

## Homework 10: IR and Raman

1. For NaI,  $\tilde{\nu}_e = 286.0 \text{ cm}^{-1}$  and  $\chi_e \tilde{\nu}_e = 0.750 \text{ cm}^{-1}$ . Calculate the force constant, zero-point energy, and dissociation energy,  $D_o$ .

*Answers:* The reduced mass is:

$$\mu_{\text{NaI}} = \frac{(22.9898)(126.9045)}{22.9898+126.9045} (\text{g mol}^{-1}) \frac{1}{N_A} (1\text{kg}/1000 \text{ g}) = 3.2321 \times 10^{-26} \text{ kg}$$

The spectroscopic constants are:

with Eq. 27.5.4:  $\tilde{\kappa} = 4\pi^2 c^2 \tilde{\nu}_e^2 \mu = 4\pi^2 (2.99792 \times 10^{10} \text{ cm s}^{-1})^2 (286.0 \text{ cm}^{-1})^2 (3.2321 \times 10^{-26} \text{ kg})$   
 $\tilde{\kappa} = 93.81 \text{ N m}^{-1}$

with Eq. 27.5.8:  $ZPE = \tilde{G}_o = \frac{1}{2} \tilde{\nu}_e - \frac{1}{4} \tilde{\nu}_e \chi_e = \frac{1}{2}(286.0 \text{ cm}^{-1}) - \frac{1}{4}(0.750 \text{ cm}^{-1})$   
 $= 142.8 \text{ cm}^{-1} = 0.0177 \text{ eV}$

with Eq. 27.5.18:  $\tilde{D}_e = \tilde{\nu}_e^2 / 4\chi_e \tilde{\nu}_e = (286.0 \text{ cm}^{-1} \text{ cm}^{-1})^2 / (4(0.750 \text{ cm}^{-1}))$   
 $\tilde{D}_e = 27,265 \text{ cm}^{-1}$

with Eq. 27.5.12:  $\tilde{D}_o = \tilde{D}_e - ZPE = 27,265 \text{ cm}^{-1} - 142.8 \text{ cm}^{-1} = 27122. \text{ cm}^{-1}$   
 $\tilde{D}_o = 3.362 \text{ eV} = 324.4 \text{ kJ mol}^{-1}$

2. Calculate the normal mode frequencies of formaldehyde at B3LYP/6-31G\* and compare to the experimental frequencies. Provide a printout of the thermodynamic corrections to the electronic energy. See the attached instructions for this problem.

*Answer:* The calculated and experimental modes are in good agreement on the basis of mode symmetry and relative order. The percent errors both before and after correction by 0.9 are shown below:

	cm-1	exp	B3LYP	error %	x0.9	error %	exp/calc	x0.961	error %
a1	CH2 symmetric-stretch	2783	2916.3	4.79	2624.7	-5.69	0.954	2802.6	0.70
	CO stretch	1746	1847.9	5.84	1663.1	-4.75	0.945	1775.9	1.71
	CH2 scissor	1500	1562.9	4.20	1406.7	-6.22	0.960	1502.0	0.13
b1	CH2 asymmetric-stretch	2843	2966.9	4.36	2670.2	-6.08	0.958	2851.2	0.29
	CH2 rock	1249	1279.5	2.45	1151.6	-7.80	0.976	1229.6	-1.55
b2	CH2wag	1167	1197.5	2.62	1077.8	-7.65	0.975	1150.8	-1.39

A correction of 0.9 is clearly too large. The ratio of the B3LYP calculated to the experimental frequencies are given in the 8<sup>th</sup> column, which averages to a correction of 0.961. Applying 0.961 as a correction gives much smaller errors, which is no surprise. However, a multiplicative correction of about 0.96 for other B3LYP/6-31G\* calculations is commonly used (but now you know why).

The thermodynamic analysis is:

Standard Thermodynamic quantities at 298.15 K and 1.00 atm

Term		ZPE	Enthalpy	Entropy	Cv	%	in
	cm-1	kJ/mol	kJ/mol	J/mol K	J/mol.K	Ground	IR Int.
1	B2	1197.520	7.1628	0.0444	0.1748	0.8639	1.45
2	B1	1279.548	7.6534	0.0319	0.1244	0.6626	12.59
3	A1	1562.945	9.3485	0.0099	0.0377	0.2510	6.55
4	A1	1847.942	11.0531	0.0030	0.0111	0.0886	98.63
5	A1	2916.302	17.4434	0.0000	0.0001	0.0013	55.95
6	B1	2966.941	17.7462	0.0000	0.0001	0.0010	164.79
Total Vibrations		70.4074	0.0893	0.3481	1.8684		
Ideal Gas			2.4789				
Translation			3.7184	151.1751	12.4716		
Rotation			3.7184	67.0499	12.4716		
Totals			80.4124	218.5731	26.8117		

Vibrational(v) Corrections:

Temp. Correction Hv 80.4124

Entropy Correction (Hv-TSv) 15.2449 (Gibbs energy correction to electronic energy  $\text{kJ mol}^{-1}$ )

3. In molecules with a center of symmetry, a given normal mode vibration is either allowed in IR and not allowed in the Raman or allowed in the Raman and not allowed in the IR. In molecules lacking a center of symmetry, the exclusions are not complete but the intensity variation between the IR and Raman often mirrors this pattern. View the IR and Raman spectra of benzaldehyde, which are available from the SDBS Integrated Spectral Data Base System for Organic Compounds:

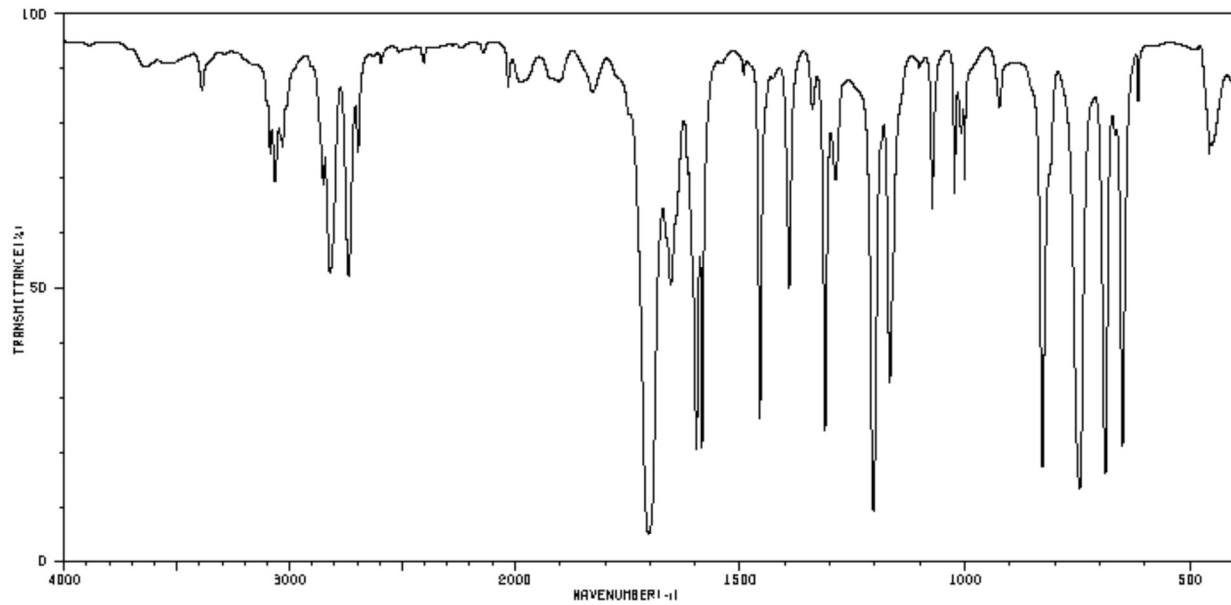
<http://sdb.db.aist.go.jp>

The symmetric ring stretching vibration near  $1000 \text{ cm}^{-1}$  is weak in the IR and strong in the Raman spectrum as expected for a symmetric vibration. Find this vibration for benzaldehyde in both the IR and Raman. Calculate the normal modes of benzaldehyde and the IR and Raman intensities at the HF/6-31G\* level, in a similar fashion as done for formaldehyde using the instructions below. To speed the calculation, do a geometry optimization at HF/3-21G\* first (about 10 seconds). Then as a second step geometry optimize and calculate the normal modes at the HF/6-31G\* level. The normal mode calculation requires about three minutes. Find the symmetric ring stretching mode. Remember the normally applied correction for anharmonicity for Hartree-Fock level calculations of 0.9. How well does the calculated frequency (in  $\text{cm}^{-1}$ ) agree with the experimental frequency after applying the 0.9 factor correction?

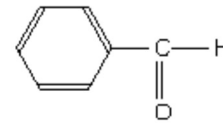
*Answer:* The spectra are shown below. The IR peak at  $1009 \text{ cm}^{-1}$  and the Raman  $1003 \text{ cm}^{-1}$  are consistent with the ring breathing mode. The small difference in frequency between the IR and Raman is consistent with expected experimental error.

The HF/6-31G\* calculations, given below, give the ring breathing mode at  $1090 \text{ cm}^{-1}$  or multiplying by 0.9 gives  $981 \text{ cm}^{-1}$ . Before correction the error is 8.7% and after correction by 0.9 the error is -2.2%. The correction is a bit too large but helpful. The exact correction for this particular case is:  $1003 \text{ cm}^{-1}/1090 \text{ cm}^{-1} = 0.920$ .

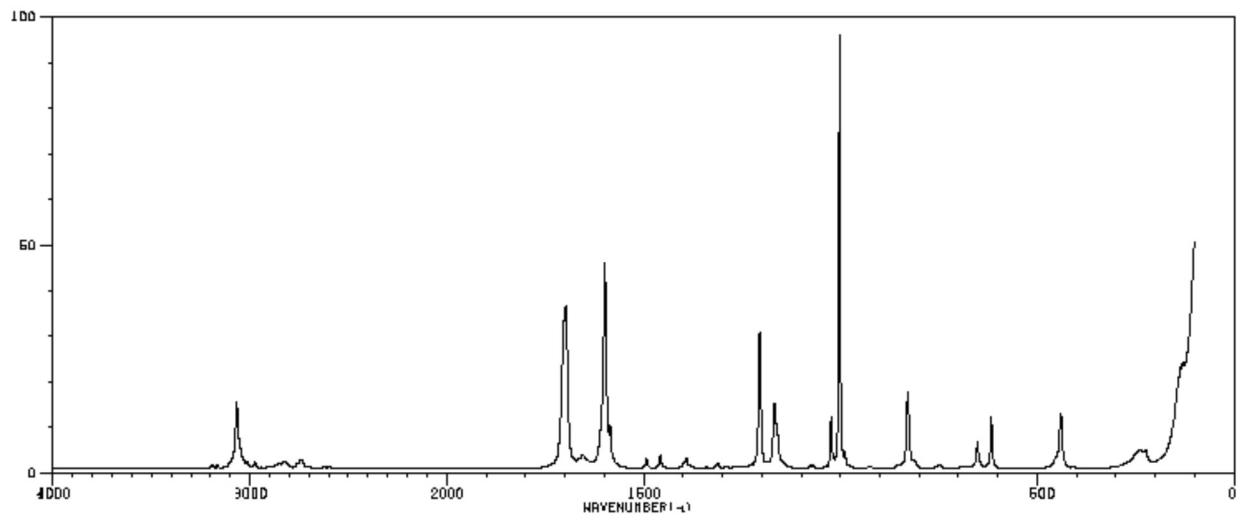
## Infrared: Benzaldehyde



3086	72	1981	84	1697	20	1204	8	828	16
3065	66	1916	84	1584	20	1168	31	746	13
3031	72	1909	84	1456	25	1073	62	688	15
2850	66	1901	84	1391	47	1023	64	667	74
2820	50	1828	81	1339	79	1008	74	650	20
2738	50	1703	4	1311	23	1001	66	615	61
2696	72	1664	48	1288	68	924	78	457	72



## Raman



BENZALDEHYDE  
SDBSN0 = 672

$C_7H_6O$

RM-01-00833 : 4880A.150M.LIQUID

3068	16	441	12
1701	36		
1599	46		
1587	10		
1207	30		
1169	14		
1025	12		
1003	95		
831	17		
617	12		

## Benzaldehyde normal mode calculation:

HF/6-31G\*

Infrared:

Term		ZPE	Enthalpy	Entropy	Cv	%	in
	cm-1	kJ/mol	kJ/mol	J/mol.K	J/mol.K	Ground	IR Int.
1*	A"	126.638	0.7575	1.2395	8.3144	4.1572	45.73 8.26
2*	A'	240.315	1.4374	1.2395	7.5334	4.1572	68.64 9.95
3*	A"	251.956	1.5070	1.2395	7.1832	4.1572	70.35 10.04
4*	A"	458.106	2.7401	0.6747	3.2285	4.1572	89.04 0.20
5*	A'	472.524	2.8263	0.6439	3.0564	4.1572	89.77 0.08
6*	A"	507.075	3.0330	0.5748	2.6805	4.1572	91.34 5.81
7	A'	675.150	4.0383	0.3231	1.4097	3.6716	96.15 0.90
8	A'	706.734	4.2272	0.2887	1.2477	3.4157	96.70 33.81
9	A"	762.880	4.5630	0.2358	1.0030	2.9867	97.48 22.89
10	A"	840.771	5.0289	0.1770	0.7388	2.4513	98.27 60.49
11	A'	896.147	5.3601	0.1438	0.5932	2.1143	98.68 38.31
12	A"	962.822	5.7590	0.1116	0.4545	1.7561	99.04 0.03
13	A"	1052.048	6.2926	0.0790	0.3171	1.3539	99.38 2.73
14	A'	1090.103	6.5203	0.0681	0.2716	1.2072	99.48 0.52
15	A"	1112.440	6.6539	0.0623	0.2479	1.1276	99.53 0.13
16	A'	1124.443	6.7257	0.0594	0.2360	1.0866	99.56 0.47
17	A"	1133.787	6.7816	0.0573	0.2272	1.0556	99.58 0.02
18	A"	1151.909	6.8899	0.0533	0.2109	0.9977	99.61 0.05
19	A'	1180.290	7.0597	0.0476	0.1877	0.9125	99.66 0.40
20	A'	1231.004	7.3630	0.0388	0.1522	0.7760	99.74 6.82
21	A'	1290.008	7.7160	0.0306	0.1191	0.6402	99.80 22.12
22	A'	1318.850	7.8885	0.0272	0.1056	0.5819	99.83 43.14
23	A'	1354.720	8.1030	0.0235	0.0909	0.5161	99.86 15.34
24	A'	1465.010	8.7627	0.0149	0.0571	0.3540	99.91 17.34
25	A'	1558.156	9.3198	0.0101	0.0385	0.2553	99.95 18.49
26	A'	1620.808	9.6946	0.0078	0.0294	0.2041	99.96 11.34
27	A'	1666.439	9.9675	0.0064	0.0242	0.1731	99.97 0.68
28	A'	1785.357	10.6788	0.0039	0.0145	0.1119	99.98 8.79
29	A'	1806.749	10.8068	0.0035	0.0132	0.1034	99.98 23.06
30	A'	2002.942	11.9803	0.0015	0.0056	0.0493	99.99 333.25
31	A'	3160.135	18.9018	0.0000	0.0000	0.0005	100.00 114.39
32	A'	3354.125	20.0621	0.0000	0.0000	0.0002	100.00 6.74
33	A'	3364.280	20.1229	0.0000	0.0000	0.0002	100.00 4.13
34	A'	3378.252	20.2064	0.0000	0.0000	0.0002	100.00 26.28
35	A'	3389.792	20.2755	0.0000	0.0000	0.0002	100.00 23.64
36	A'	3404.437	20.3630	0.0000	0.0000	0.0002	100.00 5.76

Total Vibrations 310.4141 7.4872 39.7919 52.8467

Ideal Gas 2.4789

Translation 3.7184 166.9211 12.4716

Rotation 3.7184 116.4907 12.4716

Totals 327.8171 323.2037 77.7900

Vibrational(v) Corrections:

Temp. Correction Hv 327.8171

Entropy Correction (Hv-TSv) 231.4540

## Raman:

Energy : -343.433510 hartrees

Solvation : -12.73 kJ/mol (SM54/AM1)

uncorrected Intensity Raman Raman

	cm <sup>-1</sup>	a.u.	Abs.	
1	127	8.26	1.0000	1.87
2	240	9.95	0.1346	0.75
3	252	10.04	0.3167	1.92
4	458	0.20	0.0023	0.03
5	473	0.08	0.2620	4.18
6	507	5.81	0.0132	0.23
7	675	0.90	0.2099	5.62
8	707	33.81	0.0805	2.30
9	763	22.89	0.0070	0.22
10	841	60.49	0.0226	0.83
11	896	38.31	0.2454	9.92
12	963	0.03	0.0633	2.85
13	1052	2.73	0.0060	0.31
14	1090	0.52	0.5152	28.01
15	1112	0.13	0.0011	0.06
16	1124	0.47	0.1225	6.99
17	1134	0.02	0.0084	0.48
18	1152	0.05	0.1485	8.80
19	1180	0.40	0.0074	0.46
20	1231	6.82	0.1330	8.77
21	1290	22.12	0.1426	10.15
22	1319	43.14	0.2663	19.65
23	1355	15.34	0.0221	1.70
24	1465	17.34	0.0204	1.80
25	1558	18.49	0.0341	3.36
26	1621	11.34	0.0058	0.61
27	1666	0.68	0.0049	0.55
28	1785	8.79	0.0548	6.96
29	1807	23.06	0.5875	76.32
30	2003	333.25	0.4788	76.57
31	3160	114.39	0.2094	104.37
32	3354	6.74	0.0723	43.39
33	3364	4.13	0.1487	90.14
34	3378	26.28	0.1102	67.67
35	3390	23.64	0.2656	165.00
36	3404	5.76	0.1831	115.36

(Raman assumed using 1064.0 nm laser and 298.15 K temperature)