$	*	$\frac{7}{2}$	0.049 40	0.57	2.6	0.70
$^{147}\text{Sm}$	15.0	$\frac{7}{2}$	0.001 52	0.177 47	−0.814 9	−0.26
$^{149}\text{Sm}$	13.8	$\frac{7}{2}$	0.000 85	0.146 31	−0.671 8	0.094
$^{151}\text{Eu}$	47.8	$\frac{5}{2}$	0.179 29	1.058 54	3.471 8	0.903
$^{153}\text{Eu}$	52.2	$\frac{5}{2}$	0.015 44	0.467 44	1.533 1	2.41
$^{155}\text{Gd}$	14.80	$\frac{3}{2}$	0.000 15	0.131 7	−0.259 1	1.27
$^{157}\text{Gd}$	15.65	$\frac{3}{2}$	0.000 33	0.1727	−0.339 9	1.35
$^{159}\text{Tb}$	100	$\frac{3}{2}$	0.069 45	1.023	2.014	1.432
$^{161}\text{Dy}$	18.9	$\frac{5}{2}$	0.000 48	1.465 3	−0.480 6	2.47
$^{163}\text{Dy}$	24.9	$\frac{5}{2}$	0.001 30	0.205 07	0.672 6	2.65
$^{165}\text{Ho}$	100	$\frac{7}{2}$	0.204 23	0.908 81	4.173	3.58
$^{167}\text{Er}$	22.95	$\frac{7}{2}$	0.000 507	0.122 81	−0.563 9	3.57
$^{169}\text{Tm}$	100	$\frac{1}{2}$	0.000 566	3.531	−0.231 6	
$^{171}\text{Yb}$	14.3	$\frac{1}{2}$	0.005 52	0.752 59	0.493 67	
$^{173}\text{Yb}$	16.12	$\frac{5}{2}$	0.001 35	0.207 301	−0.679 89	2.80
$^{175}\text{Lu}$	97.41	$\frac{7}{2}$	0.031 28	0.486 24	2.232 7	3.49
$^{176}\text{Lu}$	* 2.59	7	0.039 75	0.345 1	3.169	4.97
$^{177}\text{Hf}$	18.606	$\frac{7}{2}$	0.001 40	0.172 81	0.793 5	3.36
$^{179}\text{Hf}$	13.629	$\frac{9}{2}$	0.000 55	0.108 56	−0.640 9	3.79
$^{180}\text{Ta}$	0.012	9	0.102 51	0.404	4.77	
$^{181}\text{Ta}$	99.988	$\frac{7}{2}$	0.037 44	0.516 25	2.3705	3.17
$^{183}\text{W}$	14.3	$\frac{1}{2}$	0.000 08	0.179 56	0.117 785	
$^{185}\text{Re}$	37.40	$\frac{5}{2}$	0.138 70	0.971 7	3.1871	2.18
$^{187}\text{Re}$	* 62.60	$\frac{5}{2}$	0.143 00	0.981 7	3.219 7	2.07
$^{187}\text{Os}$	1.6	$\frac{1}{2}$	0.000 01	0.098 56	0.064 652	
$^{189}\text{Os}$	16.1	$\frac{3}{2}$	0.002 44	0.335 35	0.659 933	0.856
$^{191}\text{Ir}$	37.3	$\frac{3}{2}$	0.000 03	0.076 6	0.150 7	0.816
$^{193}\text{Ir}$	62.7	$\frac{3}{2}$	0.000 04	0.0832	0.163 7	0.751
$^{195}\text{Pt}$	33.8	$\frac{1}{2}$	0.010 39	0.929 20	0.609 52	
$^{197}\text{Au}$	100	$\frac{3}{2}$	0.000 03	0.074 06	0.145 746	0.547
$^{199}\text{Hg}$	16.87	$\frac{1}{2}$	0.005 94	0.771 21	0.505 885	
$^{201}\text{Hg}$	13.18	$\frac{3}{2}$	0.001 49	0.284 68	−0.560 226	0.386
$^{203}\text{Tl}$	29.524	$\frac{1}{2}$	0.195 981	2.473 10	1.622 258	
$^{205}\text{Tl}$	70.476	$\frac{1}{2}$	0.201 82	2.497 42	1.638 215	
$^{207}\text{Pb}$	22.1	$\frac{1}{2}$	0.009 55	0.903 38	0.592 58	
$^{209}\text{Bi}$	100	$\frac{9}{2}$	0.144 33	0.696 28	4.110 6	−0.50
$^{229}\text{Th}$	*	$\frac{5}{2}$	0.000 42	0.140	0.46	4.30
$^{231}\text{Pa}$	*	$\frac{3}{2}$	0.069 03	1.02	2.01	−1.72
$^{235}\text{U}$	* 0.7200	$\frac{7}{2}$	0.000 15	0.083	−0.38	4.936
$^{237}\text{Np}$	*	$\frac{5}{2}$	0.132 64	0.957	3.14	3.886
$^{239}\text{Pu}$	*	$\frac{1}{2}$	0.000 38	0.309	0.203	
$^{243}\text{Am}$	*	$\frac{5}{2}$	0.017 88	0.491	1.61	4.21

**TABLE 7.42** Proton Chemical Shifts

Values are given on the officially approved  $\delta$  scale;  $\tau = 10.00 - \delta$ .

**Abbreviations Used in the Table**

R, alkyl group      Ar, aryl group

Substituent group	Methyl protons	Methylene protons	Methine proton
HC—C—CH <sub>2</sub>	0.95	1.20	1.55
HC—C—NR <sub>2</sub>	1.05	1.45	1.70
HC—C—C=C	1.00	1.35	1.70
HC—C—C=O	1.05	1.55	1.95
HC—C—NRAr	1.10	1.50	1.80
HC—C—H(C=O)R	1.10	1.50	1.90
HC—C—(C=O)NR <sub>2</sub>	1.10	1.50	1.80
HC—C—(C=O)Ar	1.15	1.55	1.90
HC—C—(C=O)OR	1.15	1.70	1.90
HC—C—Ar	1.15	1.55	1.80
HC—C—OH	1.20	1.50	1.75
HC—C—OR	1.20	1.50	1.75
HC—C—C≡CR	1.20	1.50	1.80
HC—C—C≡N	1.25	1.65	2.00
HC—C—SR	1.25	1.60	1.90
HC—C—OAr	1.30	1.55	2.00
HC—C—O(C=O)R	1.30	1.60	1.80
HC—C—SH	1.30	1.60	1.65
HC—C—(S=O)R and HC—C—SO <sub>2</sub> R	1.35	1.70	
HC—C—NR <sub>3</sub> <sup>+</sup>	1.40	1.75	2.05
HC—C—O—N=O	1.40		
HC—C—O(C=O)CF <sub>3</sub>	1.40	1.65	
HC—C—CL	1.55	1.80	1.95
HC—C—F	1.55	1.85	2.15
HC—C—NO <sub>2</sub>	1.60	2.05	2.50
HC—C—O(C=O)Ar	1.65	1.75	1.85
HC—C—I	1.75	1.80	2.10
HC—C—Br	1.80	1.85	1.90
HC—CH <sub>2</sub>	0.90	1.30	1.50
HC—C=C	1.60	2.05	
HC—C≡C	1.70	2.20	2.80
HC—(C=O)OR	2.00	2.25	2.50
HC—(C=O)NR <sub>2</sub>	2.00	2.25	2.40
HC—SR	2.05	2.55	3.00
HC—O—O	2.10	2.30	2.55
HC—(C=O)R	2.10	2.35	2.65
HC—C≡N	2.15	2.45	2.90
HC—I	2.15	3.15	4.25
HC—CHO	2.20	2.40	
HC—Ar	2.25	2.45	2.85
HC—NR <sub>2</sub>	2.25	2.40	2.80
HC—SSR	2.35	2.70	
HC—(C=O)Ar	2.40	2.70	3.40
HC—SAr	2.40		
HC—NRAr	2.60	3.10	3.60
HC—SO <sub>2</sub> R and HC—(SO)R	2.60	3.05	
HC—Br	2.70	3.40	4.10
HC—NR <sub>3</sub> <sup>+</sup>	2.95	3.10	3.60


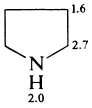

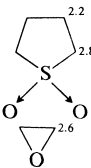

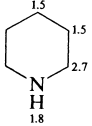


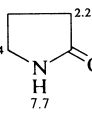
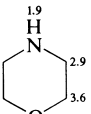


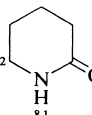


TABLE 7.42 Proton Chemical Shifts (Continued)

Substituent group	Methyl protons	Methylene protons	Methine proton
HC—NH(C=O)R	2.95	3.35	3.85
HC—SO <sub>3</sub> R	2.95		
HC—Cl	3.05	3.45	4.05
HC—OH and HC—OR	3.20	3.40	3.60
HC—PAr <sub>3</sub>	3.20	3.40	
HC—NH <sub>2</sub>	3.50	3.75	4.05
HC—O(C=O)R	3.65	4.10	4.95
HC—OAr	3.80	4.00	4.60
HC—O(C=O)Ar	3.80	4.20	5.05
HC—O(C=O)CF <sub>1</sub>	3.95	4.30	
HC—F	4.25	4.50	4.80
HC—NO <sub>2</sub>	4.30	4.35	4.60
Cyclopropane		0.20	0.40
Cyclobutane		2.45	
Cyclopentane		1.65	
Cyclohexane		1.50	1.80
Cycloheptane		1.25	

Substituent group	Proton shift	Substituent group	Proton shift
HC≡CH	2.35	HO—C=O	10–12
HC≡CAr	2.90	HO—SO <sub>2</sub>	11–12
HC≡C—C=C	2.75	HO—Ar	4.5–6.5
HAr	7.20	HO—R	0.5–4.5
HCO—O	8.1	HS—Ar	2.8–3.6
HCO—R	9.4–10.0	HS—R	1–2
HCO—Ar	9.7–10.5	HN—Ar	3–6
HO—N=C (oxime)	9–12	HN—R	0.5–5

## Saturated heterocyclic ring systems

**TABLE 7.42** Proton Chemical Shifts (*Continued*)

Unsaturated cyclic systems			

**TABLE 7.43** Estimation of Chemical Shift for Protons of  $-\text{CH}_2-$  and Methine Groups

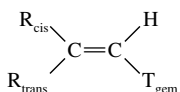
$$\delta_{\text{CH}_2} = 0.23 + C_1 + C_2 \quad \delta_{\text{CH}} = 0.23 + C_1 + C_2 + C_3$$

X*	C	X*	C	X*	C
$-\text{CH}_3$	0.5	$-\text{SR}$	1.6	$-\text{OR}$	2.4
$-\text{CF}_3$	1.1	$-\text{C}\equiv\text{C}-\text{Ar}$	1.7	$-\text{Cl}$	2.5
$>\text{C}=\text{C}<$	1.3	$-\text{CN}$	1.7	$-\text{OH}$	2.6
$-\text{C}\equiv\text{C}-\text{R}$	1.4	$-\text{CO}-\text{R}$	1.7	$-\text{N}=\text{C}=\text{S}$	2.9
$-\text{COOR}$	1.5	$-\text{I}$	1.8	$-\text{OCOR}$	3.1
$-\text{NR}_2$	1.6	$-\text{Ph}$	1.8	$-\text{OPh}$	3.2
$-\text{CONR}_2$	1.6	$-\text{Br}$	2.3		

\* R, alkyl group; Ar, aryl group; Ph, phenyl group.

**TABLE 7.44** Estimation of Chemical Shift for Proton Attached to a Double Bond

Positive Z values indicate a downfield shift, and an arrow indicates the point of attachment of the substituent group to the double bond.

$$\delta_{\text{C}=\text{C}-\text{H}} = 5.25 - Z_{\text{gem}} + Z_{\text{cis}} + Z_{\text{trans}}$$


R	$Z_{\text{gem}}$ , ppm	$Z_{\text{cis}}$ , ppm	$Z_{\text{trans}}$ , ppm
→H	0	0	0
→alkyl	0.45	-0.22	-0.28
→alkyl—ring (5- or 6-member)	0.69	-0.25	-0.28
→CH <sub>2</sub> O—	0.64	-0.01	-0.02
→CH <sub>2</sub> S—	0.71	-0.13	-0.22
→CH <sub>2</sub> X (X: F, Cl, Br)	0.70	0.11	-0.04
→CH <sub>2</sub> N<	0.58	-0.10	-0.08
↘C=C (isolated)	1.00	-0.09	-0.23
↘C=C (conjugated)	1.24	0.02	-0.05
→C≡N	0.27	0.75	0.55
→C≡C—	0.47	0.38	0.12
↘C=O (isolated)	1.10	1.12	0.87
↘C=O (conjugated)	1.06	0.91	0.74
→COOH (isolated)	0.97	1.41	0.71
→COOH (conjugated)	0.80	0.98	0.32
→COOR (isolated)	0.80	1.18	0.55
→COOR (conjugated)	0.78	1.01	0.46
$\begin{array}{c} \text{H} \\   \\ \rightarrow \text{C}=\text{O} \\   \\ \text{N} \end{array}$	1.02	0.95	1.17
$\begin{array}{c} \text{Cl} \\   \\ \rightarrow \text{C}=\text{O} \end{array}$	1.37	0.98	0.46
→C=O	1.11	1.46	1.01
→OR (R: aliphatic)	1.22	-1.07	-1.21
→OR (R: conjugated)	1.21	-0.60	-1.00
→OCOR	2.11	-0.35	-0.64
→CH <sub>2</sub> —C=O; →CH <sub>2</sub> —C≡N	0.69	-0.08	-0.06
→CH <sub>2</sub> —aromatic ring	1.05	-0.29	-0.32
→F	1.54	-0.40	-1.02
→Cl	1.08	0.18	0.13
→Br	1.07	0.45	0.55
→I	1.14	0.81	0.88
→N—R (R: aliphatic)	0.80	-1.26	-1.21
→N—R (R: conjugated)	1.17	-0.53	-0.99

**TABLE 7.44** Estimation of Chemical Shift for Proton Attached to a Double Bond (*Continued*)

R	$Z_{\text{gem}}$ , ppm	$Z_{\text{cis}}$ , ppm	$Z_{\text{trans}}$ , ppm
$\begin{array}{c}   \quad   \\ \rightarrow \text{N} - \text{C} = \text{O} \end{array}$	2.08	-0.57	-0.72
$\rightarrow$ aromatic	1.38	0.36	-0.07
$\rightarrow \text{CF}_3$	0.66	0.61	0.32
$\rightarrow$ aromatic ( <i>o</i> -substituted)	1.65	0.19	0.09
$\rightarrow \text{SR}$	1.11	-0.29	-0.13
$\rightarrow \text{SO}_2$	1.55	1.16	0.93

**TABLE 7.45** Chemical Shifts in Monosubstituted Benzene

$$\delta = 7.27 + \Delta_i$$

Substituent	$\Delta_{\text{ortho}}$	$\Delta_{\text{meta}}$	$\Delta_{\text{para}}$
$\text{NO}_2$	0.94	0.18	0.39
$\text{CHO}$	0.58	0.20	0.26
$\text{COOH}$	0.80	0.16	0.25
$\text{COOCH}_3$	0.71	0.08	0.20
$\text{COCl}$	0.82	0.21	0.35
$\text{CCl}_3$	0.8	0.2	0.2
$\text{COCH}_3$	0.62	0.10	0.25
$\text{CN}$	0.26	0.18	0.30
$\text{CONH}_2$	0.65	0.20	0.22
$\text{NH}_3^+$	0.4	0.2	0.2
$\text{CH}_2\text{X}^*$	0.0-0.1	0.0-0.1	0.0-0.1
$\text{CH}_3$	-0.16	-0.09	-0.17
$\text{CH}_2\text{CH}_3$	-0.15	-0.06	-0.18
$\text{CH}(\text{CH}_3)_2$	-0.14	-0.09	-0.18
$\text{C}(\text{CH}_3)_2$	-0.09	0.05	-0.23
$\text{F}$	-0.30	-0.02	-0.23
$\text{Cl}$	0.01	-0.06	-0.08
$\text{Br}$	0.19	-0.12	-0.05
$\text{I}$	0.39	-0.25	-0.02
$\text{NH}_2$	-0.76	-0.25	-0.63
$\text{OCH}_3$	-0.46	-0.10	-0.41
$\text{OH}$	-0.49	-0.13	-0.2
$\text{OCOR}$	-0.2	0.1	-0.2
$\text{NHCH}_3$	-0.8	-0.3	-0.6
$\text{N}(\text{CH}_3)_2$	-0.60	-0.10	-0.62

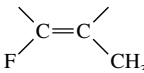

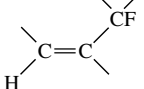
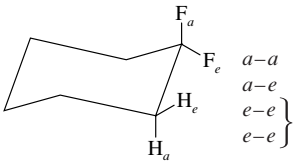
\* X = Cl, alkyl, OH, or  $\text{NH}_2$ .



TABLE 7.46 Proton Spin Coupling Constants

Structure	<i>J</i> , Hz	Structure	<i>J</i> , Hz
	12–15		2–3 3–4 2–4 2–5 5–6 3.5–5.0 1.5 3.4
$\text{CH}-\text{CH}$ (free rotation)	6–8		<i>o</i> <i>m</i> <i>p</i> 6–12 4–8
$\text{CH}-\text{OH}$ (no exchange)	5		<i>o</i> <i>m</i> <i>p</i> 1.5–2.5 2.5 1.5 0
$\text{CH}-\text{NH}$	4–8		
$\text{CH}-\text{SH}$	6–8		<i>a-a</i> <i>a-e</i> <i>e-e</i> 8–10 2–3 2–3
$\text{CH}-\text{C}(=\text{O})\text{H}$	1–3	Cyclopentane	<i>cis</i> <i>trans</i> 4–6 4–6
$-\text{N}=\text{C}(\text{H})_2$	8–16	Cyclobutane	<i>cis</i> <i>trans</i> 8 8
	0–3 6–14 11–18	Cyclopropane	<i>cis</i> <i>trans</i> <i>gem</i> 9–11 6–8 4–6
	0.5–3 0.5–3		<i>o</i> <i>m</i> <i>p</i> 6–10 1–3 0–1
$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$	4–10 10–13 6		1–2 2–3 8–9 6
$-\text{CH}_2-\text{C}\equiv\text{C}-\text{CH}$	0–3		2–3 3–4 2–4 3–5 2–5 2–6 5–6 7–9 1–2 1–2 0–1 0–1
$\text{CH}=\text{C}\equiv\text{CH}$	0–3		1–2 1–3 2–3 2–3 3–4 1–2 1–3
	0–2 2–4 5–7 6–9 10–13 4–5 3 5–6 0 7 6 2 6 4		45–52
			<i>gauche</i> <i>trans</i> 0–12 10–45
			<i>gem</i> <i>cis</i> <i>trans</i> 72–90 –3 to 20 12–40
	2–3 3–4 2–4 2–5		

**TABLE 7.46** Proton Spin Coupling Constants (*Continued*)

Structure	<i>J</i> , Hz	Structure	<i>J</i> , Hz
	2–4		21
	0–6		34 12 < 5–8

**TABLE 7.47** Proton Chemical Shifts of Reference Compounds*Relative to tetramethylsilane.*

Compound	$\delta$ , ppm	Solvent(s)
Sodium acetate	1.90	D <sub>2</sub> O
1,2-Dibromoethane	3.63	CDCl <sub>3</sub>
1,1,2,2-Tetrachloroethane	5.95	CDCl <sub>3</sub> ; CCl <sub>4</sub>
1,4-Benzoquinone	6.78	CDCl <sub>3</sub> ; CCl <sub>4</sub>
1,4-Dichlorobenzene	7.23	CCl <sub>4</sub>
1,3,5-Trinitrobenzene	9.21	DMSO- <i>d</i> <sub>6</sub> *
	9.55	CHCl <sub>3</sub>

\* DMSO, dimethyl sulfoxide.

**TABLE 7.48** Solvent Positions of Residual Protons in Incompletely Deuterated Solvents*Relative to tetramethylsilane.*

Solvent	Group	$\delta$ , ppm
Acetic- <i>d</i> <sub>3</sub> acid- <i>d</i> <sub>1</sub>	Methyl	2.05
	Hydroxyl	11.5*
Acetone- <i>d</i> <sub>6</sub>	Methyl	2.057
Acetonitrile- <i>d</i> <sub>3</sub>	Methyl	1.95
Benzene- <i>d</i> <sub>6</sub>	Methine	6.78
<i>tert</i> -Butanol- <i>d</i> <sub>1</sub> (CH <sub>3</sub> ) <sub>3</sub> COD	Methyl	1.28
Chloroform- <i>d</i> <sub>1</sub>	Methine	7.25
Cyclohexane- <i>d</i> <sub>12</sub>	Methylene	1.40
Deuterium oxide	Hydroxyl	4.7*
Dimethyl- <i>d</i> <sub>6</sub> -formamide- <i>d</i> <sub>1</sub>	Methyl	2.75; 2.95
	Formyl	8.05
Dimethyl- <i>d</i> <sub>6</sub> sulfoxide	Methyl	2.51
	Absorbed water	3.3*
1,4-Dioxane- <i>d</i> <sub>8</sub>	Methylene	3.55
Hexamethyl- <i>d</i> <sub>18</sub> -phosphoramidate	Methyl	2.60
Methanol- <i>d</i> <sub>4</sub>	Methyl	3.35
	Hydroxyl	4.8*
Dichloromethane- <i>d</i> <sub>2</sub>	Methylene	5.35

\* These values may vary greatly, depending upon the solute and its concentration.

**TABLE 7.48** Solvent Positions of Residual Protons in Incompletely Deuterated Solvents (*Continued*)

Solvent	Group	$\delta$ , ppm
Pyridine- $d_5$	C-2 Methine	8.5
	C-3 Methine	7.0
	C-4 Methine	7.35
Toluene- $d_8$	Methyl	2.3
	Methine	7.2
Trifluoroacetic acid- $d_1$	Hydroxyl	11.3*

\* These values may vary greatly, depending upon the solute and its concentration.

**TABLE 7.49** Carbon-13 Chemical Shifts

Values given in ppm on the  $\delta$  scale, relative to tetramethylsilane.

Substituent group	Primary carbon	Secondary carbon	Tertiary carbon	Quaternary carbon
<i>Alkanes</i>				
C—C	5–30	25–45	23–58	28–50
C—O	45–60	42–71	62–78	73–86
C—N	13–45	44–58	50–70	60–75
C—S	10–30	22–42	55–67	53–62
C—halide (I to Cl)	3–25	3–40	34–58	35–75
Substituent group	$\delta$ , ppm	Substituent group		$\delta$ , ppm
Cyclopropane	–5–5	Aromatics:		
Cycloalkane C <sub>4</sub> –C <sub>10</sub>	5–25	Aryl-C		125–145
Mercaptanes	5–70	Aryl-P		119–128
Amines:		Aryl-N		128–138
R <sub>2</sub> N—C	20–70	Aryl-O		133–152
Aryl—N	128–138	Azomethines		145–162
Sulfoxides, sulfones	35–55	Carbonates		159–162
Alcohols R—OH	45–87	Ureas		150–170
Ethers R—O—R	57–87	Anhydrides		150–175
Nitro R—NO <sub>2</sub>	60–78	Amides		154–178
Alkynes:		Oximes		155–165
HC≡CR	63–73	Esters:		
RC≡CR	72–95	Saturated		158–165
Acetals, ketals	88–112	$\alpha,\beta$ -Unsaturated		165–176
Thiocyanates R—SCN	96–118	Isocyanides R—NC		162–175
Alkenes:		Carboxylic acids:		
H <sub>2</sub> C=	100–122	Nonconjugated		162–165
R <sub>2</sub> C=	110–150	Conjugated		165–184
Heteroaromatics:		Salts (anion)		175–195
C=N	100–152	Ketones:		
C <sub><math>\alpha</math></sub>	142–160	$\alpha$ -Halo		160–200
Cyanates R—OCN	105–120	Nonconjugated		192–202
Isocyanates R—NCO	115–135	$\alpha,\beta$ -Unsaturated		202–220
Isothiocyanates R—NCS	115–142	Imides		165–180
Nitriles, cyanides	117–124	Acyl chlorides R—CO—Cl		165–183

**TABLE 7.49** Carbon-13 Chemical Shifts (*Continued*)

Substituent group	$\delta$ , ppm	Substituent group	$\delta$ , ppm
Thioureas	165–185	Thioketones $R-CS-R$	190–202
Aldehydes:		Carbonyl $M(CO)_n$	190–218
$\alpha$ -Halo	170–190	Allenes $=C=$	197–205
Nonconjugated	182–192		
Conjugated	192–208		

## Saturated heterocyclic ring systems


## Unsaturated cyclic systems


**TABLE 7.49** Carbon-13 Chemical Shifts (*Continued*)

Unsaturated cyclic systems ( <i>continued</i> )			
Saturated alicyclic ring systems			

**TABLE 7.50** Estimation of Chemical Shifts of Alkane Carbons*Relative to tetramethylsilane.*

Positive terms indicate a downfield shift.

$$\delta_C = -2.6 + 9.1n_\alpha + 9.4n_\beta - 2.5n_\gamma + 0.3n_\delta + 0.1n_\epsilon \quad (\text{plus any correction factors})$$

where  $n_\alpha$  is the number of carbons bonded directly to the  $i$ th carbon atom and  $n_\beta$ ,  $n_\gamma$ ,  $n_\delta$ , and  $n_\epsilon$  are the number of carbon atoms two, three, four, and five bonds removed. The constant is the chemical shift for methane.

Chain branching*	Correction factor	Chain branching*	Correction factor
1°(3°)	-1.1	4°(1°)	-1.5
1°(4°)	-3.4	2°(4°)	-7.2
2°(3°)	-2.5	3°(3°)	-9.5
3°(2°)	-3.7	4°(2°)	-8.4

\* 1° signifies a CH<sub>3</sub>— group; 2°, a —CH<sub>2</sub>— group; 3°, a >CH— group; and 4°, a >C< group. 1° (3°) signifies a methyl group bound to a >CH— group, and so on.

**Examples:** For 3-methylpentane, CH<sub>3</sub>—CH<sub>2</sub>—CH(CH<sub>3</sub>)—CH<sub>2</sub>—CH<sub>3</sub>,

$$\delta_{C=2} = -2.6 + 9.1(2) + 9.4(2) - 2.5 - 1(1)[2^\circ(3^\circ)] = 29.4$$

$$\delta_{C=3} = -2.6 + 9.1(3) + 9.4(2) + (2)[3^\circ(2^\circ)] = 36.2$$

**TABLE 7.51** Effect of Substituent Groups on Alkyl Chemical Shifts

These increments are added to the shift value of the appropriate carbon atom as calculated from Table 7.50.



Substituent group Y*	$\alpha$ carbon		$\beta$ carbon		$\gamma$ carbon
	Straight	Branched	Straight	Branched	
—CO—OH	20.9	16	2.5	2	-2.2
—COO <sup>-</sup> (anion)	24.4	20	4.1	3	-1.6
—CO—OR	20.5	17	2.5	2	-2
—CO—Cl	33	28		2	
—CO—NH <sub>2</sub>	22	2.5			-0.5
—CHO	31		0		-2
—CO—R	30	24	1	1	-2
—OH	48.3	40.8	10.2	7.7	-5.8
—OR	58	51	8	5	-4
—O—CO—NH <sub>2</sub>	51		8		
—O—CO—R	51	45	6	5	-3
—C—CO—Ar	53				
—F	68	63	9	6	-4
—Cl	31.2	32	10.5	10	-4.6
—Br	20.0	25	10.6	10	-3.1

\* R, alkyl group; Ar, aryl group.

**TABLE 7.51** Effect of Substituent Groups on Alkyl Chemical Shifts (*Continued*)

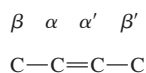
Substituent group Y*	$\alpha$ carbon		$\beta$ carbon		$\gamma$ carbon
	Straight	Branched	Straight	Branched	
—I	—8	4	11.3	12	—1.0
—NH <sub>2</sub>	29.3	24	11.3	10	—4.6
—NH <sub>3</sub> <sup>+</sup>	26	24	8	6	—5
—NHR	36.9	31	8.3	6	—3.5
—NR <sub>2</sub>	42		6		—3
—NR <sub>3</sub> <sup>+</sup>	31		5		—7
—NO <sub>2</sub>	63	57	4	4	
—CN	4	1	3	3	—3
—SH	11	11	12	11	—6
—SR	20		7		—3
—CH=CH <sub>2</sub>	20		6		—0.5
—C <sub>6</sub> H <sub>5</sub>	23	17	9	7	—2
—C≡CH	4.5		5.5		—3.5

\* R, alkyl group; Ar, aryl group.

**TABLE 7.52** Estimation of Chemical Shifts of Carbon Attached to a Double Bond

The olefinic carbon chemical shift is calculated from the equation

$$\delta_C = 123.3 + 10.6n_\alpha + 7.2n_\beta - 7.9n_{\alpha'} - 1.8n_{\beta'} \quad (\text{plus any steric correction terms})$$

where  $n$  is the number of carbon atoms at the particular position, namely,

Substituents on both sides of the double bond are considered separately. Additional vinyl carbons are treated as if they were alkyl carbons. The method is applicable to alicyclic alkenes; in small rings carbons are counted twice, i.e., from both sides of the double bond where applicable. The constant in the equation is the chemical shift for ethylene. The effect of other substituent groups is tabulated below.

Substituent group	$\beta$	$\alpha$	$\alpha'$	$\beta'$
—OR	2	29	—39	—1
—OH	6			—1
—O—CO—CH <sub>3</sub>	—3	18	—27	4
—CO—CH <sub>3</sub>		15	6	
—CHO		13.6	13.2	
—CO—OH		5.2	9.1	
—CO—OR		6	7	
—CN		—15.4	14.3	
—F		24.9	—34.3	
—Cl	—1	3.3	—5.4	2
—Br	0	—7.2	—0.7	2
—I		—37.4	7.7	
—C <sub>6</sub> H <sub>5</sub>		12	—11	

**TABLE 7.52** Estimation of Chemical Shifts of Carbon Attached to a Double Bond (*Continued*)

Substituent pair		Steric correction term
$\alpha, \alpha'$	<i>trans</i>	0
$\alpha, \alpha'$	<i>cis</i>	-1.1
$\alpha, \alpha$	<i>gem</i>	-4.8
$\alpha', \alpha'$		+2.5
$\beta, \beta$		+2.3

**TABLE 7.53** Carbon-13 Chemical Shifts in Substituted Benzenes

$$\delta_C = 128.5 + \Delta$$

Substituent group	$\Delta_{C-1}$	$\Delta_{ortho}$	$\Delta_{meta}$	$\Delta_{para}$
-CH <sub>3</sub>	9.3	0.8	-0.1	-2.9
-CH <sub>2</sub> CH <sub>3</sub>	15.6	-0.4	0	-2.6
-CH(CH <sub>3</sub> ) <sub>2</sub>	20.2	-2.5	0.1	-2.4
-C(CH <sub>3</sub> ) <sub>3</sub>	22.4	-3.1	-0.1	-2.9
-CH <sub>2</sub> O-CO-CH <sub>3</sub>	7.7	0	0	0
-C <sub>6</sub> H <sub>5</sub>	13.1	-1.1	0.4	-1.2
-CH=CH <sub>2</sub>	9.5	-2.0	0.2	-0.5
-C≡CH	-6.1	3.8	0.4	-0.2
-CH <sub>2</sub> OH	12.3	-1.4	-1.4	-1.4
-CO-OH	2.1	1.5	0	5.1
-COO <sup>-</sup> (anion)	8	1	0	3
-CO-OCH <sub>3</sub>	2.1	1.1	0.1	4.5
-CO-CH <sub>3</sub>	9.1	0.1	0	4.2
-CHO	8.6	1.3	0.6	5.5
-CO-Cl	4.6	2.4	1	6.2
-CO-CF <sub>3</sub>	-5.6	1.8	0.7	6.7
-CO-C <sub>6</sub> H <sub>5</sub>	9.4	1.7	-0.2	3.6
-CN	-15.4	3.6	0.6	3.9
-OH	26.9	-12.7	1.4	-7.3
-OCH <sub>3</sub>	31.4	-14.0	1.0	-7.7
-OC <sub>6</sub> H <sub>5</sub>	29.2	-9.4	1.6	-5.1
-O-CO-CH <sub>3</sub>	23.0	-6.4	1.3	-2.3
-NH <sub>2</sub>	18.0	-13.3	0.9	-9.8
-N(CH <sub>3</sub> ) <sub>2</sub>	22.4	-15.7	0.8	-11.5
-N(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	19	-4	1	-6
-NHC <sub>6</sub> H <sub>5</sub>	14.6	-10.7	0.7	-7.7
-NH-CO-CH <sub>3</sub>	11.1	-9.9	0.2	-5.6
-NO <sub>2</sub>	20.0	-4.8	0.9	5.8
-F	34.8	-12.9	1.4	-4.5
-Cl	6.2	0.4	1.3	-1.9
-Br	-5.5	3.4	1.7	-1.6
-I	-32.2	9.9	2.6	-1.4
-CF <sub>3</sub>	-9.0	-2.2	0.3	3.2
-NCO	5.7	-3.6	1.2	-2.8
-SH	2.3	1.1	1.1	-3.1
-SCH <sub>3</sub>	10.2	-1.8	0.4	-3.6
-SO <sub>2</sub> -NH <sub>2</sub>	15.3	-2.9	0.4	3.3
-Si(CH <sub>3</sub> ) <sub>3</sub>	13.4	4.4	-1.1	-1.1



**TABLE 7.54** Carbon-13 Chemical Shifts in Substituted Pyridines\*

$$\delta_C(k) = C_k + \Delta_i$$

Substituent group	$C_2 = C_6 = 149.6$ $\Delta_{C-2}$ or $\Delta_{C-6}$	$\Delta_{23}$	$\Delta_{24}$	$\Delta_{25}$	$\Delta_{26}$
—CH <sub>3</sub>	9.1	−1.0	−0.1	−3.4	−0.1
—CH <sub>2</sub> CH <sub>3</sub>	14.0	−2.1	0.1	−3.1	0.2
—CO—CH <sub>3</sub>	4.3	−2.8	0.7	3.0	−0.2
—CHO	3.5	−2.6	1.3	4.1	0.7
—OH	14.9	−17.2	0.4	−3.1	−6.8
—OCH <sub>3</sub>	15.3	−13.1	2.1	−7.5	−2.2
—NH <sub>2</sub>	11.3	−14.7	2.3	10.6	−0.9
—NO <sub>2</sub>	8.0	−5.1	5.5	6.6	0.4
—CN	−15.8	−5.0	−1.7	3.6	1.9
—F	14.4	−14.7	5.1	−2.7	−1.7
—Cl	2.3	0.7	3.3	−1.2	0.6
—Br	−6.7	4.8	3.3	−0.5	1.4

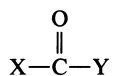
Substituent group	$\Delta_{32}$	$C_3 = C_5 = 124.2$ $\Delta_{C-3}$ or $\Delta_{C-5}$	$\Delta_{34}$	$\Delta_{35}$	
—CH <sub>3</sub>	1.3	9.0	0.2	−0.8	−2.3
—CH <sub>2</sub> CH <sub>3</sub>	0.3	15.0	−1.5	−0.3	−1.8
—CO—CH <sub>3</sub>	0.5	−0.3	−3.7	−2.7	4.2
—CHO	2.4	7.9	0	0.6	5.4
—OH	−10.7	31.4	−12.2	1.3	−8.6
—NH <sub>2</sub>	−11.9	21.5	−14.2	0.9	−10.8
—CN	3.6	−13.7	4.4	0.6	4.2
—Cl	−0.3	8.2	−0.2	0.7	−1.4
—Br	2.1	−2.6	2.9	1.2	−0.9
—I	7.1	−28.4	9.1	2.4	0.3

Substituent group	$\Delta_{42} = \Delta_{46}$	$\Delta_{43} = \Delta_{45}$	$C_4 = 136.2$ $\Delta_{C-4}$
—CH <sub>3</sub>	0.5	0.8	10.8
—CH <sub>2</sub> CH <sub>3</sub>	0	−0.3	15.9
—CH=CH <sub>2</sub>	0.3	−2.9	8.6
—CO—CH <sub>3</sub>	1.6	−2.6	6.8
—CHO	1.7	−0.6	5.5
—NH <sub>2</sub>	0.9	−13.8	19.6
—CN	2.1	2.2	−15.7
—Br	3.0	3.4	−3.0

\* May be used for disubstituted, polyheterocyclic, and polynuclear systems if deviations due to steric and mesomeric effects are allowed for.

TABLE 7.55 Carbon-13 Chemical Shifts of Carbonyl Group






X	Y	$\delta_{\text{C}}$	X	Y	$\delta_{\text{C}}$
H—	—CH <sub>3</sub>	199.7	CH <sub>3</sub> —	—CH=CH <sub>2</sub>	196.9
H—	—CCl <sub>3</sub>	175.3	CH <sub>3</sub> —	—C <sub>6</sub> H <sub>5</sub>	197.6
H—	—NH <sub>2</sub>	165.5	CH <sub>3</sub> —	—CH <sub>2</sub> —CO—CH <sub>3</sub>	201.9
H—	—N(CH <sub>3</sub> ) <sub>2</sub>	162.4		(keto)	191.4
				(enol)	167.7
H—	2-Furyl	153.3	CH <sub>3</sub> —	—CH <sub>2</sub> CHO	167.7
H—	2-Pyrrolyl	134.0	CH <sub>3</sub> —	—C <sub>6</sub> H <sub>5</sub> —CH <sub>3</sub>	196 ( <i>m, p</i> )
H—	2-Thienyl	143.3		199 ( <i>o</i> )	
(CH <sub>3</sub> ) <sub>2</sub> CH—	—OH	184.8	CH <sub>3</sub> —	—2,6-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	206
C <sub>6</sub> H <sub>5</sub> —	—OH	172.6	CH <sub>3</sub> —	—OH	178
CF <sub>3</sub> —	—OH	163.0	CH <sub>3</sub> —	—O <sup>−</sup> (anion)	181.5
CCl <sub>3</sub> —	—OH	168.0	CH <sub>3</sub> —	—OCH <sub>3</sub>	170.7
CH <sub>3</sub> CH(NH <sub>2</sub> )—	—OH	176.5	CH <sub>3</sub> —	—O—CH=CH <sub>2</sub>	167.7
CF <sub>3</sub> —	—OCH <sub>2</sub> CH <sub>3</sub>	158.1	CH <sub>3</sub> —	—O—CH(CH <sub>3</sub> ) <sub>2</sub>	170.3
H <sub>2</sub> N—	—OCH <sub>2</sub> CH <sub>3</sub>	157.8	CH <sub>3</sub> —	—O—CO—CH <sub>3</sub>	167.3
2-Furyl	—OCH <sub>3</sub>	159.1	CH <sub>3</sub> —	—NH <sub>2</sub>	172.7
(CH <sub>3</sub> ) <sub>2</sub> N—	—C <sub>6</sub> H <sub>5</sub>	170.8	CH <sub>3</sub> —	—NHCH <sub>3</sub>	172
CH <sub>2</sub> =CHCH <sub>2</sub> O—CO—	—OCH <sub>2</sub> CH=CH <sub>2</sub>	157.6	CH <sub>3</sub> —	—N(CH <sub>3</sub> ) <sub>2</sub>	169.5
CH <sub>3</sub> CH <sub>2</sub> —	—CH <sub>2</sub> CH <sub>3</sub>	211.4	CH <sub>3</sub> —	—Cl	169.6
CH <sub>3</sub> —CH <sub>2</sub> —	—O—CO—CH <sub>2</sub> CH <sub>3</sub>	170.3	CH <sub>3</sub> —	—Br	165.6
CH <sub>3</sub> —	—CH <sub>3</sub>	205.8	CH <sub>3</sub> —	—I	158.9
CH <sub>3</sub> —	—CH <sub>2</sub> CH <sub>3</sub>	207			

$\text{C}=\text{O}$		
<i>n</i>	$\delta_{\text{C}}$	
3	207.9	
4	218.2	
5	211.3	
6	211.4	
7	216.0	

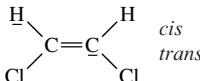
TABLE 7.56 One-Bond Carbon-Hydrogen Spin Coupling Constants

Structure	$J_{\text{CH}}$ , Hz	Structure	$J_{\text{CH}}$ , Hz
$\text{H}-\text{CH}_3$	125.0	$\text{H}-\text{CH}=\text{O}; \text{CH}_3-\underline{\text{CH}}=\text{O}$	172
$\text{H}-\text{CH}_2\text{CH}_3$	124.9	$\text{H}_2\text{N}-\text{CH}=\text{O}$	188.3
$\text{CH}_3-\text{CH}_2-\text{CH}_3$	119.2	$(\text{CH}_3)_2\text{N}-\underline{\text{CH}}=\text{O}$	191
$\text{H}-\text{C}(\text{CH}_3)_2$	114.2	$\text{H}-\text{COOH}$	222
$\text{H}-\text{CH}_2\text{CH}_2\text{OH}$	126.9	$\text{H}-\text{COO}^-$ (anion)	195
$\text{H}-\text{CH}_2\text{CH}=\text{CH}_2$	122.4	$\text{H}-\text{CO}-\text{OCH}_3$	226
$\text{H}-\text{CH}_2\text{C}_6\text{H}_5$	129.4	$\text{H}-\text{CO}-\text{F}$	267
$\text{H}-\text{CH}_2\text{C}\equiv\text{CH}$	132.0	$\text{CH}_3\text{CH}_2-\text{O}-\underline{\text{CHO}}$	225.6
$\text{H}-\text{CH}_2\text{CN}$	136.1	$\text{Cl}_3-\text{CHO}$	207
$\text{H}-\text{CH}(\text{CN})_2$	145.2	$\text{H}-\text{C}\equiv\text{CH}$	249
$\text{H}-\text{CH}_2-\text{halogen}$	149–152	$\text{H}-\text{C}\equiv\text{CCH}_3$	248
$\text{H}-\text{CHF}_2$	184.5	$\text{H}-\text{C}\equiv\text{CC}_6\text{H}_5$	251
$\text{H}-\text{CHCl}_2$	178.0	$\text{H}-\text{C}\equiv\text{CCH}_2\text{OH}$	241
$\text{H}-\text{CH}_2\text{NH}_2$	133.0	$\text{H}-\text{CN}$	269
$\text{H}-\text{CH}_2\text{NH}_3^+$	145.0	Cyclopropane	161
$\text{H}-\text{CH}_2\text{OH}$ (or $\text{H}-\text{CH}_2\text{OR}$ )	140–141	Cyclobutane	136
$\text{H}-\text{CH}(\text{OR})_2$	161–162	Cyclopentane	131
$\text{H}-\text{C}(\text{OR})_3$	186	Cyclohexane	123
$\text{H}-\text{C}(\text{OH})\text{R}_2$	143	Tetrahydrofuran 2,5	149
$\text{H}-\text{CH}_2\text{NO}_2$	146.0	3,4	133
$\text{H}-\text{CH}(\text{NO}_2)_2$	169.4	1,4-Dioxane	145
$\text{H}-\text{CH}_2\text{COOH}$	130.0	Benzene	159
$\text{H}-\text{CH}(\text{COOH})_2$	132.0	Fluorobenzene 2,6	155
$\text{H}-\text{CH}=\text{CH}_2$	156.2	3,5	163
$\text{H}-\text{C}(\text{CH}_3)=\text{C}(\text{CH}_3)_2$	148.4	4	161
$\text{H}-\text{CH}=\text{C}(\text{tert-C}_4\text{H}_9)_2$	152	Bromobenzene 2,6	171
$\text{H}-\text{C}(\text{tert-C}_4\text{H}_9)=$	143	3,5	164
$\text{C}(\text{tert-C}_4\text{H}_9)_2$		4	161
Methylenecycloalkane $\text{C}_4-\text{C}_7$	153–155	Benzonitrile 2,6	173
$\text{H}-\text{CH}=\text{C}=\text{CH}_2$	168	3,6	166
$\text{H}-\text{C}(\text{C}_6\text{H}_5)=\text{CH}(\text{C}_6\text{H}_5)$		4	163
<i>cis</i>	155	Nitrobenzene 2,6	171
<i>trans</i>	151	3,5	167
Cyclopropene	220	4	163
$\begin{array}{c} \text{H}_t \quad \quad \text{H}_g \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{H}_c \quad \quad \text{F} \end{array}$	200	Mesitylene 2,6	170
<i>gem</i>		3,5	163
<i>cis</i>	159	4	152
<i>trans</i>	162		
$\begin{array}{c} \text{H}_t \quad \quad \text{H}_g \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{H}_c \quad \quad \text{Cl} \end{array}$	195	2,4,6-Trimethylpyridine	158
<i>gem</i>			
<i>cis</i>	163		
<i>trans</i>	161		
$\begin{array}{c} \text{H}_t \quad \quad \text{H}_g \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{H}_c \quad \quad \text{CHO} \end{array}$	162		
<i>gem</i>	162		
<i>cis</i>	157		
<i>trans</i>	162		
$\begin{array}{c} \text{H}_t \quad \quad \text{H}_g \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{H}_c \quad \quad \text{CN} \end{array}$	177		
<i>gem</i>			
<i>cis</i>	163		
<i>trans</i>	165		
$\begin{array}{c} \text{H} \quad \quad \text{OH} \\ \diagdown \quad \diagup \\ \text{C}=\text{N} \\ \diagup \quad \diagdown \\ \text{CH}_3 \end{array}$	163		
<i>cis</i>			
<i>trans</i>	177		

**TABLE 7.56** One-Bond Carbon-Hydrogen Spin Coupling Constants (*Continued*)

Structure	$J_{\text{CH}}$ , Hz	Structure	$J_{\text{CH}}$ , Hz
 2 4	208 199	 216	
 205			

**TABLE 7.57** Two-Bond Carbon-Hydrogen Spin Coupling Constants

Structure	$^2J_{\text{CH}}$ , Hz	Structure	$^2J_{\text{CH}}$ , Hz
$\text{CH}_3\text{—CH}_2\text{—H}$	−4.5	$(\text{CH}_2)_n\text{—C=CH}_2$ $n = 4$	4.2
$\text{CCl}_3\text{—CH}_2\text{—H}$	5.9	$(\text{CH}_2)_n\text{—C=CH}_2$ $n = 5$	5.2
$\text{ClCH}_2\text{—CH}_2\text{Cl}$	−3.4	$(\text{CH}_2)_n\text{—C=CH}_2$ $n = 6$	5.5
$\text{Cl}_2\text{CH—CHCl}_2$	1.2	 cis trans	16.0 0.8
$\text{CH}_3\text{—CHO}$	26.7	$\text{HC}\equiv\text{CH}$	49.3
$\text{CH}_2=\text{CH}_2$	−2.4	$\text{C}_6\text{H}_5\text{O—C}\equiv\text{CH}$	61.0
$(\text{CH}_3)_2\text{C=O}$	5.5	$\text{HC}\equiv\text{C—CHO}$	33.2
$\text{CH}_2=\text{CH—CH=O}$	26.9	$\text{ClCH}_2\text{—CHO}$	32.5
$(\text{C}_2\text{H}_5)\text{CH—CHO}$	26.9	$\text{Cl}_2\text{CH—CHO}$	35.3
$\text{H}_2\text{NCH=CH—CHO}$	6.0	$\text{Cl}_3\text{C—CHO}$	46.3
$\text{H}_2\text{NCH—CH—CHO}$	20.0	$\text{C}_6\text{H}_5\text{—C}\equiv\text{C}\equiv\text{CH}_3$	10.8
$\text{C}_6\text{H}_6$	1.0		

**TABLE 7.58** Carbon-Carbon Spin Coupling Constants

Structure*	$J_{\text{CC}}$ , Hz	Structure	$J_{\text{CC}}$ , Hz
$\text{H}_3\text{C—CH}_3$	35	$\text{C—CO—OR}$	59
$\text{H}_3\text{C—CHR}_2$	37	$\text{C—CN}$	52–57
$\text{H}_3\text{C—CH}_2\text{Ar}$	34	$\text{C—C}\equiv\text{C}$ $^2J_{\text{CC}} = 11.8$	67
$\text{H}_3\text{C—CH}_2\text{CN}$	33	$\text{H}_2\text{C=CH}_2$	68
$\text{H}_3\text{C—CH}_2\text{—CH}_2\text{OH}$		$\text{>C=C—CO—OH}$	70–71
C-1, C-2	38	$\text{>C=C—CN}$	71
C-2, C-3	34	$\text{>C=C—Ar}$	67–70
$\text{H}_3\text{C—CH}_2\text{NH}_2$	37	$\text{C}_6\text{H}_6$	57
$\text{C—C=O}$	38–40	$\text{C}_3\text{H}_5\text{NO}_2$	
$\text{C—C—C=O}$	36	1-2	55
$\text{C—C—Ar}$	43	2-3, 3-4	56
$\text{C—CO—O}^-$ (anion)	52	$^3J_{2-5}$	7.6
$\text{C—CO—N}$	52		
$\text{C—CO—OH}$	57		

\* R, alkyl group; Ar, aryl group.

**TABLE 7.58** Carbon-Carbon Spin Coupling Constants (*Continued*)

Structure*	$J_{CC}$ , Hz	Structure	$J_{CC}$ , Hz
$C_6H_5I$		Pyridine	
1-2	60	2-3	54
2-3	53	3-4	56
3-4	58	$^3J_{2,5}$	14
$^3J_{2,5}$	8.6	Furan	69
$C_6H_5-OCH_3$		Pyrrole	69
2-3	58	Thiophene	64
3-4	56	$H_2C=C=C(CH_3)_2$	100
$C_6H_5NH_2$		$-C\equiv C-$	170-176
1-2	61		
2-3	58	Structure	$^2J_{CC}$ , Hz
3-4	57		
$^3J_{2,5}$	7.9	$CH_3-CO=CH_3$	16
$C_6H_5CH_3$	44	$CH_3-C\equiv CH$	11.8
		$CH_3CH_2-CN$	33

\* R, alkyl group; Ar, aryl group.

**TABLE 7.59** Carbon-Fluorine Spin Coupling Constants

Structure*	$J_{CF}$ , Hz	Structure*	$J_{CF}$ , Hz
	-158	$p-F-C_6H_4-CF_3$	-252
	-235	$p-F-C_6H_4-CO-CH_3$	-253
	-274	$p-F-C_6H_4-NO_2$	-257
	-259	$F-C_6H_5$	
	-271	$^2J_{CF} = 21.0$	-244
	-165	$^3J_{CF} = 7.7$	
$F-CH_2CH_2-$ or $F-CR_3$	-167	$^4J_{CF} = 3.4$	
$p-F-C_6H_4-OR$	-237		-287
$p-F-C_6H_4-R$	-241		-308
			-353
			-369
			-241

\* Ar, aryl group; R, alkyl group.

**TABLE 7.59** Carbon-Fluorine Spin Coupling Constants (*Continued*)

Structure*	$J_{\text{CF}}$ , Hz	Structure*	$J_{\text{CF}}$ , Hz
$\begin{array}{c} \text{F} \quad \text{F} \\ \diagdown \quad \diagup \\ \text{C} \\ \diagup \quad \diagdown \\ \text{F} \quad \text{CH}_2\text{OH} \\ \text{F} \quad \text{F} \\ \diagdown \quad \diagup \\ \text{C} \\ \diagup \quad \diagdown \\ \text{F} \quad \text{OCF}_3 \end{array}$	-278	$\begin{array}{c} \text{F} \quad \text{F} \\ \diagdown \quad \diagup \\ \text{C} \\ \diagup \quad \diagdown \\ \text{F} \quad \text{CO}-\text{CH}_3 \end{array}$	-289
	-265		

\* Ar, aryl group; R, alkyl group.

**TABLE 7.60** Carbon-13 Chemical Shifts of Deuterated Solvents*Relative to tetramethylsilane.*

Solvent	Group	$\delta$ , ppm
Acetic- $d_3$ acid- $d_1$	Methyl	20.0
	Carbonyl	205.8
Acetone- $d_6$	Methyl	28.1
	Carbonyl	178.4
Acetonitrile- $d_3$	Methyl	1.3
	Carbonyl	117.7
Benzene- $d_6$		128.5
Carbon disulfide		193
Carbon tetrachloride		97
Chloroform- $d_1$		77
Cyclohexane- $d_{12}$		25.2
Dimethyl sulfoxide- $d_6$		39.5
1,4-Dioxane- $d_6$		67
Formic- $d_1$ acid- $d_1$	Carbonyl	165.5
Methanol- $d_4$		47–49
Methylene chloride- $d_2$		53.8
Nitromethane- $d_3$		57.3
Pyridine- $d_5$	$\text{C}_3, \text{C}_5$	123.5
	$\text{C}_4$	135.5
	$\text{C}_2, \text{C}_6$	149.9

**TABLE 7.61** Carbon-13 Spin Coupling Constants with Various Nuclei

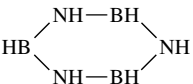
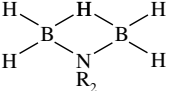
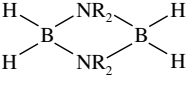
Nuclei	Structure	$^1J$ , Hz	$^2J$ , Hz	$^3J$ , Hz	$^4J$ , Hz
$^2\text{H}$	$\text{CDCl}_3$	32			
	$\text{CD}_3-\text{CO}-\text{CD}_3$	20			
	$(\text{CD}_3)_2\text{SO}$	22			
	$\text{C}_6\text{D}_6$	26			

**TABLE 7.61** Carbon-13 Spin Coupling Constants with Various Nuclei (*Continued*)

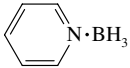
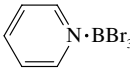
Nuclei	Structure	$^1J$ , Hz	$^2J$ , Hz	$^3J$ , Hz	$^4J$ , Hz
$^7\text{Li}$	$\text{CH}_3\text{Li}$	15			
$^{11}\text{B}$	$(\text{C}_6\text{H}_5)_4\text{B}^-$	49		3	
$^{14}\text{N}$	$(\text{CH}_3)_4\text{N}^+$	10			
	$\text{CH}_3\text{NC}$	8			
$^{29}\text{Si}$	$(\text{CH}_3)_4\text{Si}$	52			
$^{31}\text{P}$	$(\text{CH}_3)_3\text{P}$	14			
	$(\text{C}_4\text{H}_9)_3\text{P}$	11	12	5	
	$(\text{C}_6\text{H}_5)_3\text{P}$	12	20	7	0
	$(\text{CH}_3)_4\text{P}^+$	56			
	$(\text{C}_4\text{H}_9)_4\text{P}^+$	48	4	15	
	$(\text{C}_6\text{H}_5)_4\text{P}^+$	88	11	13	3
	$\text{R}(\text{RO})_2\text{P}=\text{O}$	142	5–7		
	$(\text{C}_4\text{H}_9\text{O})_3\text{P}=\text{O}$		6	7	
$^{77}\text{Se}$	$(\text{CH}_3)_2\text{Se}$	62			
	$(\text{CH}_3)_3\text{Se}^+$	50			
$^{113}\text{Cd}$	$(\text{CH}_3)_2\text{Cd}$	513, 537			
$^{119}\text{Sn}$	$(\text{CH}_3)_4\text{Sn}$	340			
	$(\text{CH}_3)_3\text{SnC}_6\text{H}_5$	474	37	47	11
$^{125}\text{Te}$	$(\text{CH}_3)_2\text{Te}$	162			
$^{199}\text{Hg}$	$(\text{CH}_3)_2\text{Hg}$	687			
	$(\text{C}_6\text{H}_5)_2\text{Hg}$	1186	88	102	18
$^{207}\text{Pb}$	$(\text{CH}_3)_2\text{Pb}$	250			
	$(\text{C}_6\text{H}_5)_4\text{Pb}$	481	68	81	20

**TABLE 7.62** Boron-11 Chemical Shifts

Values given in ppm on the  $\delta$  scale, relative to  $\text{B}(\text{OCH}_3)_3$ .

Structure	$\delta$ , ppm	Structure	$\delta$ , ppm
$\text{R}_3\text{B}$	– 67 to – 68		– 12
$\text{Ar}_3\text{B}$	– 43		
$\text{BF}_3$	24		
$\text{BCl}_3$	– 12		
$\text{BBr}_3$	– 6		37
$\text{BI}_3$	41		
$\text{B}(\text{OH})_3$	36		
$\text{B}(\text{OR})_3$	0–1		
$\text{B}(\text{NR}_2)_3$	– 13		15
$\text{C}_6\text{H}_5\text{BCl}_2$	– 36		
$\text{C}_6\text{H}_5\text{B}(\text{OH})_2$	– 14		
$\text{C}_6\text{H}_5\text{B}(\text{OR})_2$	– 10		
$\text{M}(\text{BH}_4)$	55–61	$(\text{CH}_3)_2\text{N}-\text{B}(\text{CH}_3)_2$	62
$\text{B}(\text{BF}_4)$	19–20		

**TABLE 7.62** Boron-11 Chemical Shifts (*Continued*)

Structure	$\delta$ , ppm	Structure	$\delta$ , ppm	
<b>Addition complexes</b>		<b>Boranes</b>		
$R_2O \cdot BH_3$	18–19	$B_2H_6$	1	
$R_3N \cdot BH_3$	25	$B_4H_{10}$	25	
$R_2NH \cdot BH_3$	33	( $BH_2$ )	60	
	31	(BH)		
$R_2O(\text{or } ROH) \cdot BF_3$	17–19		Base	Apex
$R_2O(\text{or } ROH) \cdot BCl_3$	–7 to –8	$B_5H_9$	31	70
$R_2O(\text{or } ROH) \cdot BBr_3$	23–24	$B_5H_{11}$	–16	50
$R_2O(\text{or } ROH) \cdot BI_3$	74–82	$B_{10}H_{14}$	7	54
	24			

**TABLE 7.63** Nitrogen-15 (or Nitrogen-14) Chemical Shifts

Values given in ppm on the  $\delta$  scale, relative to  $NH_3$  liquid.


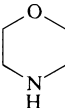
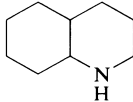
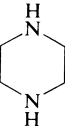
Substituent group	$\delta$ , ppm	Substituent group	$\delta$ , ppm
Aliphatic amines		Amides ( <i>continued</i> )	
Primary	1–59	$HCO-NH-Aryl$	138–141
Secondary	7–81	$RCO-NHR$ or $RCO-NR_2$	103–130
Tertiary	14–44	$RCO-NH-Aryl$	131–136
Cyclo, primary	29–44	$Aryl-CO-H-Aryl$	ca 126
Aryl amines	40–100	Guanidines	
Aryl hydrazines	40–100	Amino	30–60
Piperidines, decahydroquino- lines	30–82	Imino	166–207
Amine cations		Thioureas	85–111
Primary	19–59	Thioamides	135–154
Secondary	40–74	Cyanamides	
Tertiary	30–67	$R_2N-$	–12 to –38
Quaternary	43–70	$-CN$	175–200
Enamines, tertiary type		Carbodiimides	95–120
Alkyl	29–82	Isocyanates	
Cycloalkyl	55–104	Alkyl, primary	14–32
Aminophosphines	59–100	Alkyl, secondary and tertiary	54–57
Amine <i>N</i> -oxides	95–122	Aryl	ca 46
Ureas		Isothiocyanates	90–107
Aliphatic	63–84	Azides	52–80
Aryl	105–108		108–122
Sulfonamides	79–164		240–260
Amides		Lactams	113–122
$HCO-NHR$		Hydrazones	
R = primary	100–115	Amino	141–167
R = secondary	104–148	Imino	319–327
R = tertiary	96–133	Cyanates	155–182
		Nitrile <i>N</i> -oxides, fulminates	195–225











**TABLE 7.63** Nitrogen-15 (or Nitrogen-14) Chemical Shifts (*Continued*)

Substituent group	$\delta$ , ppm	Substituent group	$\delta$ , ppm
Isonitriles		Oximes	340–380
Alkyl, primary	162–178	Nitramines	
Alkyl, secondary	191–199	Amine	252–280
Aryl	ca 180	—NO <sub>2</sub>	328–355
Nitriles		Nitrates	310–353
Alkyl	235–241	<i>gem</i> -Polynitroalkanes	310–353
Aryl	258–268	Nitro	
Thiocyanates	265–280	Aryl	350–382
Diazonium		Alkyl	372–410
Internal	222–230	Hetero, unsaturated	354–367
Terminal	315–322	Azoxy	330–356
Diazo		Azo	504–570
Internal	226–303	Nitrosamines	222–250
Terminal	315–440		525–550
Nitrilium ions	123–150	Nitrites	555–582
Azinium ions	185–220	Thionitrites	720–790
Azine <i>N</i> -oxides	230–300	Nitroso	
Nitrones	270–285	Aliphatic amines, NO	535–560
Imides	170–178	Aryl	804–913
Imines	310–359		


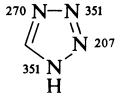




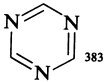
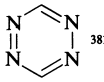
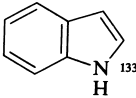
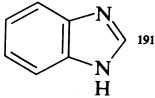
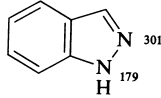
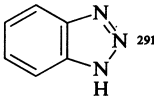
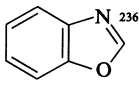
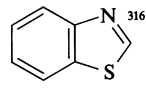
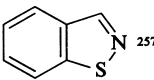
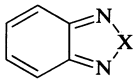
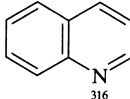
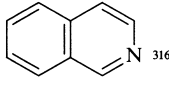
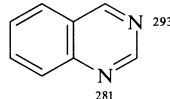
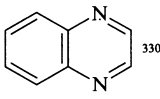
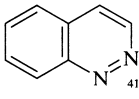
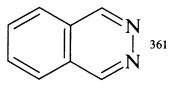
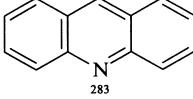
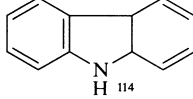
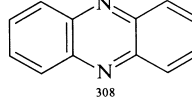
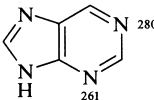
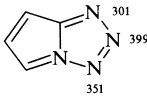
## Saturated cyclic systems

$(\text{CH}_2)_n \text{N-H}$ $n = 2$ $n = 3$ $n = 4$ $n = 5$	    		7.5 (in C <sub>6</sub> H <sub>6</sub> ) 18.0 (in H <sub>2</sub> O)
	32.1		
	35.5	<i>cis</i> <i>trans</i>	42.4 52.9

## Unsaturated cyclic systems

**TABLE 7.63** Nitrogen-15 (or Nitrogen-14) Chemical Shifts (*Continued*)

Unsaturated cyclic systems (continued)											
											
											
											
											
		<table><tr><th>X</th><th><math>\delta</math>, ppm</th></tr><tr><td>O</td><td>517</td></tr><tr><td>S</td><td>331</td></tr><tr><td>Se</td><td>373</td></tr></table>		X	$\delta$ , ppm	O	517	S	331	Se	373
X	$\delta$ , ppm										
O	517										
S	331										
Se	373										
											
											
											
											

**TABLE 7.64** Nitrogen-15 Chemical Shifts in Monosubstituted Pyridine

$$\delta = 317.3 + \Delta_i$$

Substituent	$\Delta_{C-2}$	$\Delta_{C-3}$	$\Delta_{C-4}$
—CH <sub>3</sub>	−0.4	0.3	−8.0
—CH <sub>2</sub> CH <sub>3</sub>	−1.8		−6.6
—CH(CH <sub>3</sub> ) <sub>2</sub>	−5.1		−5.9
—C(CH <sub>3</sub> ) <sub>3</sub>	−2.5		−5.8
—CN	−0.9	−0.8	10.6
—CHO	10	11	29
—CO—CH <sub>3</sub>	−9	15	11
—CO—OCH <sub>2</sub> CH <sub>3</sub>	11.8		−5
—OCH <sub>3</sub>	−49	0	−23
—OH	−126	−2	−118
—NO <sub>2</sub>	−23	1	22
—NH <sub>2</sub>	−45	10	−46
—F	−42	−18	
—Cl	−4	4	−6
—Br	2	8	7

**TABLE 7.65** Nitrogen-15 Chemical Shifts for Standards

Values given in ppm, relative to NH<sub>3</sub> liquid at 23°C.

Substance	$\delta$ , ppm	Conditions
Nitromethane (neat)	380.2	For organic solvents and acidic aqueous solutions
Potassium (or sodium) nitrate (saturated aqueous solution)	376.5	For neutral and basic aqueous solutions
C(NO <sub>2</sub> ) <sub>4</sub>	331	For nitro compounds
(CH <sub>3</sub> ) <sub>2</sub> —CHO (neat)	103.8	For organic solvents and aqueous solutions
(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> N <sup>+</sup> Cl <sup>−</sup>	64.4	Saturated aqueous solution
(CH <sub>3</sub> ) <sub>4</sub> N <sup>+</sup> Cl <sup>−</sup>	43.5	Saturated aqueous solution
NH <sub>4</sub> Cl	27.3	Saturated aqueous solution
NH <sub>4</sub> NO <sub>3</sub>	20.7	Saturated aqueous solution
NH <sub>3</sub>	0.0	Liquid, 25°C
	−15.9	Vapor, 5 atm

**TABLE 7.66** Nitrogen-15 to Hydrogen-1 Spin Coupling Constants

Structure	$J$ , Hz	Structure	$J$ , Hz
R—NH <sub>2</sub> and R <sub>2</sub> NH	61–67	Aryl—NHNH <sub>2</sub>	90
Aryl—NH <sub>2</sub>	78	<i>p</i> -O <sub>2</sub> N—aryl—NHNH <sub>2</sub>	99
<i>p</i> -CH <sub>3</sub> O—aryl—NH <sub>2</sub>	79	Aryl—SO <sub>2</sub> —NH <sub>2</sub>	81
<i>p</i> -O <sub>2</sub> N—aryl—NH <sub>2</sub>	90–93	Aryl—SO <sub>2</sub> —NHR	86
Amine salts (alkyl and aryl)	73–76	O=C—N—H <sub>syn</sub> (to —CO—)	88
Aryl—NHOH	79	H—C—N—H <sub>anti</sub>	92–93
Aryl—NHCH <sub>3</sub>	87		
Aryl—NHCH <sub>2</sub> F	90		

**TABLE 7.66** Nitrogen-15 to Hydrogen-1 Spin Coupling Constants (*Continued*)

Structure	<i>J</i> , Hz	Structure	<i>J</i> , Hz
$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{N}-\text{H} \\ \diagup \quad \diagdown \\ \text{R} \quad \text{R} \end{array}$	88–92	(R <sub>3</sub> Si) <sub>2</sub> NH	67
Pyrrole	97	CF <sub>3</sub> —S—NH <sub>2</sub>	81
HC≡NH <sup>+</sup>	133–136	(CF <sub>3</sub> —S) <sub>2</sub> NH	99
>P—NH <sub>2</sub>	82–90	Pyridinium ion	90
		Quinolinium ion	96





**TABLE 7.67** Nitrogen-15 to Carbon-13 Spin Coupling Constants

Structure	<i>J</i> , Hz	Structure	<i>J</i> , Hz
Alkyl amines	4–4.5	Alkyl—NO <sub>2</sub>	11
Cyclic alkyl amines	2–2.5	R—CN	18
Alkyl amines protonated	4–5	CH <sub>3</sub> —N <sup>+</sup> ≡C <sup>−</sup>	
Aryl amines	10–14	H <sub>3</sub> C—N	10
Aryl amines protonated	9	—N≡C	9
CH <sub>3</sub> CO—NH <sub>2</sub>	14–15	Diaryl azoxy	
H <sub>2</sub> N—CO—NH <sub>2</sub>	20	<i>anti</i>	18
Aryl—NO <sub>2</sub>	15	<i>syn</i>	13

**TABLE 7.68** Nitrogen-15 to Fluorine-19 Spin Coupling Constants

Structure	<i>J</i> , Hz	Structure	<i>J</i> , Hz
NF <sub>3</sub>	155	Pyridine	
F <sub>4</sub> N <sub>2</sub>	164	2-F	52
FNO <sub>2</sub>	158	3-F	4
F <sub>3</sub> NO	190	2,6-di-F	37
F <sub>3</sub> C—O—NF <sub>2</sub>	164–176	Pyridinium ion	
FCO—NF <sub>2</sub>	221	2-F	23
(NF <sub>4</sub> ) <sup>+</sup> SbF <sub>6</sub> <sup>−</sup>	323	3-F	3
(NF <sub>4</sub> ) <sup>+</sup> AsF <sub>6</sub> <sup>−</sup>	328	Quinoline, 8-F	3
(N <sub>2</sub> F) <sup>+</sup> AsF <sub>6</sub> <sup>−</sup>	459	Aniline	
F <sub>3</sub> C—NO <sub>2</sub>	215	2-F	0
$\begin{array}{c} \text{F} \\ \diagdown \\ \text{N}=\text{N} \\ \diagup \\ \text{F} \end{array} \quad (^2J = 10)$	190	3-F	0
$\begin{array}{c} \text{F} \quad \text{F} \\ \diagdown \quad \diagup \\ \text{N}=\text{N} \end{array} \quad (^2J = 52)$	203	4-F	1.5
		Anilinium ion	
		2-F	1.4
		3-F	0.2
		4-F	0

**TABLE 7.69** Fluorine-19 Chemical ShiftsValues given in ppm on the  $\delta$  scale, relative to  $\text{CCl}_3\text{F}$ .

Substituent group	$\delta$ , ppm	Substituent group	$\delta$ , ppm
$-\text{SO}_2-\text{F}$	-67 to -42 (aryl)(alkyl)	Cyclohexane-F	210 (axial)
$-\text{CO}-\text{F}$	-29 to -20		to
$\text{>N}-\text{CO}-\text{F}$	-5		240
Aryl- $\text{CF}_2\text{Cl}$	49		(equatorial)
$-\text{CF}_2\text{I}$	56	Perfluorocycloalkane	131-138
$-\text{CF}_2\text{Br}$	63	$\text{>CF}-\text{CF}_3$	163-198
$\text{R}-\text{CF}_2\text{Cl}$	61-71	$\text{>CF}(\text{CF}_3)_2$	180-191
$\text{>C}-\text{CF}_3$ and aryl- $\text{CF}_3$	56-73	$-\text{CFH}-$	198-231
$-\text{CS}-\text{CF}_3$	70	$-\text{CFH}_2$	235-244
$\text{>CF}-\text{CF}_3$	71-73	$\text{F}_2\text{C}=\text{CF}_2$	133
$-\text{S}-\text{CF}_3$	41	$\text{F}_c \quad \text{CF}_2-\text{CF}_2\text{H}$ $\quad \quad \quad \diagup \quad \diagdown$ $\quad \quad \quad \text{C}=\text{C}$ $\quad \quad \quad \diagdown \quad \diagup$ $\text{F}_t \quad \quad \quad \text{F}_g$	
$-\text{S}-\text{CF}_2-\text{S}-$	39	<i>cis</i>	108
$\text{>P}-\text{CF}_3$	46-66	<i>trans</i>	92
$\text{>N}-\text{CF}_3$	40-58	<i>gem</i>	192
$\text{>N}-\text{CF}_2-\text{C}$	85-127	$\text{F}_2 \quad \text{F}_3$ $\quad \quad \quad \diagup \quad \diagdown$ $\quad \quad \quad \text{C}=\text{C}$ $\quad \quad \quad \diagdown \quad \diagup$ $\text{H} \quad \quad \quad \text{H}$ $\quad \quad \quad \text{F}_1$	
$-\text{O}-\text{CF}_2-\text{R}$	70-91	F-1	126
$-\text{O}-\text{CF}_2-\text{CF}_3$	70-91	F-2	155
$-\text{CH}_2-\text{CF}_3$	76-77	F-3	162
$\text{HO}-\text{CO}-\text{CF}_3$	77	$\text{ClFC}=\text{CH}-\text{CF}_3$	61
$-\text{CHF}-\text{CF}_3$	81	Cycloalkenes	
$-\text{CF}_2-\text{CF}_3$	78-88	$=\text{CF}-\text{CF}_2-$	
$-\text{CS}-\text{F}$	81	$\text{C}(\text{CF}_3 \text{ or } \text{H})-$	101-113
$\text{CF}_3-\text{C}-\text{N} <$	84-96	$-\text{CF}_2-\text{CF}_2-$	
$-\text{CO}-\text{CF}_2-\text{CF}_3$	83	$\text{C}(\text{CF}_3 \text{ or } \text{CH}_3)=$	110-114
$-\text{CF}_2-$	86-126	$-\text{CF}_2-\text{CF}_2-\text{CH}=\text{}$	113-116
$-\text{CF}_2\text{Br}$	91	$-\text{CF}_2-\text{CF}_2-\text{CF}=\text{}$	119-122
$-\text{C}-\text{CF}_2-\text{S}-$	91-98	Aryl-F	113
$-\text{CF}=\text{}$	180-192	$\text{C}_{10}\text{H}_7-\text{F}$	
$-\text{CF}_2-\text{CF}_3$	111	F-1	127
$-\text{CO}-\text{CF}_2-$	116-131	F-2	114
$-\text{C}(\text{halide})-\text{CF}_2-$	119-128	$\text{C}_6\text{H}_5-\text{C}_6\text{H}_4-\text{F}$	
$-\text{CF}_2-\text{CF}_3$	121-125	F-2	117
$-\text{CF}_2-\text{CF}_2-$	121-129	F-3	113
$-\text{CF}_2-\text{CH}_2-$	122-133	F-4	109
$-\text{CF}_2-\text{CHF}_2$	128-132	$\text{C}_6\text{F}_6$	163
$-\text{CF}_2\text{H}$	136-143		
 $\text{F}_2$	151-156		
 $\text{F}_2$	147		
 $\text{F}_2$	96-133		
 $\text{F}$	159		

**TABLE 7.70** Fluorine-19 Chemical Shifts for Standards

Substance	Formula	$\delta$ , ppm
Trichlorofluoromethane	$\text{CFCl}_3$	0.0
$\alpha,\alpha,\alpha$ -Trifluorotoluene	$\text{C}_6\text{H}_5\text{CF}_3$	63.8
Trifluoroacetic acid	$\text{CF}_3\text{COOH}$	76.5
Carbon tetrafluoride	$\text{CF}_4$	76.7
Fluorobenzene	$\text{C}_6\text{H}_5\text{F}$	113.1
Perfluorocyclobutane	$\text{C}_4\text{F}_8$	138.0

**TABLE 7.71** Fluorine-19 to Fluorine-19 Spin Coupling Constants

Structure	$J_{\text{FF}}$ , Hz
$\text{F}_2\text{C} \begin{array}{c} \text{---} \\ \text{---} \end{array} \text{cycloalkane}$	
<i>gem</i>	212–260
Unsaturated compounds $\text{>C=C<}$	
<i>gem</i>	30–90
<i>trans</i>	115–130
<i>cis</i>	9–58
Aromatic compounds, monocyclic	
<i>ortho</i>	18–22
<i>meta</i>	0–7
<i>para</i>	12–15
Alkanes	
$\text{CFCl}_2\text{---CF}_2\text{---CFCl}_2$	6
$\text{CFCl}_2\text{---CF}_2\text{---CCl}_3$	5
$\text{CF}_2\text{Cl---CF}_2\text{---CF}_2\text{Cl}$	1
$\text{CF}_3\text{---CF}_2\text{---CF}_2\text{Cl}$ (or $\text{---CF}_3$ )	<1
$\text{CF}_3\text{---CF}_2\text{---CF}_2\text{Cl}$	2
$\text{CF}_3\text{---CF}_2\text{---CF}_2\text{Cl}$	9
$\text{CF}_3\text{---CF}_2\text{---CF}_3$	7

**TABLE 7.72** Silicon-29 Chemical Shifts

Values given in ppm on the  $\delta$  scale relative to tetramethylsilane.

Substituent group X in $(\text{CH}_3)_{4-n}\text{SiX}_n$	$n$			
	1	2	3	4
—F	35	9	–52	–109
—Cl	30	32	13	–19
—Br	26	20	–18	–94
—I	9	–34	–18	–346
—H	–19	–42	–65	–93
— $\text{C}_2\text{H}_5$	2	5	7	8
— $\text{C}_6\text{H}_5$	–5	–9	–12	
— $\text{CH=CH}_2$	–7	–14	–21	–23
—Oalkyl	14–17	–3 to –6	–41 to –45	–79 to –83
—Oaryl	17	–6	–54	–101
— $\text{O---CO---alkyl}$	22	4	–43	–75
— $\text{N}(\text{CH}_3)_2$	6	–2	–18	–28

**TABLE 7.72** Silicon-29 Chemical Shifts (*Continued*)

Structure	$\delta$ , ppm	Structure	$\delta$ , ppm
<b>Hydrides</b>			
$\text{H}_3\text{Si}-$	-39 to -60	$\begin{array}{c} \text{O}- \\   \\ \text{CH}_3\text{Si}-\text{O}- \end{array}$ (branching)	-65 to -66
$-\text{H}_2\text{Si}-$	-5 to -37	$\begin{array}{c} \text{O}- \\   \\ -\text{O}-\text{Si}-\text{O}- \end{array}$ (cross-linked)	-105 to -110
$\text{HSi}\equiv$	-2 to -39	<b>Polysilanes</b>	
<b>Silicates</b>		$\text{F}_3\text{Si}-\text{SiF}_3$	-74
Orthosilicate anions	-69 to -72	$\text{Cl}_3\text{Si}-\text{SiCl}_3$	-8
Silicon in end position	-77 to -81	$(\text{CH}_3\text{O})_3\text{Si}-\text{Si}(\text{OCH}_3)_3$	-53
Silicon in middle	-85 to -89	$(\text{CH}_3)_3\text{Si}-\text{Si}(\text{CH}_3)_3$	-20
Branching silicons	-93 to -97	$(\text{CH}_3)_2\text{Si}[\text{Si}(\text{CH}_3)_3]_2$	-48
Cross-linked silicons	-107 to -120	$\text{HSi}[\text{Si}(\text{CH}_3)_3]_3$	-117
<b>Methyl siloxanes</b>		$\text{Si}[\text{Si}(\text{CH}_3)_3]_4$	-135
$(\text{CH}_3)_2\text{Si}-\text{O}-$ (end position)	6-8		
$\begin{array}{c} \text{O}- \\   \\ (\text{CH}_3)_2\text{Si} \end{array}$ (middle)	-18 to -23		
$\begin{array}{c} \text{O}- \\   \\ \text{CH}_3\text{Si}(\text{H}) \end{array}$ (middle)	-35 to -36		

**TABLE 7.73** Phosphorus-31 Chemical Shifts

Values given in ppm on the  $\delta$  scale, relative to 85%  $\text{H}_3\text{PO}_4$ .

Structure	Identical atoms attached directly to phosphorus	Non-identically substituted phosphorus		
		R = $\text{CH}_3$	R = $\text{C}_2\text{H}_5$	R = $\text{C}_6\text{H}_5$
$\text{P}_4$	461			
$\text{PR}_3$		62	20	6
$\text{PHR}_2$		99	56	41
$\text{PH}_2\text{R}$		164	128	122
$\text{PH}_3$	241			
$\text{PF}_3$	-97			
$\text{PRF}_2$			-168	-207
$\text{PCl}_3$	-220			
$\text{PRCl}_2$		-192	-196	-162
$\text{PR}_2\text{Cl}$		-94	-119	-81
$\text{PBr}_3$	-227			
$\text{PRBr}_2$		-184	-194	-152
$\text{PR}_2\text{Br}$		-91	-116	-71
$\text{PI}_3$	-178			
$\text{P}(\text{CN})_3$	136			
$\text{P}(\text{SiR}_3)_3$		251		
$\text{P}(\text{OR})_3$		-141	-139	-127
$\text{P}(\text{OR})_2\text{Cl}$		-169	-165	-157
$\text{P}(\text{OR})\text{Cl}_2$		-114	-177	-173
$\text{P}(\text{SR})_3$		-125	-115	-132
$\text{P}(\text{SR})_2\text{Cl}$		-188	-186	-183
$\text{P}(\text{SR})\text{Cl}_2$		-206	-211	-204
$\text{P}(\text{SR})_2\text{Br}$				-184

**TABLE 7.73** Phosphorus-31 Chemical Shifts (*Continued*)

Structure	Identical atoms attached directly to phosphorus	Non-identically substituted phosphorus		
		R = CH <sub>3</sub>	R = C <sub>2</sub> H <sub>5</sub>	R = C <sub>6</sub> H <sub>5</sub>
P(SR)Br <sub>2</sub>		− 204		
P(NR <sub>2</sub> ) <sub>3</sub>		− 123	− 118	
P(NR <sub>2</sub> )Cl <sub>2</sub>		− 166	− 162	− 151
PR(NR <sub>2</sub> ) <sub>2</sub>		− 86	− 100	− 100
PR <sub>2</sub> (NR <sub>2</sub> )		− 39	− 62	
F <sub>2</sub> P—PF <sub>2</sub>	− 226			
Cl <sub>2</sub> P—PCl <sub>2</sub>	− 155			
I <sub>2</sub> P—PI <sub>2</sub>	− 170			
PH <sub>2</sub> <sup>−</sup> K <sup>+</sup>	255			
P(CF <sub>3</sub> ) <sub>3</sub>	3			
P <sub>4</sub> O <sub>6</sub>	− 113			
Structure	Identical atoms attached directly to phosphorus	Non-identically substituted phosphorus		
		X = F	X = Cl	X = Br
P(NCO) <sub>3</sub>	− 97			
P(NCO) <sub>2</sub> X		− 128	− 128	− 127
P(NCO)X <sub>2</sub>		− 131	− 166	
P(NCS) <sub>3</sub>	− 86			
P(NCS) <sub>2</sub> X			− 114	− 112
P(NCS)X <sub>2</sub>			− 155	− 153
Structure	Identical atoms attached directly to phosphorus	Non-identically substituted phosphorus		
		R = CH <sub>3</sub>	R = C <sub>2</sub> H <sub>5</sub>	R = C <sub>6</sub> H <sub>5</sub>
O=PR <sub>3</sub>		− 36	− 48	− 25
O=PHR <sub>2</sub>		− 63		− 23
O=PF <sub>3</sub>	36			
O=PRF <sub>2</sub>		− 27	− 29	− 11
O=PCl <sub>3</sub>	− 2			
O=PRCl <sub>2</sub>		− 45	− 53	− 34
O=PR <sub>2</sub> Cl		− 65	− 77	− 43
O=P(OR) <sub>3</sub>		− 1	1	18
O=P(OR) <sub>2</sub> Cl		− 6	− 3	6
O=P(OR)Cl <sub>2</sub>		− 6	− 6	− 2
O=PH(OR) <sub>2</sub>		− 19	− 15	
O=PR <sub>2</sub> (OC <sub>2</sub> H <sub>5</sub> )		− 50	− 52	− 31
O=PR(OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>		− 30	− 33	− 17
O=P(NR <sub>2</sub> ) <sub>3</sub>		− 23	− 24	− 2
O=PR <sub>2</sub> (NR <sub>2</sub> )		− 44		− 26
O=P(OR) <sub>2</sub> NH <sub>2</sub>		− 15	− 12	− 3
O=P(OR) <sub>2</sub> (NCS)			19	29
O=P(SR) <sub>3</sub>		− 66	− 61	− 55
O=PBr <sub>3</sub>	103			
O=P(NCO) <sub>3</sub>	41			
O=P(NCS) <sub>3</sub>	62			
O=P(NH <sub>2</sub> ) <sub>3</sub>	− 22			



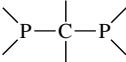
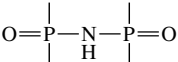
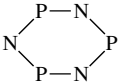
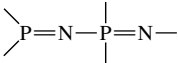
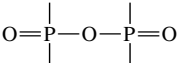
**TABLE 7.73** Phosphorus-31 Chemical Shifts (*Continued*)

Structure	Identical atoms attached directly to phosphorus	Structure	Identical atoms attached directly to phosphorus
PF <sub>5</sub>	35	<div><div><div>O</div><div>—O—P—O—</div><div>OR</div><div>(middle group)</div></div><div><div>O</div><div>—O—P—O—</div><div>O</div><div>P (etc.)</div><div>(branch group)</div></div></div>	ca 18
PF <sub>6</sub> <sup>-</sup> H <sup>+</sup>	144		
PBr <sub>5</sub>	101		
P(OC <sub>2</sub> H <sub>5</sub> ) <sub>5</sub>	71		
PO <sub>4</sub> <sup>3-</sup>	−6		
O=P[OSi(CH <sub>3</sub> ) <sub>3</sub> ] <sub>3</sub>	33		
H <sub>4</sub> P <sub>2</sub> O <sub>7</sub>	11		
Phosphonates	−24 to −2		
Phosphonium cations			
Alkyl	−43 to −32		
Aryl	−35 to −18		
(O <sub>3</sub> P—PO <sub>3</sub> ) <sup>4-</sup>	−9		ca 30
Polyphosphates			
O=P—O—   (OR) <sub>2</sub> (end group)	ca 6		

Structure	Identical atoms attached directly to phosphorus	Non-identically substituted phosphorus		
		R = CH <sub>3</sub>	R = C <sub>2</sub> H <sub>5</sub>	R = C <sub>6</sub> H <sub>5</sub>
S=PR <sub>3</sub>	−29	−59	−55	−43
S=PCl <sub>3</sub>				
S=PRCl <sub>2</sub>	112	−80	−94	−75
S=PR <sub>2</sub> Cl		−87	−109	−80
S=PBr <sub>3</sub>				
S=PRBr <sub>2</sub>		−21	−42	−20
S=PR <sub>2</sub> Br		−64	−98	
S=P(OR) <sub>3</sub>		−73	−68	−53
S=P(OR)Cl <sub>2</sub>		−59	−56	−54
S=P(OR) <sub>2</sub> Cl		−73	−68	−59
S=PH(OR) <sub>2</sub>		−74	−69	−59
S=P(SR) <sub>3</sub>		−98	−92	−92
S=P(NH <sub>2</sub> ) <sub>3</sub>	−60			
S=P(NR <sub>2</sub> ) <sub>3</sub>		−82	−78	
Se=P(OR) <sub>3</sub>		−78	−71	−58
Se=P(SR) <sub>3</sub>		−82	−76	
P(OR) <sub>5</sub>			71	86
PRF <sub>4</sub>		30	30	42
PR <sub>2</sub> F <sub>3</sub>		−9	−6	



**TABLE 7.74** Phosphorus-31 Spin Coupling Constants (*Continued*)

Substituent group	$J_{PP}$ , Hz	Substituent group	$J_{PP}$ , Hz
	ca 70		8–30
$\text{>P-O-P<}$	20–40		5–66
$\text{>P-S-P<}$	86–90		5–65
	15–25		

## 7.8 MASS SPECTROMETRY

### 7.8.1 Correlation of Mass Spectra with Molecular Structure

**7.8.1.1 Molecular Identification.** In the identification of a compound, the most important information is the molecular weight. The mass spectrometer is able to provide this information, often to four decimal places. One assumes that no ions heavier than the molecular ion form when using electron-impact ionization. The chemical ionization spectrum will often show a cluster around the nominal molecular weight.

Several relationships aid in deducing the empirical formula of the parent ion (and also molecular fragments). From the empirical formula hypothetical molecular structures can be proposed, using the entries in the formula indices of Beilstein and *Chemical Abstracts*.

**7.8.1.2 Natural Isotopic Abundances.** The relative abundances of natural isotopes produce peaks one or more mass units larger than the parent ion (Table 7.75a). For a compound  $\text{C}_w\text{H}_x\text{O}_z\text{N}_y$ , a formula allows one to calculate the percent of the heavy isotope contributions from a monoisotopic peak,  $P_M$ , to the  $P_{M+1}$  peak:

$$100 \frac{P_{M+1}}{P_M} = 0.015x + 1.11w + 0.37y + 0.037z$$

Tables of abundance factors have been calculated for all combinations of C, H, N, and O up to mass 500 (J. H. Beynon and A. E. Williams, *Mass and Abundance Tables for Use in Mass Spectrometry*, Elsevier, Amsterdam, 1963).

Compounds that contain chlorine, bromine, sulfur, or silicon are usually apparent from prominent peaks at masses 2, 4, 6, and so on, units larger than the nominal mass of the parent or fragment ion. For example, when one chlorine atom is present, the  $P + 2$  mass peak will be about one-third the intensity of the parent peak. When one bromine atom is present, the  $P + 2$  mass peak will be about the same intensity as the parent peak. The abundance of heavy isotopes is treated in terms of the binomial expansion  $(a + b)^m$ , where  $a$  is the relative abundance of the light isotope,  $b$  is the relative abundance of the heavy isotope, and  $m$  is the number of atoms of the particular element present in the molecule. If two bromine atoms are present, the binomial expansion is

$$(a + b)^2 = a^2 + 2ab + b^2$$

**TABLE 7.75** Isotopic Abundances and Masses of Selected Elements

(a) Abundances of some polyisotopic elements, %					
Element	Abundance	Element	Abundance	Element	Abundance
$^1\text{H}$	99.985	$^{16}\text{O}$	99.76	$^{33}\text{S}$	0.76
$^2\text{H}$	0.015	$^{17}\text{O}$	0.037	$^{34}\text{S}$	4.22
$^{12}\text{C}$	98.892	$^{18}\text{O}$	0.204	$^{35}\text{Cl}$	75.53
$^{13}\text{C}$	1.108	$^{28}\text{Si}$	92.18	$^{37}\text{Cl}$	24.47
$^{14}\text{N}$	99.63	$^{29}\text{Si}$	4.71	$^{79}\text{Br}$	50.52
$^{15}\text{N}$	0.37	$^{30}\text{Si}$	3.12	$^{81}\text{Br}$	49.48

(b) Selected isotope masses			
Element	Mass	Element	Mass
$^1\text{H}$	1.0078	$^{31}\text{P}$	30.9738
$^{12}\text{C}$	12.0000	$^{32}\text{S}$	31.9721
$^{14}\text{N}$	14.0031	$^{35}\text{Cl}$	34.9689
$^{16}\text{O}$	15.9949	$^{56}\text{Fe}$	55.9349
$^{19}\text{F}$	18.9984	$^{79}\text{Br}$	78.9184
$^{28}\text{Si}$	27.9769	$^{127}\text{I}$	126.9047

Now substituting the percent abundance of each isotope ( $^{79}\text{Br}$  and  $^{81}\text{Br}$ ) into the expansion,

$$(0.505)^2 + 2(0.505)(0.495) + (0.495)^2$$

gives

$$0.255 + 0.500 + 0.250$$

which are the proportions of  $P:(P+2):(P+4)$ , a triplet that is slightly distorted from a 1:2:1 pattern. When two elements with heavy isotopes are present, the binomial expansion  $(a+b)^m(c+d)^n$  is used.

Sulfur-34 enhances the  $P+2$  peak by 4.2%; silicon-29 enhances the  $P+1$  peak by 4.7% and the  $P+2$  peak by 3.1%.

**7.8.1.3 Exact Mass Differences.** If the exact mass of the parent or fragment ions are ascertained with a high-resolution mass spectrometer, this relationship is often useful for combinations of C, H, N, and O (Table 7.75b):

$$\frac{\text{Exact mass difference from nearest integral mass} + 0.0051z - 0.0031y}{0.0078} = \text{number of hydrogens}$$

One substitutes integral numbers (guesses) for  $z$  (oxygen) and  $y$  (nitrogen) until the divisor becomes an integral multiple of the numerator within 0.0002 mass unit.

For example, if the exact mass is 177.0426 for a compound containing only C, H, O, and N (note the odd mass which indicates an odd number of nitrogen atoms), then

$$\frac{0.0426 + 0.0051z - 0.0031y}{0.0078} = 7 \text{ hydrogen atoms}$$

when  $z = 3$  and  $y = 1$ . The empirical formula is  $C_9H_7NO_3$  since

$$\frac{177 - 7(1) - 1(14) - 3(16)}{12} = 9 \text{ carbon atoms}$$

**7.8.1.4 Number of Rings and Double Bonds.** The total number of rings and double bonds can be determined from the empirical formula ( $C_wH_xO_zN_y$ ) by the relationship

$$\frac{1}{2(2w - x + y + z)}$$

when covalent bonds comprise the molecular structure. Remember the total number for a benzene ring is four (one ring and three double bonds); a triple bond has two.

#### 7.8.1.5 General Rules

1. If the nominal molecular weight of a compound containing only C, H, O, and N is even, so is the number of hydrogen atoms it contains.
2. If the nominal molecular weight is divisible by four, the number of hydrogen atoms is also divisible by four.
3. When the nominal molecular weight of a compound containing only C, H, O, and N is odd, the number of nitrogen atoms must be odd.

**7.8.1.6 Metastable Peaks.** If the mass spectrometer has a field-free region between the exit of the ion source and the entrance to the mass analyzer, metastable peaks  $m^*$  may appear as a weak, diffuse (often humped-shape) peak, usually at a nonintegral mass. The one-step decomposition process takes the general form:



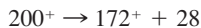
The relationship between the original ion and daughter ion is given by

$$m^* = \frac{(\text{mass of daughter ion})^2}{\text{mass of original ion}}$$

For example, a metastable peak appeared at 147.9 mass units in a mass spectrum with prominent peaks at 65, 91, 92, 107, 108, 155, 172, and 200 mass units. Try all possible combinations in the above expression. The fit is given by

$$147.9 = \frac{(172)^2}{200}$$

which provides this information:



The probable neutral fragment lost is either  $CH_2=CH_2$  or CO.

### 7.8.2 Mass Spectra and Structure

The mass spectrum is a fingerprint for each compound because no two molecules are fragmented and ionized in exactly the same manner on electron-impact ionization. In reporting mass spectra the data are normalized by assigning the most intense peak (denoted as base peak) a value of 100. Other peaks are reported as percentages of the base peak.

A very good general survey for interpreting mass spectral data is given by R. M. Silverstein, G. C. Bassler, and T. C. Morrill, *Spectrometric Identification of Organic Compounds*, 4th ed., Wiley, New York, 1981.

#### 7.8.2.1 Initial Steps in Elucidation of a Mass Spectrum

1. Tabulate the prominent ion peaks, starting with the highest mass.
2. Usually only one bond is cleaved. In succeeding fragmentations a new bond is formed for each additional bond that is broken.
3. When fragmentation is accompanied by the formation of a new bond as well as by the breaking of an existing bond, a rearrangement process is involved. These will be even mass peaks when only C, H, and O are involved. The migrating atom is almost exclusively hydrogen; six-membered cyclic transition states are most important.
4. Tabulate the probable groups that (a) give rise to the prominent charged ion peaks and (b) list the neutral fragments.

#### 7.8.2.2 General Rules for Fragmentation Patterns

1. Bond cleavage is more probable at branched carbon atoms: tertiary > secondary > primary. The positive charge tends to remain with the branched carbon.
2. Double bonds favor cleavage beta to the carbon (but see rule 6).
3. A strong parent peak often indicates a ring.
4. Saturated ring systems lose side chains at the alpha carbon. Upon fragmentation, two ring atoms are usually lost.
5. A heteroatom induces cleavage at the bond beta to it.
6. Compounds that contain a carbonyl group tend to break at this group; the positive charge remains with the carbonyl portion.
7. For linear alkanes, the initial fragment lost is an ethyl group (never a methyl group), followed by propyl, butyl, and so on. An intense peak at mass 43 suggests a chain longer than butane.
8. The presence of Cl, Br, S, and Si can be deduced from the unusual isotopic abundance patterns of these elements. These elements can be traced through the positively charged fragments until the pattern disappears or changes due to the loss of one of these atoms to a neutral fragment.
9. When unusual mass differences occur between some fragments ions, the presence of F (mass difference 19), I (mass difference 127), or P (mass difference 31) should be suspected.

#### 7.8.2.3 Characteristic Low-Mass Fragment Ions

Mass 30 = Primary amines

Masses 31, 45, 59 = Alcohol or ether

Masses 19 and 31 = Alcohol

Mass 66 = Monobasic carboxylic acid

Masses 77 and 91 = Benzene ring

#### 7.8.2.4 Characteristic Low-Mass Neutral Fragments from the Molecular Ion

Mass 18 ( $\text{H}_2\text{O}$ ) = From alcohols, aldehydes, ketones

Mass 19 (F) and 20 (HF) = Fluorides

Mass 27 (HCN) = Aromatic nitriles or nitrogen heterocycles

Mass 29 = Indicates either CHO or  $\text{C}_2\text{H}_5$

Mass 30 = Indicates either  $\text{CH}_2\text{O}$  or NO

Mass 33 (HS) and 34 ( $\text{H}_2\text{S}$ ) = Thiols

Mass 42 =  $\text{CH}_2\text{CO}$  via rearrangement from a methyl ketone or an aromatic acetate or an aryl- $\text{NHCOCH}_3$  group

Mass 43 =  $\text{C}_3\text{H}_7$  or  $\text{CH}_3\text{CO}$

Mass 45 = COOH or  $\text{OC}_2\text{H}_5$

Table 7.76 is condensed, with permission, from the Catalog of Mass Spectral Data of the American Petroleum Institute Research Project 44. These, and other tables, should be consulted for further and more detailed information.

Included in the table are all compounds for which information was available through the  $\text{C}_7$  compounds. The mass number for the five most important peaks for each compound are listed, followed in each case by the relative intensity in parentheses. The intensities in all cases are normalized to the *n*-butane 43 peak taken as 100. Another method for expressing relative intensities is to assign the base peak a value of 100 and express the relative intensities of the other peaks as a ratio to the base peak. Taking ethyl nitrate as an example, the tabulated values would be

Ethyl nitrate	91(0.01)(P)	46(100)	29(44.2)	30(30.5)	76(24.2)
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The compounds are arranged in the table according to their molecular formulas. Each formula is arranged alphabetically, except that C is first if carbon occurs in the molecules, followed by H if it occurs. The formulas are then arranged alphabetically and according to increasing number of atoms of each kind, all  $\text{C}_4$  compounds being listed before any  $\text{C}_5$  compounds, and so on.

Nearly all these spectra have been recorded using 70-V electrons to bombard the sample molecules.

TABLE 7.76 Condensed Table of Mass Spectra

Molecular formula	Name	Mass numbers (and intensities) of:				
		Parent peak	Base peak	Three next most intense peaks		
B <sub>2</sub> H <sub>6</sub>	Diborane	28(0.13)	26(54)	27(52)	24(48)	25(30)
B <sub>3</sub> H <sub>6</sub> N <sub>3</sub>	Triborine triamine	81(21)	80(58)	79(37)	53(29)	52(22)
B <sub>5</sub> H <sub>9</sub>	Pentaborane	64(15)	59(30)	60(30)	62(24)	61(21)
CBrClF <sub>2</sub>	Diffuorochlorobromomethane	164(0.23)	85(86)	87(27)	129(17)	131(16)
CBr <sub>2</sub> F <sub>2</sub>	Diffuorodibromomethane	208(1.7)	129(70)	131(68)	79(18)	31(18)
CCl <sub>2</sub> F <sub>2</sub>	Diffuorodichloromethane	120(0.07)	85(33)	87(11)	50(3.9)	101(2.8)
CCl <sub>3</sub> F	Fluorotrichloromethane	136(0.04)	101(54)	103(35)	66(7.0)	35(5.8)
CCl <sub>4</sub>	Tetrachloromethane	152(0.0)	117(39)	119(37)	35(16)	47(16)
CF <sub>3</sub> I	Trifluoroiodomethane	196(51)	196(51)	127(49)	69(40)	177(16)
CF <sub>4</sub>	Tetrafluoromethane	88(0.0)	69(57)	50(6.8)	19(3.9)	31(2.8)
CHBrClF	Fluorochlorobromomethane	148(5.5)	67(120)	69(38)	31(13)	111(11)
CHBrF <sub>2</sub>	Diffuorobromomethane	130(13)	51(83)	31(18)	132(13)	79(13)
CHCl <sub>3</sub>	Trichloromethane	118(1.3)	83(69)	85(44)	47(24)	35(13)
CHF <sub>3</sub>	Trifluoromethane	70(0.25)	69(20)	51(18)	31(9.9)	50(2.9)
CHN	Hydrogen cyanide	27(92)	27(92)	26(15)	12(3.8)	28(1.6)
CH <sub>2</sub> ClF	Fluorochloromethane	68(48)	68(48)	33(25)	70(15)	49(11)
CH <sub>2</sub> Cl <sub>2</sub>	Dichloromethane	84(41)	49(71)	86(26)	51(21)	47(13)
CH <sub>2</sub> F <sub>2</sub>	Diffuoromethane	52(2.7)	33(26)	51(25)	31(7.3)	32(2.9)
CH <sub>2</sub> O	Methanal (formaldehyde)	30(19)	29(21)	28(6.6)	14(0.94)	13(0.92)
CH <sub>2</sub> O <sub>2</sub>	Methanoic acid (formic)	46(72)	29(118)	45(56)	28(20)	17(20)
CH <sub>3</sub> Cl	Chloromethane	50(66)	50(66)	15(54)	52(21)	49(6.6)
CH <sub>3</sub> F	Monofluoromethane	34(29)	15(31)	33(28)	14(5.3)	31(3.2)
CH <sub>3</sub> I	Iodomethane	142(78)	142(78)	127(29)	141(11)	15(10)
CH <sub>3</sub> NO <sub>2</sub>	Nitromethane	61(35)	30(65)	15(34)	46(23)	29(5.3)
CH <sub>4</sub>	Methane	16(67)	16(67)	15(58)	14(11)	13(5.5)
CH <sub>4</sub> O	Methanol	32(26)	31(38)	29(25)	28(2.4)	18(0.7)
CH <sub>4</sub> S	Methanethiol	48(49)	47(65)	45(40)	46(9.5)	15(8.9)
CH <sub>5</sub> N	Aminomethane (methylamine)	31(30)	30(53)	28(47)	29(8.7)	27(8.6)
CO	Carbon monoxide	28(78)	28(78)	12(3.7)	16(1.3)	29(0.9)
COS	Carbonyl sulfide	60(83)	60(83)	32(48)	28(6.9)	12(5.0)
CO <sub>2</sub>	Carbon dioxide	44(76)	44(76)	28(5.0)	16(4.7)	12(1.9)
CS <sub>2</sub>	Carbon disulfide	76(184)	76(184)	32(40)	44(33)	78(16)
C <sub>2</sub> F <sub>4</sub>	Tetrafluoroethene	100(20)	31(47)	81(34)	50(14)	12(3.6)
C <sub>2</sub> F <sub>6</sub>	Hexafluoroethane	138(0.14)	69(95)	119(39)	31(17)	50(9.6)
C <sub>2</sub> F <sub>6</sub> Hg	Hexafluorodimethylmercury	340(0.83)	69(111)	202(26)	271(22)	200(21)
C <sub>2</sub> H <sub>2</sub>	Ethyne	26(102)	26(102)	25(20)	24(5.7)	13(5.7)
C <sub>2</sub> H <sub>2</sub> ClN	Chloroethanenitrile	75(51)	75(51)	48(46)	40(23)	77(16)
C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub>	<i>cis</i> -1,2-Dichloroethene	96(53)	61(72)	98(34)	63(23)	26(22)
C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub>	<i>trans</i> -1,2-Dichloroethene	96(49)	61(73)	98(32)	26(25)	63(23)
C <sub>2</sub> H <sub>2</sub> Cl <sub>4</sub>	1,1,2,2-Tetrachloroethane	166(5.9)	83(95)	85(60)	95(11)	87(9.7)
C <sub>2</sub> H <sub>2</sub> F <sub>2</sub>	1,1-Difluoroethene	64(32)	64(32)	45(21)	31(16)	33(13)
C <sub>2</sub> H <sub>3</sub> Cl <sub>3</sub>	1,1,1-Trichloroethane	132(0.0)	97(37)	99(24)	61(19)	117(7.1)
C <sub>2</sub> H <sub>3</sub> Cl <sub>3</sub>	1,1,2-Trichloroethane	132(3.9)	97(43)	83(41)	99(27)	85(26)
C <sub>2</sub> H <sub>3</sub> F <sub>3</sub>	1,1,1-Trifluoroethane	84(0.94)	69(81)	65(31)	15(13)	45(10)
C <sub>2</sub> H <sub>3</sub> N	Ethanenitrile	41(89)	41(89)	40(46)	39(17)	38(10)
C <sub>2</sub> H <sub>4</sub>	Ethene (ethylene)	28(66)	28(66)	27(43)	26(41)	25(7.8)
C <sub>2</sub> H <sub>4</sub> BrCl	1-Chloro-2-bromoethane	142(7.9)	63(93)	27(82)	65(30)	26(24)
C <sub>2</sub> H <sub>4</sub> Br <sub>2</sub>	1,2-Dibromoethane	186(1.6)	27(93)	107(72)	109(67)	26(23)
C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	1,1-Dichloroethane	98(5.7)	63(89)	27(64)	65(28)	26(21)



**TABLE 7.76** Condensed Table of Mass Spectra (*Continued*)

Molecular formula	Name	Mass numbers (and intensities) of:				
		Parent peak	Base peak	Three next most intense peaks		
C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	1,2-Dichloroethane	98(1.7)	62(12)	27(11)	49(4.9)	64(3.9)
C <sub>2</sub> H <sub>4</sub> N <sub>2</sub>	Diazoethane	56(16)	28(27)	27(25)	26(21)	41(5.2)
C <sub>2</sub> H <sub>4</sub> O	Ethanal (acetaldehyde)	44(30)	29(66)	43(18)	42(6.1)	26(6.1)
C <sub>2</sub> H <sub>4</sub> O	Ethylene oxide	44(30)	29(46)	15(30)	14(12)	43(7.1)
C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	Ethanoic acid (acetic)	60(19)	43(37)	45(33)	15(21)	14(8.0)
C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	Methyl formate	60(27)	31(96)	29(60)	32(33)	28(6.8)
C <sub>2</sub> H <sub>5</sub> Br	Bromoethane	108(35)	29(54)	27(48)	110(33)	26(16)
C <sub>2</sub> H <sub>5</sub> Cl	Chloroethane	64(36)	64(36)	28(32)	29(30)	27(27)
C <sub>2</sub> H <sub>5</sub> F	Fluoroethane	48(2.4)	47(24)	27(8.9)	33(8.2)	26(3.0)
C <sub>2</sub> H <sub>5</sub> N	Ethylenimine	43(31)	42(56)	28(44)	15(20)	41(11)
C <sub>2</sub> H <sub>5</sub> NO <sub>2</sub>	Nitroethane	75(0.0)	29(85)	27(74)	30(19)	26(11)
C <sub>2</sub> H <sub>5</sub> NO <sub>3</sub>	Ethyl nitrate	91(0.01)	46(95)	29(42)	30(29)	76(23)
C <sub>2</sub> H <sub>6</sub>	Ethane	30(26)	28(99)	27(33)	26(23)	29(21)
C <sub>2</sub> H <sub>6</sub> O	Ethanol	46(9.7)	31(63)	45(22)	29(14)	27(14)
C <sub>2</sub> H <sub>6</sub> O	Dimethyl ether	46(32)	45(71)	29(56)	15(41)	14(8.9)
C <sub>2</sub> H <sub>6</sub> O <sub>2</sub>	Dimethyl peroxide	62(28)	29(47)	31(45)	15(16)	30(12)
C <sub>2</sub> H <sub>6</sub> S	2-Thiapropane	62(56)	47(69)	45(42)	46(29)	35(24)
C <sub>2</sub> H <sub>6</sub> S	Ethanethiol	62(44)	62(44)	29(43)	47(36)	27(35)
C <sub>2</sub> H <sub>6</sub> S <sub>2</sub>	2,3-Dithiabutane	94(95)	94(95)	45(59)	79(56)	46(34)
C <sub>2</sub> H <sub>6</sub> S <sub>3</sub>	2,3,4-Trithiapentane	126(54)	126(54)	45(32)	79(27)	47(19)
C <sub>2</sub> H <sub>7</sub> N	Aminoethane (ethylamine)	45(18)	30(96)	28(28)	44(19)	27(13)
C <sub>2</sub> H <sub>7</sub> N	N-Methylaminomethane	45(36)	44(71)	28(48)	15(14)	42(13)
C <sub>2</sub> H <sub>8</sub> N <sub>2</sub>	1,2-Diaminoethane	60(2.7)	30(111)	18(14)	42(6.9)	43(5.9)
C <sub>3</sub> F <sub>6</sub>	Hexafluoropropene	150(16)	31(56)	69(44)	131(41)	100(20)
C <sub>3</sub> F <sub>8</sub>	Octafluoropropane	188(0.0)	69(171)	31(49)	169(42)	50(16)
C <sub>3</sub> H <sub>3</sub> N	Propenenitrile	53(55)	26(55)	52(41)	51(18)	27(10)
C <sub>3</sub> H <sub>4</sub>	Propadiene	40(72)	40(72)	39(69)	38(29)	37(23)
C <sub>3</sub> H <sub>4</sub>	Propyne (methylacetylene)	40(79)	40(79)	39(73)	38(29)	37(22)
C <sub>3</sub> H <sub>4</sub> ClN	3-Chloropropanenitrile	89(12)	49(68)	54(54)	51(29)	26(20)
C <sub>3</sub> H <sub>4</sub> O	Propenal (acrolein)	56(16)	27(25)	26(15)	28(13)	55(11)
C <sub>3</sub> H <sub>5</sub> Cl	1-Chloro-1-propene	76(30)	41(70)	39(43)	40(10)	78(9.6)
C <sub>3</sub> H <sub>5</sub> ClO	3-Chloro-1,2-epoxypropane	92(0.19)	57(55)	27(53)	29(40)	31(21)
C <sub>3</sub> H <sub>5</sub> ClO <sub>2</sub>	Methyl chloroacetate	109(0.23)	59(56)	49(44)	15(43)	29(37)
C <sub>3</sub> H <sub>5</sub> Cl <sub>3</sub>	1,2,3-Trichloropropane	146(0.71)	75(61)	110(22)	77(19)	61(18)
C <sub>3</sub> H <sub>5</sub> N	Propanenitrile	55(8.3)	28(83)	54(51)	26(17)	27(15)
C <sub>3</sub> H <sub>6</sub>	Cyclopropane	42(64)	42(64)	41(58)	39(44)	27(23)
C <sub>3</sub> H <sub>6</sub>	Propene	42(39)	41(58)	39(41)	27(22)	40(17)
C <sub>3</sub> H <sub>6</sub> Cl <sub>2</sub>	1,1-Dichloropropane	112(0.0)	63(27)	41(25)	77(22)	62(19)
C <sub>3</sub> H <sub>6</sub> Cl <sub>2</sub>	1,2-Dichloropropane	112(2.6)	63(51)	62(36)	27(29)	41(25)
C <sub>3</sub> H <sub>6</sub> O	1-Propen-3-ol (allyl alc.)	58(12)	57(43)	29(34)	31(26)	27(19)
C <sub>3</sub> H <sub>6</sub> O	Propanal	58(25)	29(66)	28(46)	27(38)	26(14)
C <sub>3</sub> H <sub>6</sub> O	Propanone (acetone)	58(24)	43(85)	15(26)	27(5.9)	42(5.9)
C <sub>3</sub> H <sub>6</sub> O	1,2-Epoxypropane	58(19)	28(44)	29(30)	27(28)	26(18)
C <sub>3</sub> H <sub>6</sub> O <sub>2</sub>	1,3-Dioxolane	74(3.1)	73(52)	43(36)	44(30)	29(30)
C <sub>3</sub> H <sub>6</sub> O <sub>2</sub>	Propanoic acid	74(27)	28(34)	29(28)	27(21)	45(19)
C <sub>3</sub> H <sub>6</sub> O <sub>2</sub>	Ethyl formate	74(5.8)	31(82)	28(60)	29(54)	27(36)
C <sub>3</sub> H <sub>6</sub> O <sub>2</sub>	Methyl acetate	74(22)	43(148)	29(16)	42(15)	59(8.4)
C <sub>3</sub> H <sub>6</sub> O <sub>3</sub>	Methyl carbonate	90(3.3)	15(93)	45(54)	29(43)	31(34)
C <sub>3</sub> H <sub>7</sub> Br	1-Bromopropane	122(14)	43(94)	27(55)	41(47)	39(22)

TABLE 7.76 Condensed Table of Mass Spectra (*Continued*)

Molecular formula	Name	Mass numbers (and intensities) of:				
		Parent peak	Base peak	Three next most intense peaks		
C <sub>3</sub> H <sub>7</sub> Br	2-Bromopropane	122(11)	43(100)	27(50)	41(47)	39(24)
C <sub>3</sub> H <sub>7</sub> Cl	1-Chloropropane	78(3.6)	42(60)	29(27)	27(22)	41(14)
C <sub>3</sub> H <sub>7</sub> Cl	2-Chloropropane	78(14)	43(58)	27(20)	63(15)	41(13)
C <sub>3</sub> H <sub>7</sub> F	2-Fluoropropane	62(1.0)	47(84)	46(24)	61(12)	27(7.6)
C <sub>3</sub> H <sub>7</sub> N	2-Methylethylenimine	57(22)	28(76)	56(34)	30(24)	29(19)
C <sub>3</sub> H <sub>7</sub> N	<i>N</i> -Methylethylenimine	57(31)	42(94)	15(46)	28(25)	27(17)
C <sub>3</sub> H <sub>7</sub> NO	<i>N,N</i> -Dimethylformamide	73(54)	44(63)	42(29)	28(25)	15(24)
C <sub>3</sub> H <sub>7</sub> NO <sub>2</sub>	1-Nitropropane	89(0.0)	43(68)	27(67)	41(58)	39(24)
C <sub>3</sub> H <sub>7</sub> NO <sub>2</sub>	2-Nitropropane	89(0.0)	43(75)	41(55)	27(53)	39(23)
C <sub>3</sub> H <sub>8</sub>	Propane	44(25)	29(85)	28(50)	27(33)	43(19)
C <sub>3</sub> H <sub>8</sub> O	1-Propanol	60(7.2)	31(115)	27(18)	29(17)	59(10)
C <sub>3</sub> H <sub>8</sub> O	2-Propanol	60(0.45)	45(112)	43(19)	27(18)	29(11)
C <sub>3</sub> H <sub>8</sub> O	Methyl ethyl ether	60(24)	45(94)	29(46)	15(23)	27(19)
C <sub>3</sub> H <sub>8</sub> O <sub>2</sub>	Dimethoxymethane	76(1.6)	45(117)	29(51)	75(51)	15(48)
C <sub>3</sub> H <sub>8</sub> O <sub>2</sub>	2-Methoxy-1-ethanol	76(7.3)	45(122)	29(44)	15(38)	31(32)
C <sub>3</sub> H <sub>8</sub> S	2-Thiabutane	76(47)	61(73)	48(40)	47(30)	27(27)
C <sub>3</sub> H <sub>8</sub> S	1-Propanethiol	76(30)	47(43)	43(34)	27(34)	41(32)
C <sub>3</sub> H <sub>8</sub> S	2-Propanethiol	76(41)	43(65)	41(44)	27(41)	61(26)
C <sub>3</sub> H <sub>9</sub> N	1-Aminopropane	59(1.5)	30(20)	28(2.5)	27(1.3)	41(1.0)
C <sub>3</sub> H <sub>9</sub> N	Trimethylamine	59(37)	58(95)	42(44)	15(32)	30(17)
C <sub>3</sub> H <sub>12</sub> B <sub>3</sub> N <sub>3</sub>	<i>B,B',B''</i> -Trimethylborazole	123(30)	108(102)	107(77)	67(38)	66(34)
C <sub>4</sub> F <sub>6</sub>	Hexafluorocyclobutene	162(21)	93(80)	31(51)	143(15)	74(6.9)
C <sub>4</sub> F <sub>6</sub>	Hexafluoro-1,3-butadiene	162(27)	93(90)	31(45)	74(10)	112(10)
C <sub>4</sub> F <sub>6</sub>	Hexafluoro-2-butyne	162(18)	93(47)	143(38)	31(25)	69(20)
C <sub>4</sub> F <sub>8</sub>	Octafluorocyclobutane	200(0.12)	100(97)	131(84)	31(53)	69(24)
C <sub>4</sub> F <sub>8</sub>	Octafluoromethylpropene	200(14)	69(74)	181(54)	31(44)	93(22)
C <sub>4</sub> F <sub>8</sub>	Octafluoro-1-butene	200(11)	131(122)	31(86)	69(44)	93(16)
C <sub>4</sub> F <sub>10</sub>	Decafluorobutane	238(0.0)	69(178)	119(33)	31(22)	100(15)
C <sub>4</sub> HF <sub>7</sub> O <sub>2</sub>	Heptafluorobutanoic acid	214(0.0)	45(26)	69(24)	119(17)	100(14)
C <sub>4</sub> H <sub>2</sub>	1,3-Butadiyne	50(133)	50(133)	49(57)	48(14)	25(12)
C <sub>4</sub> H <sub>4</sub>	1-Buten-3-yne	52(55)	52(55)	51(28)	50(23)	49(7.2)
C <sub>4</sub> H <sub>4</sub> O	Furan	68(36)	39(58)	38(9.7)	29(9.3)	40(6.7)
C <sub>4</sub> H <sub>4</sub> S	Thiophene	84(93)	84(93)	58(56)	45(49)	39(24)
C <sub>4</sub> H <sub>4</sub> S <sub>2</sub>	2-Thiophenethiol	116(68)	116(68)	71(64)	45(31)	39(11)
C <sub>4</sub> H <sub>5</sub> N	3-Butenenitrile	67(27)	41(80)	39(36)	27(30)	40(20)
C <sub>4</sub> H <sub>5</sub> N	Pyrrole	67(67)	67(67)	39(46)	41(42)	40(36)
C <sub>4</sub> H <sub>6</sub>	1,2-Butadiene	54(65)	54(65)	27(35)	53(29)	39(28)
C <sub>4</sub> H <sub>6</sub>	1,3-Butadiene	54(46)	39(53)	27(36)	53(31)	28(24)
C <sub>4</sub> H <sub>6</sub>	1-Butyne	54(64)	54(64)	39(49)	53(27)	27(26)
C <sub>4</sub> H <sub>6</sub>	2-Butyne	54(93)	54(93)	27(42)	53(41)	39(24)
C <sub>4</sub> H <sub>6</sub> Cl <sub>2</sub> O <sub>2</sub>	Ethyl dichloroacetate	156(0.12)	29(192)	27(58)	83(23)	28(19)
C <sub>4</sub> H <sub>6</sub> O <sub>2</sub>	2,3-Butanedione	86(13)	43(118)	15(40)	14(12)	42(8.6)
C <sub>4</sub> H <sub>6</sub> O <sub>2</sub>	Methyl 2-propenoate	86(2.0)	55(98)	27(66)	15(27)	26(22)
C <sub>4</sub> H <sub>7</sub> BrO <sub>2</sub>	2-Bromoethyl acetate	166(0.03)	43(158)	27(35)	106(31)	108(30)
C <sub>4</sub> H <sub>7</sub> Cl	2-Chloro-2-butene	90(27)	55(68)	27(21)	39(21)	29(18)
C <sub>4</sub> H <sub>7</sub> ClO <sub>2</sub>	2-Chloroethyl acetate	122(0.0)	43(162)	73(43)	15(36)	27(29)
C <sub>4</sub> H <sub>7</sub> ClO <sub>2</sub>	Ethyl chloroacetate	122(0.96)	29(130)	27(41)	77(37)	49(29)
C <sub>4</sub> H <sub>7</sub> N	2-Methylpropanenitrile	69(1.7)	42(79)	68(38)	28(26)	54(19)
C <sub>4</sub> H <sub>7</sub> N	<i>n</i> -Butanenitrile	69(0.15)	41(112)	29(70)	27(38)	28(11)

TABLE 7.76 Condensed Table of Mass Spectra (Continued)

Molecular formula	Name	Mass numbers (and intensities) of:				
		Parent peak	Base peak	Three next most intense peaks		
C <sub>4</sub> H <sub>8</sub>	Cyclobutane	56(41)	28(65)	41(58)	27(27)	26(15)
C <sub>4</sub> H <sub>8</sub>	2-Methylpropene	56(36)	41(85)	39(37)	28(18)	27(17)
C <sub>4</sub> H <sub>8</sub>	1-Butene	56(32)	41(87)	39(30)	27(26)	28(26)
C <sub>4</sub> H <sub>8</sub>	<i>cis</i> -2-Butene	56(36)	41(76)	39(27)	27(25)	28(24)
C <sub>4</sub> H <sub>8</sub>	<i>trans</i> -2-Butene	56(37)	41(80)	27(27)	39(26)	28(26)
C <sub>4</sub> H <sub>8</sub> Cl <sub>2</sub>	1,2-Dichlorobutane	126(0.30)	41(39)	77(35)	27(20)	76(16)
C <sub>4</sub> H <sub>8</sub> Cl <sub>2</sub>	1,4-Dichlorobutane	126(0.03)	55(87)	41(29)	27(24)	90(23)
C <sub>4</sub> H <sub>8</sub> Cl <sub>2</sub>	<i>dl</i> -2,3-Dichlorobutane	126(0.95)	63(63)	62(58)	27(57)	55(29)
C <sub>4</sub> H <sub>8</sub> Cl <sub>2</sub>	<i>meso</i> -2,3-Dichlorobutane	126(0.95)	63(64)	27(57)	62(54)	55(31)
C <sub>4</sub> H <sub>8</sub> N <sub>2</sub>	Acetaldazine	84(23)	42(92)	15(47)	28(46)	69(38)
C <sub>4</sub> H <sub>8</sub> O	Butanal	72(19)	27(41)	29(38)	44(34)	43(32)
C <sub>4</sub> H <sub>8</sub> O	2-Butanone	72(17)	43(97)	29(24)	27(15)	57(6.0)
C <sub>4</sub> H <sub>8</sub> O	Ethyl ethenyl ether	72(27)	44(64)	43(56)	29(49)	27(43)
C <sub>4</sub> H <sub>8</sub> O	<i>cis</i> -2,3-Epoxybutane	72(3.6)	43(67)	44(39)	27(35)	29(33)
C <sub>4</sub> H <sub>8</sub> O	<i>trans</i> -2,3-Epoxybutane	72(3.5)	43(69)	44(35)	29(32)	27(31)
C <sub>4</sub> H <sub>8</sub> O	Tetrahydrofuran	72(22)	42(76)	41(39)	27(25)	71(20)
C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	2-Methyl-1,3-dioxacyclopentane	88(0.33)	73(67)	43(48)	45(44)	29(34)
C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	1,4-Dioxane	88(42)	28(138)	29(51)	58(33)	31(24)
C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	2-Methylpropanoic acid	88(8.1)	43(77)	41(33)	27(26)	73(19)
C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	<i>n</i> -Butanoic acid	88(1.0)	60(40)	73(12)	27(9.6)	41(9.1)
C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	<i>n</i> -Propyl formate	88(0.41)	31(123)	42(89)	29(38)	27(36)
C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	Ethyl acetate	88(7.1)	43(181)	29(46)	45(24)	27(24)
C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	Methyl propanoate	88(23)	29(110)	57(83)	27(40)	59(27)
C <sub>4</sub> H <sub>8</sub> S	3-Methylthiacyclobutane	88(42)	46(101)	45(31)	39(24)	47(21)
C <sub>4</sub> H <sub>8</sub> S	Thiacyclopentane	88(44)	60(82)	45(29)	46(29)	47(22)
C <sub>4</sub> H <sub>9</sub> Br	1-Bromobutane	136(7.0)	57(86)	41(63)	29(50)	27(46)
C <sub>4</sub> H <sub>9</sub> Br	2-Bromobutane	136(0.72)	57(108)	41(65)	29(61)	27(36)
C <sub>4</sub> H <sub>9</sub> N	Pyrrolidine	71(24)	43(102)	28(38)	70(33)	42(20)
C <sub>4</sub> H <sub>9</sub> NO <sub>2</sub>	<i>n</i> -Butyl nitrite	103(0.0)	27(55)	43(54)	41(50)	30(47)
C <sub>4</sub> H <sub>10</sub>	2-Methylpropane	58(3.2)	43(117)	41(45)	42(39)	27(33)
C <sub>4</sub> H <sub>10</sub>	<i>n</i> -Butane	58(12)	43(100)	29(44)	27(37)	28(33)
C <sub>4</sub> H <sub>10</sub> Hg	Diethylmercury	260(12)	29(188)	27(54)	28(21)	231(15)
C <sub>4</sub> H <sub>10</sub> O	2-Methyl-1-propanol	74(7.5)	43(84)	31(56)	42(48)	41(47)
C <sub>4</sub> H <sub>10</sub> O	2-Methyl-2-propanol	74(0.0)	59(92)	31(31)	41(19)	43(14)
C <sub>4</sub> H <sub>10</sub> O	1-Butanol	74(0.37)	31(52)	56(44)	41(31)	43(30)
C <sub>4</sub> H <sub>10</sub> O	2-Butanol	74(0.30)	45(116)	31(23)	59(22)	27(20)
C <sub>4</sub> H <sub>10</sub> O	Diethyl ether	74(22)	31(73)	59(34)	29(29)	45(28)
C <sub>4</sub> H <sub>10</sub> O	Methyl isopropyl ether	74(8.3)	59(126)	29(42)	43(37)	15(32)
C <sub>4</sub> H <sub>10</sub> O <sub>2</sub>	1,1-Dimethoxyethane	90(0.06)	59(93)	29(52)	15(37)	31(37)
C <sub>4</sub> H <sub>10</sub> O <sub>2</sub>	1,2-Dimethoxyethane	90(12)	45(177)	29(53)	15(50)	60(16)
C <sub>4</sub> H <sub>10</sub> O <sub>2</sub>	2-Ethoxyethanol	90(0.49)	31(112)	29(57)	59(56)	27(31)
C <sub>4</sub> H <sub>10</sub> O <sub>2</sub>	Diethyl peroxide	90(20)	29(116)	15(42)	45(34)	62(30)
C <sub>4</sub> H <sub>10</sub> S	3-Methyl-2-thiabutane	90(41)	41(49)	75(47)	43(41)	48(38)
C <sub>4</sub> H <sub>10</sub> S	2-Thiapentane	90(58)	61(126)	48(50)	41(43)	27(43)
C <sub>4</sub> H <sub>10</sub> S	3-Thiapentane	90(41)	75(59)	47(51)	27(39)	61(33)
C <sub>4</sub> H <sub>10</sub> S	2-Methyl-1-propanethiol	90(35)	41(60)	43(46)	56(34)	47(29)
C <sub>4</sub> H <sub>10</sub> S	2-Methyl-2-propanethiol	90(34)	41(68)	57(61)	29(44)	39(21)
C <sub>4</sub> H <sub>10</sub> S	1-Butanethiol	90(40)	56(74)	41(65)	27(42)	47(31)
C <sub>4</sub> H <sub>10</sub> S	2-Butanethiol	90(34)	41(56)	57(50)	61(46)	29(46)

TABLE 7.76 Condensed Table of Mass Spectra (*Continued*)

Molecular formula	Name	Mass numbers (and intensities) of:				
		Parent peak	Base peak	Three next most intense peaks		
C <sub>4</sub> H <sub>10</sub> S <sub>2</sub>	2,3-Dithiahexane	122(37)	80(53)	43(36)	41(27)	27(25)
C <sub>4</sub> H <sub>10</sub> S <sub>2</sub>	3,4-Dithiahexane	122(73)	29(82)	66(81)	27(57)	94(53)
C <sub>4</sub> H <sub>10</sub> SO <sub>3</sub>	Ethyl sulfite	138(3.3)	29(131)	31(59)	45(42)	27(39)
C <sub>4</sub> H <sub>11</sub> N	<i>N</i> -Ethylaminoethane	73(17)	58(83)	30(81)	28(30)	27(24)
C <sub>4</sub> H <sub>11</sub> N	1-Amino-2-methylpropane	73(1.0)	30(22)	28(2.0)	41(1.2)	27(1.1)
C <sub>4</sub> H <sub>11</sub> N	2-Amino-2-methylpropane	73(0.25)	58(127)	41(26)	42(20)	15(18)
C <sub>4</sub> H <sub>11</sub> N	1-Aminobutane	73(12)	30(200)	28(23)	27(16)	18(12)
C <sub>4</sub> H <sub>11</sub> N	2-Aminobutane	73(1.2)	44(170)	18(25)	41(18)	58(18)
C <sub>4</sub> H <sub>12</sub> Pb	Tetramethyllead	268(0.14)	253(69)	223(59)	208(46)	251(36)
C <sub>5</sub> F <sub>10</sub>	Decafluorocyclopentane	250(0.62)	131(173)	100(41)	31(40)	69(28)
C <sub>5</sub> F <sub>12</sub>	Dodecafluoro-2-methylbutane	288(0.0)	69(277)	119(45)	131(23)	31(18)
C <sub>5</sub> F <sub>12</sub>	Dodecafluoropentane	288(0.08)	69(259)	119(76)	169(25)	31(24)
C <sub>5</sub> HF <sub>9</sub>	Nonafluorocyclopentane	232(0.07)	131(61)	113(49)	69(34)	31(19)
C <sub>5</sub> H <sub>5</sub> N	Pyridine	79(135)	79(135)	52(95)	51(48)	50(35)
C <sub>5</sub> H <sub>6</sub>	Cyclopentadiene	66(95)	66(95)	65(40)	39(35)	40(30)
C <sub>5</sub> H <sub>6</sub>	<i>trans</i> -2-Penten-4-yne	66(77)	66(77)	39(54)	65(38)	40(35)
C <sub>5</sub> H <sub>6</sub> N <sub>2</sub>	2-Methylpyrazine	94(81)	94(81)	67(48)	26(33)	39(30)
C <sub>5</sub> H <sub>6</sub> O <sub>2</sub>	Furfuryl alcohol	98(3.4)	98(3.4)	41(3.3)	39(3.3)	42(2.6)
C <sub>5</sub> H <sub>6</sub> S	2-Methylthiophene	98(68)	97(125)	45(26)	39(17)	53(11)
C <sub>5</sub> H <sub>6</sub> S	3-Methylthiophene	98(74)	97(138)	45(35)	39(14)	27(11)
C <sub>5</sub> H <sub>8</sub>	Methylenecyclobutane	68(38)	40(67)	67(48)	39(47)	53(21)
C <sub>5</sub> H <sub>8</sub>	Spiropentane	68(8.9)	67(58)	40(56)	39(52)	53(23)
C <sub>5</sub> H <sub>8</sub>	Cyclopentene	68(41)	67(99)	39(36)	53(23)	41(19)
C <sub>5</sub> H <sub>8</sub>	3-Methyl-1,2-butadiene	68(53)	68(53)	53(40)	39(28)	41(26)
C <sub>5</sub> H <sub>8</sub>	2-Methyl-1,3-butadiene	68(40)	67(48)	53(41)	39(34)	27(23)
C <sub>5</sub> H <sub>8</sub>	1,2-Pentadiene	68(39)	68(39)	53(38)	39(37)	27(31)
C <sub>5</sub> H <sub>8</sub>	<i>cis</i> -1,3-Pentadiene	68(40)	67(53)	39(43)	53(38)	41(25)
C <sub>5</sub> H <sub>8</sub>	<i>trans</i> -1,3-Pentadiene	68(41)	67(52)	39(43)	53(39)	41(26)
C <sub>5</sub> H <sub>8</sub>	1,4-Pentadiene	68(40)	39(47)	67(35)	53(33)	41(30)
C <sub>5</sub> H <sub>8</sub>	2,3-Pentadiene	68(62)	68(62)	53(42)	39(36)	41(31)
C <sub>5</sub> H <sub>8</sub>	3-Methyl-1-butyne	68(8.5)	53(74)	67(45)	27(35)	39(21)
C <sub>5</sub> H <sub>8</sub>	1-Pentyne	68(8.7)	67(50)	40(44)	39(42)	27(34)
C <sub>5</sub> H <sub>8</sub>	2-Pentyne	68(67)	68(67)	53(61)	39(32)	27(27)
C <sub>5</sub> H <sub>8</sub> N <sub>2</sub>	3,5-Dimethylpyrazole	96(47)	96(47)	95(37)	39(16)	54(12)
C <sub>5</sub> H <sub>8</sub> O <sub>2</sub>	2,4-Pentanedione	100(22)	43(120)	85(33)	15(23)	27(11)
C <sub>5</sub> H <sub>8</sub> O <sub>2</sub>	2-Propenyl acetate	100(0.16)	43(177)	41(30)	39(29)	15(28)
C <sub>5</sub> H <sub>8</sub> O <sub>2</sub>	Methyl methacrylate	100(26)	41(78)	69(52)	39(31)	15(16)
C <sub>5</sub> H <sub>9</sub> ClO <sub>2</sub>	Ethyl 3-chloropropanoate	136(0.70)	27(65)	29(62)	91(42)	63(37)
C <sub>5</sub> H <sub>10</sub>	<i>cis</i> -1,2-Dimethylcyclopropane	70(39)	55(77)	42(35)	39(32)	41(32)
C <sub>5</sub> H <sub>10</sub>	<i>trans</i> -1,2-Dimethylcyclopropane	70(42)	55(79)	42(34)	41(33)	39(30)
C <sub>5</sub> H <sub>10</sub>	Ethylcyclopropane	70(26)	42(93)	55(47)	41(39)	39(35)
C <sub>5</sub> H <sub>10</sub>	Cyclopentane	70(44)	42(148)	55(43)	41(43)	39(31)
C <sub>5</sub> H <sub>10</sub>	2-Methyl-1-butene	70(30)	55(97)	42(36)	39(34)	41(28)
C <sub>5</sub> H <sub>10</sub>	3-Methyl-1-butene	70(26)	55(102)	27(31)	42(28)	29(27)
C <sub>5</sub> H <sub>10</sub>	2-Methyl-2-butene	70(31)	55(88)	41(31)	39(28)	42(27)
C <sub>5</sub> H <sub>10</sub>	1-Pentene	70(27)	42(89)	55(53)	41(39)	39(31)
C <sub>5</sub> H <sub>10</sub>	<i>cis</i> -2-Pentene	70(30)	55(89)	42(41)	39(30)	29(26)
C <sub>5</sub> H <sub>10</sub>	<i>trans</i> -2-Pentene	70(31)	55(93)	42(41)	39(30)	41(28)
C <sub>5</sub> H <sub>10</sub> O	3-Methyl-1-butanal	86(3.0)	41(30)	43(26)	58(20)	29(20)

TABLE 7.76 Condensed Table of Mass Spectra (Continued)

Molecular formula	Name	Mass numbers (and intensities) of:				
		Parent peak	Base peak	Three next most intense peaks		
C <sub>5</sub> H <sub>10</sub> O	2-Pentanone	86(16)	43(106)	29(23)	27(23)	57(20)
C <sub>5</sub> H <sub>10</sub> O	3-Pentanone	86(15)	57(87)	29(87)	27(32)	28(9.4)
C <sub>5</sub> H <sub>10</sub> O	Ethyl-2-propenyl ether	86(6.2)	41(52)	29(48)	58(44)	57(42)
C <sub>5</sub> H <sub>10</sub> O	Ethyl isopropyl ether	86(21)	43(87)	44(69)	41(46)	27(45)
C <sub>5</sub> H <sub>10</sub> O	2-Methyltetrahydrofuran	86(8.9)	71(57)	43(55)	41(40)	27(27)
C <sub>5</sub> H <sub>10</sub> O <sub>2</sub>	Tetrahydrofurfuryl alcohol	102(0.02)	71(8.9)	43(6.8)	41(4.8)	27(3.8)
C <sub>5</sub> H <sub>10</sub> O <sub>2</sub>	2-Methoxyethyl ethenyl ether	102(3.0)	29(69)	45(58)	15(48)	58(45)
C <sub>5</sub> H <sub>10</sub> O <sub>2</sub>	2,2-Dimethylpropanoic acid	102(2.0)	57(83)	41(38)	29(27)	39(12)
C <sub>5</sub> H <sub>10</sub> O <sub>2</sub>	2-Methylbutanoic acid	102(0.32)	74(54)	57(34)	29(33)	41(28)
C <sub>5</sub> H <sub>10</sub> O <sub>2</sub>	<i>n</i> -Butyl formate	102(0.27)	56(80)	41(48)	31(47)	29(42)
C <sub>5</sub> H <sub>10</sub> O <sub>2</sub>	Isobutyl formate	102(0.27)	43(58)	56(48)	41(46)	31(38)
C <sub>5</sub> H <sub>10</sub> O <sub>2</sub>	<i>sec</i> -Butyl formate	102(0.17)	45(99)	29(49)	27(32)	41(31)
C <sub>5</sub> H <sub>10</sub> O <sub>2</sub>	<i>n</i> -Propyl acetate	102(0.07)	43(176)	61(34)	31(31)	27(26)
C <sub>5</sub> H <sub>10</sub> O <sub>2</sub>	Isopropyl acetate	102(0.17)	43(155)	45(50)	27(22)	61(18)
C <sub>5</sub> H <sub>10</sub> O <sub>2</sub>	Ethyl propanoate	102(10)	29(151)	57(97)	27(52)	28(24)
C <sub>5</sub> H <sub>10</sub> O <sub>2</sub>	Methyl 2-methylpropanoate	102(8.9)	43(69)	71(23)	41(19)	59(17)
C <sub>5</sub> H <sub>10</sub> O <sub>2</sub>	Methyl butanoate	102(1.0)	43(53)	74(37)	71(29)	27(23)
C <sub>5</sub> H <sub>10</sub> O <sub>3</sub>	Ethyl carbonate	118(0.30)	29(114)	45(80)	31(60)	27(46)
C <sub>5</sub> H <sub>10</sub> S	2-Methylthiacyclopentane	102(37)	87(88)	41(30)	45(29)	59(18)
C <sub>5</sub> H <sub>10</sub> S	3-Methylthiacyclopentane	102(40)	60(45)	41(31)	45(25)	74(23)
C <sub>5</sub> H <sub>10</sub> S	Thiacyclohexane	102(43)	87(44)	68(33)	61(32)	41(28)
C <sub>5</sub> H <sub>10</sub> S	Cyclopentanethiol	102(19)	41(48)	69(47)	39(26)	67(18)
C <sub>5</sub> H <sub>11</sub> N	Piperidine	85(22)	84(43)	57(22)	56(22)	44(17)
C <sub>5</sub> H <sub>11</sub> NO	<i>N</i> -Methylmorpholine	101(4.4)	43(18)	42(8.6)	15(3.4)	71(2.9)
C <sub>5</sub> H <sub>11</sub> NO <sub>2</sub>	3-Methylbutyl nitrite	117(0.0)	29(75)	41(68)	57(43)	30(42)
C <sub>5</sub> H <sub>12</sub>	2,2-Dimethylpropane	72(0.01)	57(126)	41(52)	29(49)	27(20)
C <sub>5</sub> H <sub>12</sub>	2-Methylbutane	72(4.7)	43(74)	42(64)	41(49)	57(40)
C <sub>5</sub> H <sub>12</sub>	<i>n</i> -Pentane	72(10)	43(114)	42(66)	41(45)	27(39)
C <sub>5</sub> H <sub>12</sub> O	2-Methyl-1-butanol	88(0.18)	57(57)	29(55)	41(53)	56(50)
C <sub>5</sub> H <sub>12</sub> O	3-Methyl-1-butanol	88(0.02)	55(47)	42(42)	43(39)	41(38)
C <sub>5</sub> H <sub>12</sub> O	2-Methyl-2-butanol	88(0.0)	59(43)	55(37)	45(25)	73(22)
C <sub>5</sub> H <sub>12</sub> O	1-Pentanol	88(0.0)	42(41)	55(30)	41(25)	70(23)
C <sub>5</sub> H <sub>12</sub> O	Methyl <i>n</i> -butyl ether	88(3.1)	45(211)	56(36)	29(36)	27(28)
C <sub>5</sub> H <sub>12</sub> O	Methyl isobutyl ether	88(12)	45(186)	41(30)	29(30)	15(27)
C <sub>5</sub> H <sub>12</sub> O	Methyl <i>sec</i> -butyl ether	88(2.0)	52(142)	29(50)	27(27)	41(25)
C <sub>5</sub> H <sub>12</sub> O	Methyl <i>tert</i> -butyl ether	88(0.02)	73(119)	41(33)	43(32)	57(32)
C <sub>5</sub> H <sub>12</sub> O	Ethyl isopropyl ether	88(2.6)	45(143)	43(46)	73(40)	27(24)
C <sub>5</sub> H <sub>12</sub> O <sub>2</sub>	Diethoxymethane	104(2.1)	31(104)	59(99)	29(62)	103(39)
C <sub>5</sub> H <sub>12</sub> O <sub>2</sub>	1,1-Dimethoxypropane	104(0.05)	75(84)	73(62)	29(43)	45(37)
C <sub>5</sub> H <sub>12</sub> S	3,3-Dimethyl-2-thiabutane	104(30)	57(83)	41(62)	29(42)	39(16)
C <sub>5</sub> H <sub>12</sub> S	4-Methyl-2-thiapentane	104(37)	41(46)	56(38)	27(29)	39(23)
C <sub>5</sub> H <sub>12</sub> S	2-Methyl-3-thiapentane	104(82)	89(119)	62(79)	43(63)	61(58)
C <sub>5</sub> H <sub>12</sub> S	2-Thiahexane	104(38)	61(77)	56(50)	41(39)	27(33)
C <sub>5</sub> H <sub>12</sub> S	3-Thiahexane	104(30)	75(72)	27(53)	47(50)	62(33)
C <sub>5</sub> H <sub>12</sub> S	2,2-Dimethyl-1-propanethiol	104(31)	57(100)	41(55)	55(48)	29(42)
C <sub>5</sub> H <sub>12</sub> S	2-Methyl-1-butanethiol	104(28)	41(65)	29(44)	57(40)	70(40)
C <sub>5</sub> H <sub>12</sub> S	2-Methyl-2-butanethiol	104(18)	43(88)	71(54)	41(46)	55(34)
C <sub>5</sub> H <sub>12</sub> S	3-Methyl-2-butanethiol	104(23)	61(73)	43(55)	27(33)	55(28)
C <sub>5</sub> H <sub>12</sub> S	1-Pentanethiol	104(35)	42(91)	55(44)	41(39)	70(39)

**TABLE 7.76** Condensed Table of Mass Spectra (*Continued*)

Molecular formula	Name	Mass numbers (and intensities) of:				
		Parent peak	Base peak	Three next most intense peaks		
C <sub>5</sub> H <sub>12</sub> S	2-Pentanethiol	104(28)	43(72)	61(52)	27(39)	55(38)
C <sub>5</sub> H <sub>12</sub> S	3-Pentanethiol	104(23)	43(56)	41(48)	75(29)	47(23)
C <sub>5</sub> H <sub>12</sub> S <sub>2</sub>	4,4-Dimethyl-2,3-dithiapentane	136(12)	57(74)	41(38)	29(36)	80(13)
C <sub>5</sub> H <sub>12</sub> S <sub>2</sub>	2-Methyl-3,4-dithiahexane	136(20)	94(49)	27(46)	43(39)	66(37)
C <sub>5</sub> H <sub>14</sub> Pb	Trimethylethyllead	282(0.64)	223(61)	253(52)	208(51)	221(33)
C <sub>6</sub> F <sub>6</sub>	Hexafluorobenzene	186(95)	186(95)	117(59)	31(58)	93(23)
C <sub>6</sub> F <sub>12</sub>	Dodecafluorocyclohexane	300(0.96)	131(138)	69(97)	100(40)	31(30)
C <sub>6</sub> F <sub>14</sub>	Tetradecafluoro-2-methylpentane	338(0.0)	69(317)	131(41)	119(36)	169(29)
C <sub>6</sub> F <sub>14</sub>	Tetradecafluorohexane	338(0.13)	69(268)	119(74)	169(51)	131(37)
C <sub>6</sub> H <sub>5</sub> Br	Bromobenzene	156(75)	77(98)	158(74)	51(41)	50(36)
C <sub>6</sub> H <sub>5</sub> Cl	Chlorobenzene	112(102)	112(102)	77(49)	114(33)	51(17)
C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	Nitrobenzene	123(39)	77(93)	51(55)	50(23)	30(15)
C <sub>6</sub> H <sub>6</sub>	Benzene	78(113)	78(113)	52(22)	77(20)	51(18)
C <sub>6</sub> H <sub>6</sub>	1,5-Hexadiyne	78(58)	39(65)	52(38)	51(32)	50(26)
C <sub>6</sub> H <sub>6</sub>	2,4-Hexadiyne	78(108)	78(108)	51(55)	52(38)	50(31)
C <sub>6</sub> H <sub>6</sub> S	Benzenethiol	110(68)	110(68)	66(26)	109(17)	51(15)
C <sub>6</sub> H <sub>7</sub> N	Aminobenzene (aniline)	93(19)	93(19)	66(6.5)	65(3.6)	39(3.5)
C <sub>6</sub> H <sub>7</sub> N	2-Methylpyridine	93(86)	93(86)	66(36)	39(28)	51(16)
C <sub>6</sub> H <sub>7</sub> NO	1-Methyl-2-pyridone	109(71)	109(71)	81(49)	39(34)	80(29)
C <sub>6</sub> H <sub>8</sub>	Methylcyclopentadiene	80(53)	79(87)	77(29)	39(19)	51(11)
C <sub>6</sub> H <sub>8</sub>	1,3-Cyclohexadiene	80(53)	79(92)	77(35)	39(21)	27(18)
C <sub>6</sub> H <sub>8</sub> O	2,5-Dimethylfuran	96(57)	43(65)	95(48)	53(37)	81(24)
C <sub>6</sub> H <sub>8</sub> S	2,3-Dimethylthiophene	112(44)	97(53)	111(44)	45(16)	27(9.4)
C <sub>6</sub> H <sub>8</sub> S	2,4-Dimethylthiophene	112(27)	111(36)	97(18)	45(9.4)	39(7.0)
C <sub>6</sub> H <sub>8</sub> S	2,5-Dimethylthiophene	112(67)	111(95)	97(59)	59(23)	45(19)
C <sub>6</sub> H <sub>8</sub> S	2-Ethylthiophene	112(27)	97(68)	45(16)	39(8.9)	27(5.4)
C <sub>6</sub> H <sub>8</sub> S	3-Ethylthiophene	112(54)	97(147)	45(38)	39(20)	27(12)
C <sub>6</sub> H <sub>9</sub> N	2,5-Dimethylpyrrole	95(73)	94(127)	26(52)	80(22)	42(19)
C <sub>6</sub> H <sub>10</sub>	Isopropenylcyclopropane	82(20)	67(92)	41(47)	39(46)	27(22)
C <sub>6</sub> H <sub>10</sub>	1-Methylcyclopentene	82(26)	67(98)	39(21)	81(16)	41(16)
C <sub>6</sub> H <sub>10</sub>	Cyclohexene	82(33)	67(83)	54(64)	41(31)	39(30)
C <sub>6</sub> H <sub>10</sub>	2,3-Dimethyl-1,3-butadiene	82(41)	67(60)	39(55)	41(44)	54(22)
C <sub>6</sub> H <sub>10</sub>	2-Methyl-1,3-pentadiene	82(23)	67(48)	39(30)	41(26)	27(13)
C <sub>6</sub> H <sub>10</sub>	1,5-Hexadiene	82(1.3)	41(98)	67(80)	39(60)	54(52)
C <sub>6</sub> H <sub>10</sub>	3,3-Dimethyl-1-butyne	82(0.57)	67(101)	41(57)	39(31)	27(11)
C <sub>6</sub> H <sub>10</sub>	4-Methyl-1-pentyne	82(2.3)	67(82)	41(74)	43(64)	39(55)
C <sub>6</sub> H <sub>10</sub>	1-Hexyne	82(1.0)	67(131)	41(88)	27(85)	43(67)
C <sub>6</sub> H <sub>10</sub>	2-Hexyne	82(56)	67(58)	53(50)	27(39)	41(36)
C <sub>6</sub> H <sub>10</sub>	3-Hexyne	82(55)	67(59)	41(55)	39(37)	53(20)
C <sub>6</sub> H <sub>10</sub> O	Cyclohexanone	98(32)	55(102)	42(86)	41(35)	27(34)
C <sub>6</sub> H <sub>10</sub> O	4-Methyl-3-penten-2-one	98(40)	55(82)	83(82)	43(64)	29(38)
C <sub>6</sub> H <sub>10</sub> O <sub>2</sub>	2,5-Hexanedione	114(4.0)	43(148)	15(25)	99(22)	14(14)
C <sub>6</sub> H <sub>10</sub> O <sub>3</sub>	Propanoic anhydride	130(0.0)	57(190)	29(119)	27(62)	28(26)
C <sub>6</sub> H <sub>10</sub> O <sub>3</sub>	Ethyl acetoacetate	130(8.3)	43(150)	29(52)	27(32)	15(27)
C <sub>6</sub> H <sub>11</sub> N	4-Methylpentanenitrile	97(0.13)	55(98)	41(51)	43(45)	27(39)
C <sub>6</sub> H <sub>11</sub> N	Hexanenitrile	97(0.54)	41(73)	54(49)	27(43)	55(40)
C <sub>6</sub> H <sub>12</sub>	1,1,2-Trimethylcyclopropane	84(38)	41(132)	69(81)	39(34)	27(24)
C <sub>6</sub> H <sub>12</sub>	1-Methyl-1-ethylcyclopropane	84(25)	41(78)	55(58)	69(53)	27(33)
C <sub>6</sub> H <sub>12</sub>	Isopropylcyclopropane	84(2.0)	56(114)	41(84)	39(30)	43(28)

TABLE 7.76 Condensed Table of Mass Spectra (Continued)

Molecular formula	Name	Mass numbers (and intensities) of:				
		Parent peak	Base peak	Three next most intense peaks		
C <sub>6</sub> H <sub>12</sub>	Ethylcyclobutane	84(3.8)	56(138)	41(89)	27(35)	55(34)
C <sub>6</sub> H <sub>12</sub>	Methylcyclopentane	84(18)	56(116)	41(74)	69(37)	42(33)
C <sub>6</sub> H <sub>12</sub>	Cyclohexane	84(58)	56(75)	41(44)	55(25)	42(21)
C <sub>6</sub> H <sub>12</sub>	2,3-Dimethyl-1-butene	84(27)	41(117)	69(96)	39(36)	27(24)
C <sub>6</sub> H <sub>12</sub>	3,3-Dimethyl-1-butene	84(23)	41(112)	69(107)	39(28)	27(26)
C <sub>6</sub> H <sub>12</sub>	2-Ethyl-1-butene	84(30)	41(74)	69(66)	55(56)	27(38)
C <sub>6</sub> H <sub>12</sub>	2,3-Dimethyl-2-butene	84(32)	41(108)	69(88)	39(35)	27(20)
C <sub>6</sub> H <sub>12</sub>	2-Methyl-1-pentene	84(29)	56(91)	41(73)	55(39)	39(36)
C <sub>6</sub> H <sub>12</sub>	3-Methyl-1-pentene	84(25)	55(85)	41(67)	69(60)	27(43)
C <sub>6</sub> H <sub>12</sub>	4-Methyl-1-pentene	84(12)	43(110)	41(80)	56(47)	27(37)
C <sub>6</sub> H <sub>12</sub>	2-Methyl-2-pentene	84(36)	41(120)	69(111)	39(35)	27(28)
C <sub>6</sub> H <sub>12</sub>	3-Methyl- <i>cis</i> -2-pentene	84(37)	41(104)	69(82)	55(46)	27(36)
C <sub>6</sub> H <sub>12</sub>	3-Methyl- <i>trans</i> -2-pentene	84(38)	41(102)	69(81)	55(47)	27(35)
C <sub>6</sub> H <sub>12</sub>	4-Methyl- <i>cis</i> -2-pentene	84(35)	41(122)	69(114)	39(35)	27(26)
C <sub>6</sub> H <sub>12</sub>	4-Methyl- <i>trans</i> -2-pentene	84(34)	41(123)	69(112)	39(34)	27(26)
C <sub>6</sub> H <sub>12</sub>	1-Hexene	84(20)	41(70)	56(60)	42(52)	27(48)
C <sub>6</sub> H <sub>12</sub>	<i>cis</i> -2-Hexene	84(27)	55(91)	42(51)	41(45)	27(45)
C <sub>6</sub> H <sub>12</sub>	<i>trans</i> -2-Hexene	84(32)	55(112)	42(54)	41(46)	27(41)
C <sub>6</sub> H <sub>12</sub>	<i>cis</i> -3-Hexene	84(28)	55(81)	41(62)	42(54)	27(32)
C <sub>6</sub> H <sub>12</sub>	<i>trans</i> -3-Hexene	84(32)	55(89)	41(72)	42(62)	27(35)
C <sub>6</sub> H <sub>12</sub> N <sub>2</sub>	Acetone azine (ketazine)	112(31)	56(99)	15(31)	97(31)	39(26)
C <sub>6</sub> H <sub>12</sub> O	Cyclopentylmethanol	100(0.02)	41(35)	68(32)	69(31)	67(24)
C <sub>6</sub> H <sub>12</sub> O	4-Methyl-2-pentanone	100(12)	43(115)	58(37)	41(22)	57(22)
C <sub>6</sub> H <sub>12</sub> O	Ethenyl <i>n</i> -butyl ether	100(5.7)	29(80)	41(59)	56(45)	57(35)
C <sub>6</sub> H <sub>12</sub> O	Ethenyl isobutyl ether	100(5.8)	29(73)	41(65)	57(58)	56(40)
C <sub>6</sub> H <sub>12</sub> O <sub>2</sub>	4-Hydroxy-4-methyl-2-pentanone	116(0.0)	43(149)	15(45)	58(32)	27(14)
C <sub>6</sub> H <sub>12</sub> O <sub>2</sub>	<i>n</i> -Butyl acetate	116(0.03)	43(172)	56(58)	41(30)	27(27)
C <sub>6</sub> H <sub>12</sub> O <sub>2</sub>	<i>n</i> -Propyl propanoate	116(0.03)	57(147)	29(84)	27(57)	75(47)
C <sub>6</sub> H <sub>12</sub> O <sub>2</sub>	Isopropyl propanoate	116(0.26)	57(116)	43(88)	29(54)	27(46)
C <sub>6</sub> H <sub>12</sub> O <sub>2</sub>	Methyl 2,2-dimethylpropanoate	116(3.2)	57(85)	41(32)	29(24)	56(21)
C <sub>6</sub> H <sub>12</sub> O <sub>2</sub>	Ethyl butanoate	116(2.2)	43(50)	71(45)	29(43)	27(31)
C <sub>6</sub> H <sub>12</sub> O <sub>3</sub>	2,4,6-Trimethyl-1,3,5-trioxacyclohexane	132(0.12)	45(196)	43(107)	29(35)	89(23)
C <sub>6</sub> H <sub>12</sub> S	1-Cyclopentyl-1-thiaethane	116(31)	68(72)	41(64)	39(37)	67(37)
C <sub>6</sub> H <sub>12</sub> S	<i>cis</i> -2,5-Dimethylthiacyclopentane	116(32)	101(85)	59(34)	41(26)	74(24)
C <sub>6</sub> H <sub>12</sub> S	<i>trans</i> -2,5-Dimethylthiacyclopentane	116(32)	101(85)	59(34)	74(25)	41(25)
C <sub>6</sub> H <sub>12</sub> S	2-Methylthiacyclohexane	116(42)	101(81)	41(37)	27(32)	67(30)
C <sub>6</sub> H <sub>12</sub> S	3-Methylthiacyclohexane	116(41)	101(55)	41(47)	39(33)	45(28)
C <sub>6</sub> H <sub>12</sub> S	4-Methylthiacyclohexane	116(46)	116(46)	101(44)	41(40)	27(39)
C <sub>6</sub> H <sub>12</sub> S	Thiacycloheptane	116(60)	87(75)	41(66)	67(48)	47(46)
C <sub>6</sub> H <sub>12</sub> S	1-Methylcyclopentanethiol	116(20)	83(76)	55(58)	41(39)	67(33)
C <sub>6</sub> H <sub>12</sub> S	<i>cis</i> -2-Methylcyclopentanethiol	116(32)	55(55)	83(54)	60(48)	41(47)
C <sub>6</sub> H <sub>12</sub> S	<i>trans</i> -2-Methylcyclopentanethiol	116(28)	67(48)	55(46)	41(42)	83(40)
C <sub>6</sub> H <sub>12</sub> S	Cyclohexanethiol	116(21)	55(56)	41(45)	67(35)	83(32)
C <sub>6</sub> H <sub>13</sub> N	Cyclohexylamine	99(8.9)	56(92)	43(25)	28(13)	30(13)
C <sub>6</sub> H <sub>13</sub> N	3-Methylpiperidine	99(23)	44(49)	30(34)	28(27)	57(26)
C <sub>6</sub> H <sub>13</sub> NO	<i>N</i> -Ethylmorpholine	115(2.0)	42(9.8)	57(7.0)	100(5.2)	28(4.3)
C <sub>6</sub> H <sub>14</sub>	2,2-Dimethylbutane	86(0.04)	43(85)	57(82)	71(61)	41(51)
C <sub>6</sub> H <sub>14</sub>	2,3-Dimethylbutane	86(5.3)	43(157)	42(136)	41(49)	27(40)



TABLE 7.76 Condensed Table of Mass Spectra (*Continued*)

Molecular formula	Name	Mass numbers (and intensities) of:				
		Parent peak	Base peak	Three next most intense peaks		
C <sub>6</sub> H <sub>14</sub>	2-Methylpentane	86(4.4)	43(147)	42(78)	41(47)	27(40)
C <sub>6</sub> H <sub>14</sub>	3-Methylpentane	86(3.2)	57(105)	56(80)	41(67)	29(64)
C <sub>6</sub> H <sub>14</sub>	<i>n</i> -Hexane	86(12)	57(87)	43(71)	41(64)	29(55)
C <sub>6</sub> H <sub>14</sub> N <sub>2</sub>	<i>cis</i> -2,5-Dimethylpiperazine	114(0.38)	58(10)	28(7.7)	30(4.7)	44(4.2)
C <sub>6</sub> H <sub>14</sub> O	2-Ethyl-1-butanol	102(0.0)	43(114)	70(40)	29(39)	27(38)
C <sub>6</sub> H <sub>14</sub> O	2-Methyl-1-pentanol	102(0.0)	42(110)	41(40)	29(34)	27(33)
C <sub>6</sub> H <sub>14</sub> O	3-Methyl-1-pentanol	102(0.0)	56(26)	41(20)	29(19)	55(18)
C <sub>6</sub> H <sub>14</sub> O	4-Methyl-2-pentanol	102(0.08)	45(111)	43(34)	41(17)	27(14)
C <sub>6</sub> H <sub>14</sub> O	1-Hexanol	102(0.0)	56(63)	43(52)	41(37)	55(36)
C <sub>6</sub> H <sub>14</sub> O	Ethyl <i>n</i> -butyl ether	102(3.8)	59(108)	31(87)	29(61)	27(42)
C <sub>6</sub> H <sub>14</sub> O	Ethyl <i>sec</i> -butyl ether	102(1.5)	45(150)	73(76)	29(51)	27(39)
C <sub>6</sub> H <sub>14</sub> O	Ethyl isobutyl ether	102(8.7)	59(124)	31(95)	29(53)	27(38)
C <sub>6</sub> H <sub>14</sub> O	Diisopropyl ether	102(1.4)	45(125)	43(66)	87(23)	27(19)
C <sub>6</sub> H <sub>14</sub> O <sub>2</sub>	1,1-Diethoxyethane	118(0.0)	45(132)	73(69)	29(36)	27(27)
C <sub>6</sub> H <sub>14</sub> O <sub>2</sub>	1,2-Diethoxyethane	118(1.2)	31(124)	59(88)	29(72)	45(53)
C <sub>6</sub> H <sub>14</sub> O <sub>3</sub>	<i>bis</i> -(2-Methoxyethyl) ether	134(0.0)	59(140)	29(74)	58(57)	15(56)
C <sub>6</sub> H <sub>14</sub> S	2,2-Dimethyl-3-thiapentane	118(33)	57(147)	41(70)	29(54)	27(40)
C <sub>6</sub> H <sub>14</sub> S	2,4-Dimethyl-3-thiapentne	118(33)	43(94)	61(85)	41(48)	103(44)
C <sub>6</sub> H <sub>14</sub> S	2-Methyl-3-thiahexane	118(206)	43(540)	41(317)	42(301)	27(287)
C <sub>6</sub> H <sub>14</sub> S	4-Methyl-3-thiahexane	118(195)	89(585)	29(343)	27(296)	41(279)
C <sub>6</sub> H <sub>14</sub> S	5-Methyl-3-thiahexane	118(171)	75(520)	41(230)	47(224)	56(217)
C <sub>6</sub> H <sub>14</sub> S	3-Thiaheptane	118(35)	75(55)	29(33)	27(33)	62(28)
C <sub>6</sub> H <sub>14</sub> S	4-Thiaheptane	118(47)	43(86)	89(74)	41(57)	27(55)
C <sub>6</sub> H <sub>14</sub> S	2-Methyl-1-pentanethiol	118(119)	43(96)	41(51)	56(32)	27(31)
C <sub>6</sub> H <sub>14</sub> S	4-Methyl-1-pentanethiol	118(30)	56(142)	41(57)	43(57)	27(32)
C <sub>6</sub> H <sub>14</sub> S	4-Methyl-2-pentanethiol	118(6.3)	43(68)	69(61)	41(56)	84(42)
C <sub>6</sub> H <sub>14</sub> S	2-Methyl-3-pentanethiol	118(20)	41(64)	43(63)	75(50)	27(28)
C <sub>6</sub> H <sub>14</sub> S	1-Hexanethiol	118(16)	56(66)	41(41)	27(40)	43(38)
C <sub>6</sub> H <sub>14</sub> S <sub>2</sub>	2,5-Dimethyl-3,4-dithiahexane	150(31)	43(152)	108(41)	41(36)	27(30)
C <sub>6</sub> H <sub>14</sub> S <sub>2</sub>	5-Methyl-3,4-dithiaheptane	150(14)	29(86)	94(66)	66(57)	27(41)
C <sub>6</sub> H <sub>14</sub> S <sub>2</sub>	6-Methyl-3,4-dithiaheptane	150(4.9)	29(42)	66(40)	122(30)	94(29)
C <sub>6</sub> H <sub>14</sub> S <sub>2</sub>	4,5-Dithiaoctane	150(44)	43(167)	27(65)	41(64)	108(35)
C <sub>6</sub> H <sub>15</sub> N	Triethylamine	101(21)	86(134)	30(46)	27(36)	58(35)
C <sub>6</sub> H <sub>15</sub> N	Di- <i>n</i> -propylamine	101(7.1)	30(89)	72(70)	44(36)	43(28)
C <sub>6</sub> H <sub>15</sub> N	Diisopropylamine	101(5.0)	44(171)	86(52)	58(24)	42(22)
C <sub>6</sub> H <sub>16</sub> Pb	Dimethyldiethyllead	296(0.98)	267(89)	223(83)	208(79)	221(44)
C <sub>7</sub> F <sub>14</sub>	Tetradecafluoromethylcyclohexane	350(0.0)	69(244)	131(107)	181(48)	100(38)
C <sub>7</sub> F <sub>16</sub>	Hexadecafluoroheptane	388(0.0)	69(330)	119(89)	169(68)	131(44)
C <sub>7</sub> H <sub>5</sub> N	Benzonitrile	103(246)	103(246)	76(80)	50(42)	51(24)
C <sub>7</sub> H <sub>7</sub> Br	1-Methyl-2-bromobenzene	170(48)	91(97)	172(46)	39(21)	63(20)
C <sub>7</sub> H <sub>7</sub> Br	1-Methyl-4-bromobenzene	170(46)	91(97)	172(45)	39(20)	65(19)
C <sub>7</sub> H <sub>7</sub> Cl	1-Methyl-2-chlorobenzene	126(44)	91(121)	63(20)	39(19)	89(18)
C <sub>7</sub> H <sub>7</sub> Cl	1-Methyl-3-chlorobenzene	126(51)	91(120)	63(19)	39(18)	128(16)
C <sub>7</sub> H <sub>7</sub> Cl	1-Methyl-4-chlorobenzene	126(44)	91(120)	125(19)	63(18)	39(17)
C <sub>7</sub> H <sub>7</sub> F	1-Methyl-3-fluorobenzene	110(79)	109(129)	83(17)	57(12)	39(12)
C <sub>7</sub> H <sub>7</sub> F	1-Methyl-4-fluorobenzene	110(73)	109(122)	83(16)	57(12)	39(9.3)
C <sub>7</sub> H <sub>8</sub>	Methylbenzene (toluene)	92(82)	91(108)	39(20)	65(14)	51(10)
C <sub>7</sub> H <sub>8</sub> S	1-Phenyl-1-thiaethane	124(76)	124(76)	109(34)	78(25)	91(19)
C <sub>7</sub> H <sub>9</sub> N	2,4-Dimethylpyridine	107(76)	107(76)	106(29)	79(16)	92(13)



TABLE 7.76 Condensed Table of Mass Spectra (Continued)

Molecular formula	Name	Mass numbers (and intensities) of:				
		Parent peak	Base peak	Three next most intense peaks		
C <sub>7</sub> H <sub>10</sub> S	2,3,4-Trimethylthiophene	126(50)	111(81)	125(47)	45(22)	39(18)
C <sub>7</sub> H <sub>12</sub>	Ethenylcyclopentane	96(13)	67(118)	39(44)	68(38)	54(35)
C <sub>7</sub> H <sub>12</sub>	Ethylidenecyclopentane	96(40)	67(180)	39(44)	41(30)	27(30)
C <sub>7</sub> H <sub>12</sub>	Bicyclo[2.2.1]heptane	96(12)	67(64)	68(50)	81(44)	54(30)
C <sub>7</sub> H <sub>12</sub>	3-Ethylcyclopentene	96(29)	67(193)	39(36)	41(35)	27(26)
C <sub>7</sub> H <sub>12</sub>	1-Methylcyclohexene	96(32)	81(83)	68(38)	67(37)	39(33)
C <sub>7</sub> H <sub>12</sub>	4-Methylcyclohexene	96(28)	81(84)	54(50)	39(44)	55(34)
C <sub>7</sub> H <sub>12</sub>	4-Methyl-2-hexyne	96(13)	81(71)	67(52)	41(48)	39(35)
C <sub>7</sub> H <sub>12</sub>	5-Methyl-2-hexyne	96(42)	43(49)	81(43)	27(39)	39(38)
C <sub>7</sub> H <sub>12</sub>	1-Heptyne	96(0.44)	41(75)	81(70)	29(65)	27(47)
C <sub>7</sub> H <sub>14</sub>	1,1,2,2,-Tetramethylcyclopropane	98(21)	55(92)	83(90)	41(69)	39(41)
C <sub>7</sub> H <sub>14</sub>	<i>cis</i> -1,2-Dimethylcyclopentane	98(19)	56(85)	70(77)	41(65)	55(65)
C <sub>7</sub> H <sub>14</sub>	<i>trans</i> -1,2-Dimethylcyclopentane	98(25)	56(93)	41(63)	55(61)	70(54)
C <sub>7</sub> H <sub>14</sub>	<i>cis</i> -1,3-Dimethylcyclopentane	98(12)	56(81)	70(78)	41(64)	55(59)
C <sub>7</sub> H <sub>14</sub>	<i>trans</i> -1,3-Dimethylcyclopentane	98(13)	56(81)	70(68)	41(63)	55(58)
C <sub>7</sub> H <sub>14</sub>	1,1-Dimethylcyclopentane	98(6.7)	56(81)	55(63)	69(56)	41(55)
C <sub>7</sub> H <sub>14</sub>	Ethylcyclopentane	98(14)	69(83)	41(78)	68(60)	55(46)
C <sub>7</sub> H <sub>14</sub>	Methylcyclohexane	98(41)	83(94)	55(78)	41(55)	42(34)
C <sub>7</sub> H <sub>14</sub>	Cycloheptane	98(37)	41(57)	55(54)	56(50)	42(49)
C <sub>7</sub> H <sub>14</sub>	2,3,3-Trimethyl-1-butene	98(20)	83(101)	55(83)	41(61)	39(33)
C <sub>7</sub> H <sub>14</sub>	3-Methyl-2-ethyl-1-butene	98(22)	41(71)	69(71)	55(62)	27(38)
C <sub>7</sub> H <sub>14</sub>	2,3-Dimethyl-1-pentene	98(13)	41(92)	69(86)	55(40)	39(35)
C <sub>7</sub> H <sub>14</sub>	2,4-Dimethyl-1-pentene	98(9.1)	56(117)	43(68)	41(61)	39(39)
C <sub>7</sub> H <sub>14</sub>	3,3-Dimethyl-1-pentene	98(9.4)	69(104)	41(85)	55(42)	27(36)
C <sub>7</sub> H <sub>14</sub>	3,4-Dimethyl-1-pentene	98(0.61)	56(75)	55(62)	43(55)	41(54)
C <sub>7</sub> H <sub>14</sub>	4,4-Dimethyl-1-pentene	98(2.6)	57(161)	41(86)	29(52)	55(49)
C <sub>7</sub> H <sub>14</sub>	3-Ethyl-1-pentene	98(19)	41(116)	69(91)	27(43)	39(37)
C <sub>7</sub> H <sub>14</sub>	2,3-Dimethyl-2-pentene	98(31)	83(80)	55(75)	41(63)	39(34)
C <sub>7</sub> H <sub>14</sub>	2,4-Dimethyl-2-pentene	98(26)	83(97)	55(71)	41(52)	39(34)
C <sub>7</sub> H <sub>14</sub>	3,4-Dimethyl- <i>cis</i> -2-pentene	98(30)	83(87)	55(82)	41(52)	27(32)
C <sub>7</sub> H <sub>14</sub>	3,4-Dimethyl- <i>trans</i> -2-pentene	98(31)	83(89)	55(83)	41(52)	27(34)
C <sub>7</sub> H <sub>14</sub>	4,4-Dimethyl- <i>cis</i> -2-pentene	98(27)	83(96)	55(92)	41(62)	39(35)
C <sub>7</sub> H <sub>14</sub>	4,4-Dimethyl- <i>trans</i> -2-pentene	98(28)	83(105)	55(89)	41(58)	39(31)
C <sub>7</sub> H <sub>14</sub>	3-Ethyl-2-pentene	98(33)	41(86)	69(80)	55(74)	27(33)
C <sub>7</sub> H <sub>14</sub>	2-Methyl-1-hexene	98(4.6)	56(105)	41(54)	27(30)	39(27)
C <sub>7</sub> H <sub>14</sub>	3-Methyl-1-hexene	98(7.7)	55(76)	41(60)	69(57)	56(48)
C <sub>7</sub> H <sub>14</sub>	4-Methyl-1-hexene	98(4.9)	41(98)	57(94)	56(80)	29(70)
C <sub>7</sub> H <sub>14</sub>	5-Methyl-1-hexene	98(1.6)	56(91)	41(75)	55(47)	27(42)
C <sub>7</sub> H <sub>14</sub>	2-Methyl-2-hexene	98(28)	69(113)	41(99)	27(36)	39(33)
C <sub>7</sub> H <sub>14</sub>	3-Methyl- <i>cis</i> -2-hexene	98(30)	41(95)	69(90)	55(42)	27(36)
C <sub>7</sub> H <sub>14</sub>	4-Methyl- <i>trans</i> -2-hexene	98(23)	69(118)	41(106)	55(40)	39(35)
C <sub>7</sub> H <sub>14</sub>	5-Methyl-2-hexene	98(13)	56(90)	55(74)	43(71)	41(57)
C <sub>7</sub> H <sub>14</sub>	2-Methyl- <i>trans</i> -3-hexene	98(24)	69(86)	41(74)	55(62)	56(37)
C <sub>7</sub> H <sub>14</sub>	3-Methyl- <i>cis</i> -3-hexene	98(28)	69(98)	41(82)	39(33)	27(33)
C <sub>7</sub> H <sub>14</sub>	3-Methyl- <i>trans</i> -3-hexene	98(28)	69(97)	41(86)	55(63)	39(35)
C <sub>7</sub> H <sub>14</sub>	1-Heptene	98(15)	41(91)	56(79)	29(64)	55(54)
C <sub>7</sub> H <sub>14</sub>	<i>trans</i> -2-Heptene	98(27)	55(64)	56(59)	41(50)	27(35)
C <sub>7</sub> H <sub>14</sub>	<i>trans</i> -3-Heptene	98(27)	41(98)	56(65)	69(55)	55(47)
C <sub>7</sub> H <sub>14</sub> O	2,4-Dimethyl-3-pentanone	114(13)	43(226)	71(62)	27(49)	41(42)

TABLE 7.76 Condensed Table of Mass Spectra (*Continued*)

Molecular formula	Name	Mass numbers (and intensities) of:				
		Parent peak	Base peak	Three next most intense peaks		
C <sub>7</sub> H <sub>14</sub> O <sub>2</sub>	<i>n</i> -Butyl propanoate	130(0.03)	57(152)	29(98)	56(54)	27(52)
C <sub>7</sub> H <sub>14</sub> O <sub>2</sub>	Isobutyl propanoate	130(0.07)	57(187)	29(87)	56(27)	27(47)
C <sub>7</sub> H <sub>14</sub> O <sub>2</sub>	<i>n</i> -Propyl <i>n</i> -butanoate	130(0.05)	43(96)	71(90)	27(54)	89(48)
C <sub>7</sub> H <sub>14</sub> O <sub>3</sub>	<i>n</i> -Propyl carbonate	146(0.02)	43(171)	27(61)	63(55)	41(49)
C <sub>7</sub> H <sub>14</sub> S	<i>cis</i> -2-Methylcyclohexanethiol	130(28)	55(138)	97(70)	81(44)	41(44)
C <sub>7</sub> H <sub>15</sub> N	2,6-Dimethylpiperidine	113(5.3)	98(73)	44(43)	42(34)	28(26)
C <sub>7</sub> H <sub>16</sub>	2,2,3-Trimethylbutane	100(0.03)	57(110)	43(84)	56(67)	41(64)
C <sub>7</sub> H <sub>16</sub>	2,2-Dimethylpentane	100(0.06)	57(130)	43(95)	41(59)	56(52)
C <sub>7</sub> H <sub>16</sub>	2,3-Dimethylpentane	100(2.1)	43(94)	56(93)	57(67)	41(64)
C <sub>7</sub> H <sub>16</sub>	2,4-Dimethylpentane	100(1.6)	43(139)	57(93)	41(59)	56(50)
C <sub>7</sub> H <sub>16</sub>	3,3-Dimethylpentane	100(0.03)	43(166)	71(103)	27(38)	41(36)
C <sub>7</sub> H <sub>16</sub>	3-Ethylpentane	100(3.1)	43(175)	70(77)	70(77)	29(45)
C <sub>7</sub> H <sub>16</sub>	2-Methylhexane	100(5.9)	43(154)	42(59)	41(57)	85(49)
C <sub>7</sub> H <sub>16</sub>	3-Methylhexane	100(4.0)	43(110)	57(52)	71(52)	41(50)
C <sub>7</sub> H <sub>16</sub>	<i>n</i> -Heptane	100(17)	43(126)	41(65)	57(60)	29(58)
C <sub>7</sub> H <sub>16</sub> O	2-Heptanol	116(0.01)	45(131)	43(29)	27(25)	29(23)
C <sub>7</sub> H <sub>16</sub> O	3-Heptanol	116(0.01)	59(61)	69(41)	41(29)	31(25)
C <sub>7</sub> H <sub>16</sub> O	4-Heptanol	116(0.02)	55(102)	73(72)	43(45)	27(32)
C <sub>7</sub> H <sub>16</sub> O	<i>n</i> -Propyl <i>n</i> -butyl ether	116(3.7)	43(120)	57(102)	41(51)	29(49)
C <sub>7</sub> H <sub>16</sub> O <sub>2</sub>	Di- <i>n</i> -propoxymethane	132(0.58)	43(194)	73(114)	27(45)	41(34)
C <sub>7</sub> H <sub>16</sub> O <sub>2</sub>	Diisopropoxymethane	132(0.16)	43(133)	45(84)	73(71)	27(28)
C <sub>7</sub> H <sub>16</sub> O <sub>2</sub>	1,1-Diethoxypropane	132(0.0)	59(138)	47(88)	87(84)	29(74)
C <sub>7</sub> H <sub>16</sub> S	2,2,4-Trimethyl-3-thiapentane	132(30)	57(149)	41(74)	29(35)	43(32)
C <sub>7</sub> H <sub>16</sub> S	2,4-Dimethyl-3-thiahexane	132(30)	61(94)	103(60)	41(51)	43(46)
C <sub>7</sub> H <sub>16</sub> S	2-Thiaoctane	132(34)	61(73)	56(53)	27(46)	41(44)
C <sub>7</sub> H <sub>16</sub> S	1-Heptanethiol	132(14)	41(48)	27(40)	56(39)	70(38)
C <sub>7</sub> H <sub>18</sub> Pb	Methyltriethyllead	310(0.84)	281(86)	208(76)	223(66)	237(60)
C <sub>7</sub> H <sub>18</sub> Pb	<i>n</i> -Butyltrimethyllead	310(0.14)	253(76)	223(75)	208(68)	295(52)
C <sub>7</sub> H <sub>18</sub> Pb	<i>sec</i> -Butyltrimethyllead	310(1.8)	253(94)	223(85)	208(74)	251(45)
C <sub>7</sub> H <sub>18</sub> Pb	<i>tert</i> -Butyltrimethyllead	310(0.09)	252(95)	223(82)	208(65)	250(46)
C <sub>8</sub> H <sub>10</sub>	1,2-Dimethylbenzene	106(52)	91(91)	105(22)	39(15)	51(14)
C <sub>8</sub> H <sub>10</sub>	1,3-Dimethylbenzene	106(58)	91(93)	105(26)	39(17)	51(14)
C <sub>8</sub> H <sub>10</sub>	1,4-Dimethylbenzene	106(52)	91(85)	105(25)	51(13)	39(13)
C <sub>8</sub> H <sub>10</sub>	Ethylbenzene	106(45)	91(146)	51(19)	39(14)	65(12)
F <sub>3</sub> N	Nitrogen trifluoride	71(10)	52(33)	33(13)	14(3.0)	19(2.7)
HCl	Hydrogen chloride	36(54)	36(54)	38(17)	35(9.2)	37(2.9)
H <sub>2</sub> S	Hydrogen sulfide	34(75)	34(75)	32(33)	33(32)	1(4.1)
H <sub>3</sub> P	Ammonia	17(32)	17(32)	16(26)	15(2.4)	14(0.7)
H <sub>3</sub> N	Phosphine	34(59)	34(59)	33(20)	31(19)	32(7.5)
H <sub>4</sub> N <sub>2</sub>	Hydrazine	32(48)	32(48)	31(23)	29(19)	30(15)
NO	Nitric oxide	30(76)	30(76)	14(5.7)	15(1.8)	16(1.1)
NO <sub>2</sub>	Nitrogen dioxide	46(6.6)	30(18)	16(4.0)	14(1.7)	47(0.02)
N <sub>2</sub>	Nitrogen	28(65)	28(65)	14(3.3)	29(0.47)	...
N <sub>2</sub> O	Nitrous oxide	44(60)	44(60)	30(19)	14(7.8)	28(6.5)
O <sub>2</sub>	Oxygen	32(54)	32(54)	16(2.7)	28(1.7)	34(0.22)
O <sub>2</sub> S	Sulfur dioxide	64(47)	64(47)	48(23)	32(4.9)	16(2.4)

**Source:** L. Meites, ed., *Handbook of Analytical Chemistry*, McGraw-Hill, New York, 1963. J. A. Dean, ed., *Analytical Chemistry Handbook*, McGraw-Hill, New York, 1995.