Supplementary Material

Table 1: H_2O molecule as example. Water has 3N-6=3 frequencies. So we need three force constants. the f_4 is automatically fixed from f_1,f_2 and f_3. In C_1 symmetry, all the off-diagonal elements are fixed by the diagonal force constants because 3N-6=number of frequencies=
number of diagonal force constants.

$$\begin{bmatrix} -0.719 & -0.719 & -0.014 \\ 0.048 & 0.048 & -1.520 \\ 0.731 & -0.731 & 0.000 \end{bmatrix} \begin{bmatrix} 1 & 3 & 4 \\ 3 & 1 & 4 \\ 4 & 4 & 2 \end{bmatrix} \begin{bmatrix} -0.719 & 0.048 & 0.731 \\ -0.719 & 0.048 & -0.731 \\ -0.014 & -1.520 & 0.000 \end{bmatrix} = \begin{bmatrix} 1 & 4 & 0 \\ 4 & 2 & 0 \\ 0 & 0 & 3 \end{bmatrix}$$

$$L^T \qquad F \qquad L \qquad = \qquad \Lambda$$

$1=\lambda_1= 1.035*f_1+0.000*f_2+1.035*f_3+0.041*f_4$
$2=\lambda_2= 0.005*f_1+2.312*f_2+0.005*f_3-0.294*f_4$
$3=\lambda_3= 1.070*f_1+0.000*f_2-1.070*f_3+0.000*f_4$
$4=0 =-0.032*f_1+0.010*f_2-0.032*f_3+1.000*f_4$

When we have several equations like 4, they constitute a set of linear homogeneous equations which could be solved by Gaussian elimination to get relations among the force constants.

Table 2: Scaled frequencies of Benzene after fitting to the experimental frequencies. The scaled frequencies are in parenthesis followed by experimental values [11].

A_{1g}
3074(3078); 993(995);
A_{2g}
1350(1365);
B_{2g}
990(992); 707(707);
E_{1g}
847(846);
E_{2g}
3057(3055); 1600(1601); 1178(1172); 608(608);
A_{2u}
674(677);
B_{1u}
3057(3048); 1010(1005);
B_{2u}
1310(1315); 1149(1155);
E_{1u}
3065(3069); 1484(1474); 1038(1039);
E_{2u}
967(966); 399(399);
———————————-
RMS error 5 cm^{-1}

Table S1: The local coordinates of benzene

1 1 1 1.000000
1 1 ν C_{ 1} C_{ 2}
2 1 2 1.000000
2 1 ν C_{ 2} C_{ 3}
3 1 3 1.000000
3 1 ν C_{ 3} C_{ 4}
4 1 4 1.000000
4 1 ν C_{ 4} C_{ 5}
5 1 5 1.000000
5 1 ν C_{ 5} C_{ 6}
6 1 6 1.000000
6 1 ν C_{ 6} C_{ 1}
7 1 7 1.000000
7 1 ν C_{ 1} H_{ 7}
8 1 8 1.000000
8 1 ν C_{ 2} H_{ 8}
9 1 9 1.000000
9 1 ν C_{ 3} H_{ 9}
10 1 10 1.000000
10 1 ν C_{ 4} H_{10}
11 1 11 1.000000
11 1 ν C_{ 5} H_{11}
12 1 12 1.000000
12 1 ν C_{ 6} H_{12}
13 1 13 1.000000
13 1 δ H_{ 7} C_{ 1} C_{ 2}
14 1 14 1.000000
14 1 δ H_{ 8} C_{ 2} C_{ 3}
15 1 15 1.000000
15 1 δ H_{ 9} C_{ 3} C_{ 4}
16 1 16 1.000000
16 1 δ H_{10} C_{ 4} C_{ 5}
17 1 17 1.000000
17 1 δ H_{11} C_{ 5} C_{ 6}
18 1 18 1.000000
18 1 δ H_{12} C_{ 6} C_{ 1}
19 6 19 0.408248 20 -0.408248 21 0.408248

19 6 δ C_{ 1} C_{ 2} C_{ 3} δ C_{ 2} C_{ 3} C_{ 4}
δ C_{3} C_{4}C_{5}
22 -0.408248 23 0.408248 24 -0.408248
δ C_{ 4} C_{ 5} C_{ 6} δ C_{ 5} C_{ 6} C_{ 1}
δ C_{6} C_{1} C_{2}
20 6 19 0.577350 20 -0.288675 21 -0.288675
20 6 δ C_{ 1} C_{ 2} C_{ 3} δ C_{ 2} C_{ 3} C_{ 4}
δ C_{3} C_{4} C_{5}
22 0.577350 23 -0.288675 24 -0.288675
δ C_{ 4} C_{ 5} C_{ 6} δ C_{ 5} C_{ 6} C_{ 1}
δ C_{ 6} C_{ 1} C_{ 2}
21 4 20 0.500000 21 -0.500000 23 0.500000
21 4 δ C_{ 2} C_{ 3} C_{ 4} δ C_{ 3} C_{ 4} C_{ 5}
δ C_{ 5} C_{ 6} C_{ 1}
24 -0.500000
δ C_{ 6} C_{ 1} C_{ 2}
22 1 25 1.000000
22 1 γ H_{ 7} C_{ 1} C_{ 2} C_{ 6}
23 1 26 1.000000
23 1 γ H_{ 8} C_{ 2} C_{ 3} C_{ 1}
24 1 27 1.000000
24 1 γ H_{ 9} C_{ 3} C_{ 4} C_{ 2}
25 1 28 1.000000
25 1 γ H_{10} C_{ 4} C_{ 5} C_{ 3}
26 1 29 1.000000
26 1 γ H_{11} C_{ 5} C_{ 6} C_{ 4}
27 1 30 1.000000
27 1 γ H_{12} C_{ 6} C_{ 1} C_{ 5}
28 6 31 0.408248 32 -0.408248 33 0.408248
28 6 τ C_{ 1} C_{ 2} τ C_{ 2} C_{ 3}
τ C_{ 3} C_{ 4}
34 -0.408248 35 0.408248 36 -0.408248
τ C_{ 4} C_{ 5} τ C_{ 5} C_{ 6}
τ C_{ 6} C_{ 1}
29 6 31 -0.288675 32 0.577350 33 -0.288675
29 6 τ C_{ 1} C_{ 2} τ C_{ 2} C_{ 3}
τ C_{ 3} C_{ 4}

34 -0.288675 35 0.577350 36 -0.288675

τ C_{ 4} C_{ 5} τ C_{ 5} C_{ 6}

τ C_{ 6} C_{ 1}

30 4 31 0.500000 33 -0.500000 34 0.500000

30 4 τ C_{ 1} C_{ 2} τ C_{ 3} C_{ 4}

τ C_{ 4} C_{ 5}

36 -0.500000

τ C_{ 6} C_{ 1}

Table S2: Symbolic local F (30x30) for benzene.
Total number of force constants:42

	1	2	3	4	5	6	7	8	9	10	11
1	1	9	10	11	10	9	12	12	13	14	14
2	9	1	9	10	11	10	13	12	12	13	14
3	10	9	1	9	10	11	14	13	12	12	13
4	11	10	9	1	9	10	14	14	13	12	12
5	10	11	10	9	1	9	13	14	14	13	12
6	9	10	11	10	9	1	12	13	14	14	13
7	12	13	14	14	13	12	2	15	16	17	16
8	12	12	13	14	14	13	15	2	15	16	17
9	13	12	12	13	14	14	16	15	2	15	16
10	14	13	12	12	13	14	17	16	15	2	15
11	14	14	13	12	12	13	16	17	16	15	2
12	13	14	14	13	12	12	15	16	17	16	15
13	18	19	20	-20	-19	-18	0	21	22	0	-22
14	-18	18	19	20	-20	-19	-21	0	21	22	0
15	-19	-18	18	19	20	-20	-22	-21	0	21	22
16	-20	-19	-18	18	19	20	0	-22	-21	0	21
17	20	-20	-19	-18	18	19	22	0	-22	-21	0
18	19	20	-20	-19	-18	18	21	22	0	-22	-21
19	0	0	0	0	0	0	26	-26	26	-26	26
20	27	27	28	27	27	28	29	30	29	29	30
21	32	-32	0	32	-32	0	33	0	-33	33	0
22	0	0	0	0	0	0	0	0	0	0	0
23	0	0	0	0	0	0	0	0	0	0	0
24	0	0	0	0	0	0	0	0	0	0	0
25	0	0	0	0	0	0	0	0	0	0	0
26	0	0	0	0	0	0	0	0	0	0	0
27	0	0	0	0	0	0	0	0	0	0	0
28	0	0	0	0	0	0	0	0	0	0	0
29	0	0	0	0	0	0	0	0	0	0	0
30	0	0	0	0	0	0	0	0	0	0	0

	12	13	14	15	16	17	18	19	20	21	22
12	2	-21	-22	0	22	21	0	-26	29	-33	0
13	-21	3	23	24	25	24	23	0	31	34	0
14	-22	23	3	23	24	25	24	0	0	35	0
15	0	24	23	3	23	24	25	0	-31	34	0
16	22	25	24	23	3	23	24	0	31	34	0

17	21	24	25	24	23	3	23	0	0	35	0
18	0	23	24	25	24	23	3	0	-31	34	0
19	-26	0	0	0	0	0	0	4	0	0	0
20	29	31	0	-31	31	0	-31	0	5	0	0
21	-33	34	35	34	34	35	34	0	0	5	0
22	0	0	0	0	0	0	0	0	0	0	6
23	0	0	0	0	0	0	0	0	0	0	36
24	0	0	0	0	0	0	0	0	0	0	37
25	0	0	0	0	0	0	0	0	0	0	38
26	0	0	0	0	0	0	0	0	0	0	37
27	0	0	0	0	0	0	0	0	0	0	36
28	0	0	0	0	0	0	0	0	0	0	39
29	0	0	0	0	0	0	0	0	0	0	0
30	0	0	0	0	0	0	0	0	0	0	41

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	23	24	25	26	27	28	29	30
23	6	36	37	38	37	-39	40	42
24	36	6	36	37	38	39	-40	42
25	37	36	6	36	37	-39	0	41
26	38	37	36	6	36	39	40	42
27	37	38	37	36	6	-39	-40	42
28	-39	39	-39	39	-39	7	0	0
29	40	-40	0	40	-40	0	8	0
30	42	42	41	42	42	0	0	8

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Table S3: The relations between the off-diagonal force constants and the 20 independent force constants. The force constant numbers are as given in Figure S2.

The meaning of these numbers is as follows:

f(33) = 0.0133*f(20)-0.0103*f(18)-0.0006*f(17)+0.0006*f(16)+0.0006*f(15)+ 0.0033*f(11)-0.0033*f(10)-0.0033*f(9)+0.0033*f(1)-0.0006*f(2)+0.0538*f(5)

We get 22 dependent force constants in terms of the other 20 independent force constants.

1 33 1.0000
20 0.0103 18 -0.0103 17 -0.0006 16 0.0006 15 0.0006 11 0.0033
10 -0.0033 9 -0.0033 1 0.0033 2 -0.0006 5 0.0538 -1 0.0000
2 30 1.0000
20 -0.0119 18 0.0119 17 0.0007 16 -0.0007 15 -0.0007 11 -0.0039
10 0.0039 9 0.0039 1 -0.0039 2 0.0007 5 -0.0621 -1 0.0000
3 29 1.0000
20 0.0059 18 -0.0059 17 -0.0003 16 0.0003 15 0.0003 11 0.0019
10 -0.0019 9 -0.0019 1 0.0019 2 -0.0003 5 0.0310 -1 0.0000
4 21 1.0000
19 0.0521 20 0.0185 18 0.0336 17 -0.0013 16 -0.0032 15 0.0013
11 -0.0010 10 0.0061 9 0.0010 1 -0.0061 2 0.0032 5 0.0046
-1 0.0000
5 22 1.0000
19 0.0521 20 0.0336 18 0.0185 17 -0.0032 16 -0.0013 15 0.0032
11 0.0061 10 -0.0010 9 -0.0061 1 0.0010 2 0.0013 5 -0.0046
-1 0.0000
6 31 1.0000
20 -0.0444 18 0.0444 17 -0.0000 16 0.0000 15 0.0000 11 0.0210
10 -0.0210 9 -0.0210 1 0.0210 2 -0.0000 5 -0.0481 -1 0.0000
7 35 1.0000
20 -0.0512 18 0.0512 17 -0.0000 16 0.0000 15 0.0000 11 0.0242
10 -0.0242 9 -0.0242 1 0.0242 2 -0.0000 5 -0.0555 -1 0.0000
8 34 1.0000
20 0.0256 18 -0.0256 17 0.0000 16 -0.0000 15 -0.0000 11 -0.0121
10 0.0121 9 0.0121 1 -0.0121 2 0.0000 5 0.0278 -1 0.0000
9 32 1.0000
20 0.2818 18 -0.2818 17 -0.0000 16 0.0000 15 0.0000 11 0.0526
10 -0.0526 9 -0.0526 1 0.0526 2 -0.0000 5 -0.4064 -1 0.0000
10 25 1.0000
19 0.8804 20 -0.3963 18 -0.3963 17 -0.0006 16 -0.0006 15 0.0006
11 0.1510 10 -0.0031 9 0.0031 1 -0.1510 2 0.0006 3 1.0000
-1 0.0000
11 24 1.0000
19 0.2421 20 0.5067 18 -0.2646 17 -0.0004 16 -0.0004 15 0.0004
11 0.0111 10 0.1384 9 -0.0111 1 -0.1384 2 0.0004 3 1.0000

5 0.0192 -1 0.0000
12 23 1.0000
19 0.6383 20 -0.1317 18 -0.9029 17 -0.0001 16 -0.0002 15 0.0001
11 0.0127 10 -0.0142 9 0.1415 1 -0.1399 2 0.0002 3 1.0000
5 0.0192 -1 0.0000
13 27 1.0000
20 -0.1627 18 0.1627 17 0.0000 16 -0.0000 15 -0.0000 11 -0.0304
10 0.0304 9 0.0304 1 -0.0304 2 0.0000 5 0.2346 -1 0.0000
14 28 1.0000
20 0.3254 18 -0.3254 17 -0.0000 16 0.0000 15 0.0000 11 0.0607
10 -0.0607 9 -0.0607 1 0.0607 2 -0.0000 5 -0.4693 -1 0.0000
15 26 1.0000
17 -0.0015 16 0.0030 15 -0.0030 2 0.0015 4 0.0776 -1 0.0000
16 14 1.0000
19 0.0340 20 0.0449 18 -0.0109 17 -0.0412 16 -0.0493 15 -0.0075
11 0.0462 10 0.0405 9 -0.0037 1 0.0020 2 0.0005 5 -0.0200
-1 0.0000
17 12 1.0000
19 -0.0340 20 0.0109 18 -0.0449 17 0.0005 16 -0.0075 15 -0.0493
11 0.0020 10 -0.0037 9 0.0405 1 0.0462 2 -0.0412 5 -0.0200
-1 0.0000
18 13 1.0000
20 -0.0558 18 0.0558 17 -0.0080 16 -0.0407 15 -0.0407 11 -0.0058
10 0.0483 9 0.0483 1 -0.0058 2 -0.0080 5 0.0400 -1 0.0000
19 40 1.0000
38 0.1536 37 -0.1536 36 -0.1536 6 0.1536 8 0.1610 -1 0.0000
20 42 1.0000
38 -0.0887 37 0.0887 36 0.0887 6 -0.0887 8 -0.0930 -1 0.0000
21 41 1.0000
38 0.1774 37 -0.1774 36 -0.1774 6 0.1774 8 0.1859 -1 0.0000
22 39 1.0000
38 -0.1321 37 0.2642 36 -0.2642 6 0.1321 7 0.1811 -1 0.0000

Table S4: The final scaled force constants obtained after fitting the calculated frequencies to the experimental ones. Diagonal scale factors 8

1	1	1	6.9729	6.7378	0.9663
2	2	7	5.5592	5.1464	0.9257
3	3	13	1.0478	1.0276	0.9808
4	4	19	1.2626	1.2626	1.0000
5	5	20	1.2849	1.2499	0.9728
6	6	22	0.4631	0.4493	0.9704
7	7	28	0.4118	0.3884	0.9431
8	8	29	0.3308	0.3125	0.9447

Off-diagonal scale factors (independent)

1	9	0	0.7008	0.6891	0.9833
2	10	0	-0.4217	-0.4217	1.0000
3	11	0	0.3833	0.3627	0.9464
4	15	0	0.0070	0.0053	0.7518
5	16	0	0.0034	0.0034	1.0000
6	17	0	0.0007	0.0005	0.7046
7	18	0	0.2384	0.2378	0.9978
8	19	0	0.0250	0.0176	0.7030
9	20	0	-0.0285	-0.0285	1.0000
10	36	0	-0.0737	-0.0678	0.9192
11	37	0	0.0033	0.0024	0.7103
12	38	0	-0.0218	-0.0199	0.9157

Off-diagonal scale factors (dependent)

1	33	0	0.0866	0.0841	0.9718
2	30	0	-0.0999	-0.0972	0.9722
3	29	0	0.0500	0.0486	0.9718
4	21	0	-0.0120	-0.0125	1.0388
5	22	0	0.0117	0.0106	0.9088
6	31	0	0.0984	0.0950	0.9649
7	35	0	0.1136	0.1097	0.9649
8	34	0	-0.0568	-0.0548	0.9649
9	32	0	-0.2253	-0.2238	0.9931
10	25	0	-0.0021	0.0036	-1.7245
11	24	0	-0.0234	-0.0135	0.5798
12	23	0	0.0121	0.0180	1.4837
13	27	0	0.1301	0.1292	0.9930
14	28	0	-0.2602	-0.2584	0.9931
15	26	0	0.1064	0.1057	0.9942
16	14	0	-0.0139	-0.0150	1.0801
17	12	0	0.0859	0.0926	1.0780
18	13	0	-0.0077	-0.0049	0.6288
19	40	0	0.1319	0.1263	0.9580
20	42	0	-0.0761	-0.0729	0.9580
21	41	0	0.1523	0.1459	0.9580
22	39	0	0.1590	0.1509	0.9489