Computational Chemistry II   2023

Text book   Cramer: Essentials of Quantum Chemistry, Wiley (2 ed.)

Chapter 4. Electronic properties (Cramer: chapter 9)

What we can get out form the ab initio calculations

We have now some kind of wave function and the total energy of
our system. What can we learn from them? As said in the first
chapter (and Comp. Chem. I) the atomic **total energy** is very
useful for many chemical properties. Most of the structural
problems in chemistry can be solved with total energy.

In this chapter, we focus on the electronic properties, which
can be computer from the wave functions.

Dipole moment

One of the simplest quantities is the electron density

$$\rho(r) = \int \int \Psi^*(r, r_2.., r_N)\Psi(r, r_2.., r_N)\, dr_2..dr_N$$

Note that the integral is over the coordinated $r_2..r_N$. In the
case of HF and DFT the

$$\rho(r) = \sum_{n,occ}|\varphi_n(r)|^2 \,.$$

Very often the dipole and higher moments of the molecule are
interesting. The importance of dipole moment is twofold. First,
when molecules are **interacting with light** (e.g. in spectroscopy,
especially the IR) the main term in this interaction is the
dipole moment. Secondly, when neutral **molecules are interacting**
and the main term is the dipole-dipole interaction.

The most general moment is

$$\langle x^n y^m z^k \rangle = \sum_{i\ atoms} Z_i x_i^n y_i^m z_i^k + \int \Psi^*(r_1, r_2 .., r_N) x^n y^m z^k \Psi(r_1, r_2 .., r_N)\, dr_1 .. dr_N$$

Again form DFT and HF

$$\langle x^n y^m z^k \rangle = \sum_{i\ atoms} Z_i x_i^n y_i^m z_i^k + \int \rho(r)\, x^n y^m z^k\, dr$$

The dipole moment is <µ>=<r> or $\langle \mu \rangle = \sqrt{\langle x \rangle^2 + \langle y \rangle^2 + \langle z \rangle^2}$. On average the DFT models will produce good dipole moments. The higher moments are also easy to compute but one need to remember that they depend on the origin of the coordinate system. This is typically the centre of mass of the molecule.

A good database for comparing the experimental and computer data can be found from:

http://cccbdb.nist.gov/compdipole2x.asp

Remember that the dipole moment can be computed for an arbitrary molecular geometry. This is useful if we are interested of IR vibrational intensities. The IR intensity will depend on the *change* of the dipole moment in the molecular vibration. Thus, the difference in dipole moment can be computed with

$\Delta \mu = \mu(R_0) - \mu(R_0 + \delta V_i)$ where V_i is the atomic displacement of the i:th vibrational mode.

Total electrostatic potential

One quantity that can be computed is the total electrostatic potential

$$V_{el}(r) = \sum_{I} \frac{Z_I}{|r - R_I|} - \int \frac{\rho(r_1)}{|r - r_1|} dr_1$$

The electrostatic potential is useful for analyzing the charge distribution of the molecules.

Point charges

In chemistry, it is interesting to know the charge of each atom. This sound simple but it is not. The true quantity is the electron density and there is no unique (correct) way to determine the atom charges.

One type of charge definition is based on the basis functions, $\varphi_n(r) = \sum_m c_{n,m}\xi_m(r)$ now we can assign the basis functions to each atom. We use notation m(I) meaning that functions m are centered to atom I. Now the total amount of electrons is N

$$N = \sum_{n\ elec} \int |\varphi_n(r)|^2\, d^3r = \sum_{n\ elec} \sum_{m,l} \int c_{n,m}c_{n,l}\xi_m(r)\xi_l(r)\, d^3r$$

$$N = \sum_{n\ elec} \left(\sum_I c_{n,m(I)}{}^2 + \sum_{J\neq I} S_{m(I),l(J)}\, c_{n,m(I)}c_{n,l(J)} \right)$$

The term in parenthesis for each atom I can be interpreted as an atomic charge. This is so called Mulliken charge. It is very easy to compute since all needed information is in the quantum chemical calculations. Unfortunately, it has strong basis function dependence (meaning that different basis function will give very different charges). The overlap contribution is also odd.

A better (?) way to compute the basis function based charge is to use a method proposed by Löwdin where an orthonormal basis is used.

$$\vartheta_n(r) = \sum_m S_{nm}^{-1/2}\xi_m(r)$$

Now

$$\varphi_n(r) = \sum_m a_{n,m}\vartheta_m(r) = \sum_{nm} c_{n,m}S_{nm}^{1/2}\vartheta_m(r)$$

Unfortunately, the Löwdin charges are not necessary better than the Mulliken ones. Similar but even more realistic method is the Natural Population Analysis (NPA).

Bader and similar charges

A completely different approach to determine the charge is the Bader method. In the Bader method, the space is divided into parts and each atom has a relevant volume Ω_I. The charge is defined as a simple integral

$$q_I = Z_I + \int_{\Omega_I} \rho(r)dr$$

Unfortunately, the integration areas are complex. Bader have one definition of the integration volumes but other volumes, like Voronoy cells, can be used. The Bader analysis is usually done with separate program.
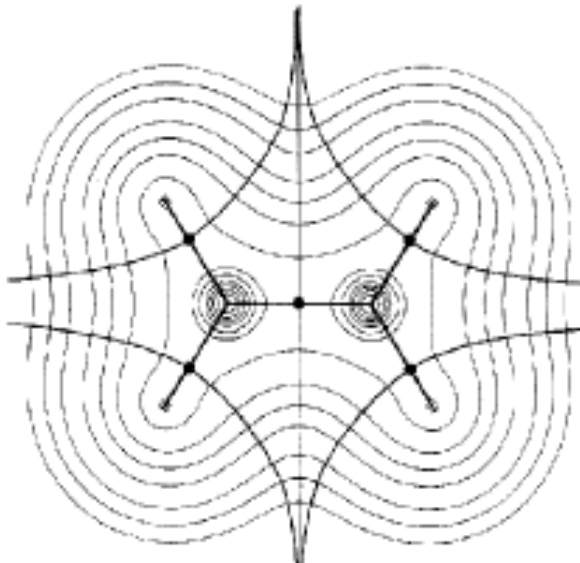
The charges can also be determined from the electrostatic potential. We can find the atomic charges that reproduced best the total el. potential.

$$V_{el}(r) = \sum_I \frac{Z_I}{|r - R_I|} - \int \frac{\rho(r_1)}{|r - r_1|} dr_1 \approx \sum_I \frac{q_I}{|r - R_I|}$$

These EPS charges are very useful for empirical modelling.

There is an example of the effective charge of some cyclic molecules. Note that the values differ a lot (AIM = Bader, MK and ChelpG are potential fitting methods, Hirshfeld method we did not discuss, GenFF is an empirical ForceField)
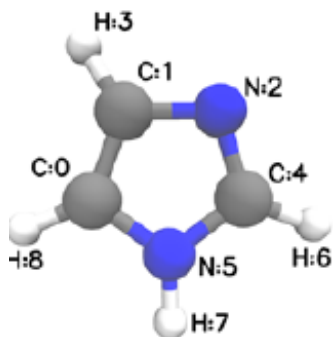
		Charmm GenFF	Hirshfeld	AIM	MK	ChelpG
	C:0	-0.048	-0.038	0.355	-0.341	-0.151
	C:1	0.225	-0.055	0.401	0.125	0.114
	N:2	-0.729	-0.236	-1.168	-0.552	-0.566
	H:3	0.102	0.048	0.048	0.106	0.073
	C:4	0.277	0.029	1.019	0.141	0.210
	N:5	-0.361	-0.039	-1.281	-0.114	-0.215
	H:6	0.121	0.064	0.076	0.119	0.087
	H:7	0.322	0.165	0.464	0.304	0.315
	H:8	0.091	0.062	0.074	0.212	0.134
	Average		0.183	0.326	0.122	0.078
Error	Median		0.157	0.176	0.121	0.067
	SD		0.155	0.307	0.099	0.052

There will be an exercise on this.

Polarization

If any molecule is in external electric field (or next to other molecules) it's charge distribution will change. We can define polarization as

$$\alpha_{ij} = \frac{\partial \mu_i}{\partial E_j}$$

Where μ is the dipole moment and E is the electric field. The polarization is useful to understand as the "rigidty" of the electrons and the Raman intensities are based on the change of polarization in the vibrational mode. (In Orca the Raman analysis require numerical frequency calculation, NumFreq)

The polarization can be significant. In the case of water, in gas phase the dipole moment is 1.85 D and in liquid water around 3.0 D. The increase is due to the polarization.

The polarization can be computed with elprop keyword.

The higher order polarization terms can be defined as

$$\mu = \mu_0 + E_i \frac{\partial \mu}{\partial E_i} + \frac{1}{2} E_i E_j \frac{\partial^2 \mu}{\partial E_i \partial E_j} = \mu_0 + E_i \alpha_i + \frac{1}{2} E_i E_j \beta_{ij} + \cdots$$

Here β is hyperpolarization. (Orca do not calculate hyperpolarization.)

Vibrations

Molecular vibrations are one of the ways to identify different molecules, IR or Raman spectroscopy.

The molecular vibrations can be calculated from the second derivative,

$$A_{IJ} = \frac{\partial^2 E_{tot}^{el}}{\partial R_I \partial R_J}$$

Often the second derivative can be computed analytically, but with more complex methods numerical second derivative has to be used. Once the A has been computed it can be used to solve the vibrational eigenvalues and –vectors. Sometimes the numerical second derivative can be unreliable especially in the case of low frequencies.

The multidimensional vibrational Schrödinger equation can be written as:

$$\left(-\sum_i \frac{1}{2m_i}\frac{d^2}{dX_i^2} + \sum_{ij} X_i\, A X_j\right)\Phi(X) = E\Phi(X)$$

This is not easy to solve and we need to choose mass weighted coordinates $Q_i = \sqrt{m_i} X_i$ and $B_{ij} = \sqrt{m_i m_j}\, A_{ij}$ this removes the mass dependence from the first term.

$$\left(-\sum_i \frac{1}{2}\frac{d^2}{dQ_i^2} + \sum_{ij} Q_i\, B Q_j\right)\Phi(Q) = E\Phi(Q)$$

The vibrational energies are the eigenvalues of matrix B and vibrational modes (Q_i) are eigenvectors of B.

In classical mechanics, the vibrational problem is easy. We can construct system of atoms connected with harmonic springs. We can take a water molecule as an example. It has 3 vibrational modes and we can build the molecules with two OH bonds (with force constant k_1) and one H-O-H bending bond (with force constant k_2). This sounds reasonable but in reality stretching one OH bond has small effect to the other OH bond (coupling constant k_{11}). We can write a matrix equation of

$$M\ddot{Q} = \begin{pmatrix} b_1 & b_{11} & b_{12} \\ b_{11} & b_1 & b_{12} \\ b_{12} & b_{12} & b_2 \end{pmatrix} Q$$

Where the b's are the proper force constants in some coordinate system. M is a matrix containing the molecular masses (it depend on the coordinate system). Note usually this coordinate system is Cartesian. We can diagonalize the B matrix and we find a new orthogonal coordinate systems ξ=ξ(Q)

$$\widetilde{M}\ddot{\xi} = \begin{pmatrix} \kappa_1 & 0 & 0 \\ 0 & \kappa_2 & 0 \\ 0 & 0 & \kappa_3 \end{pmatrix} \xi$$

We know how the vibrational coordinate system depend of the old coordinates (Q) and the values κ are the vibrational eigenvalues.

Also $\tilde{M}$ is diagonal but it depends on the atoms masses and the coordinate transform.
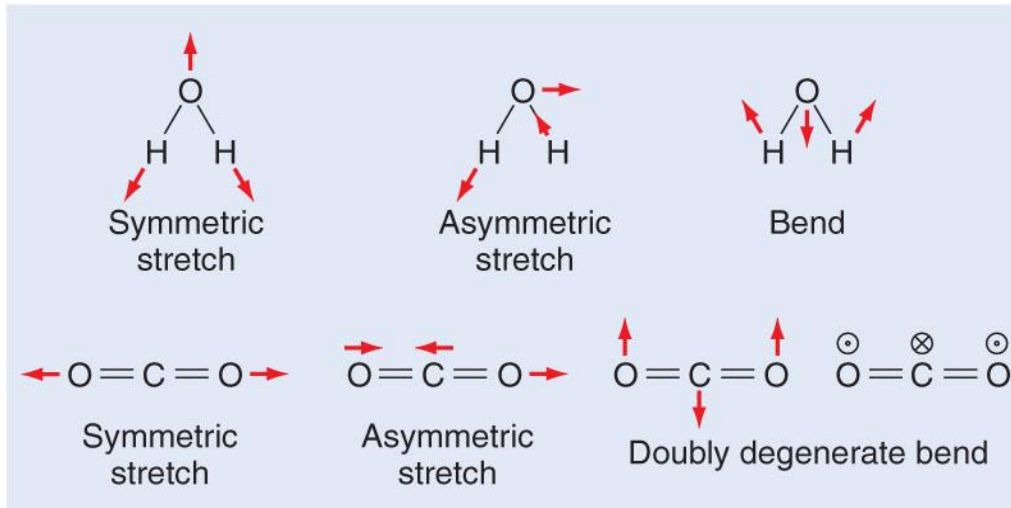
IR intensities

First, we need a term that describe the interaction of light and the molecule. The light is described with an time dependent **electric field** E(t)=E₀ sin(ωt). In the first approximation the electric field is coupled to the **dipole moment,μ(t),** of the molecule (there are higher order term like the quadrupole moment but we ignore them here.) So the coupling term is (both μ and E are vectors)

   H(t)=-μ(t)·E(t)

The main result is the transition dipole rule:

$$\mu_{nm} = \int \varphi_n^*(x)\hat{\mu}\varphi_m(x)dx \qquad (2.1)$$

In this equation, the φ_n is the wave functions of the starting state and φ_m is the wave functions of the end state. Now we can compute any transition probability when the wave functions are known. (Even a good approximation of the wf will do.)

Let us apply this to a harmonic oscillator. The wave function is $H_n(x)\exp(-\alpha x^2/2)$ but now we need to think carefully what the x means. It is the oscillation coordinate. In the case of two atom molecule it is the distance between the atoms.
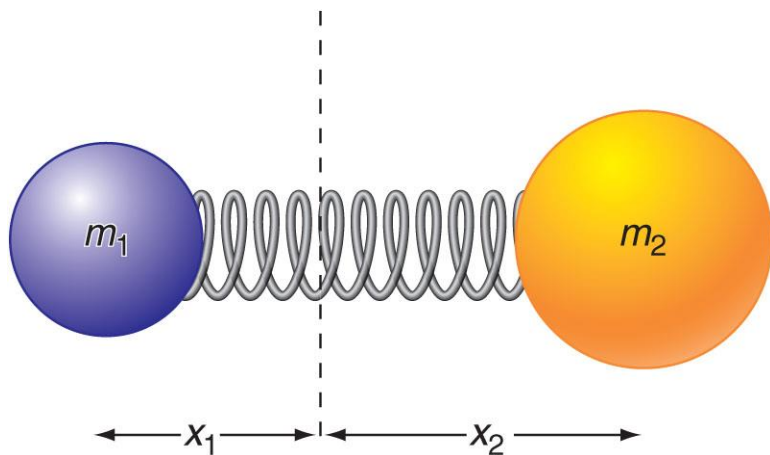
Also $\mu = \mu_x$, here μ_x is x component of the dipole moment, we can choose coordinates such that the dipole vector is in x direction.

Now the dipole moment is

$$\mu(t) = \mu_0 + \frac{\partial \mu}{\partial x} x$$

The μ_0 is the dipole moment at equilibrium distance and the derivative tells the *change* of dipole moment in the vibration. When this is inserted to (2.1) we get

$$\mu_{nm} = \int \varphi_n^*(x)\mu_0\varphi_m(x)dx + (d\mu/dx)\int \varphi_n^*(x)x\varphi_m(x)dx + ...$$

The first term is 0 when n ≠ m because the wave functions are orthogonal. The case where n=m is not interesting since nothing happens. The next term is the key term. It shows that the intensity will depend on the **change of dipole moment in the vibration**. Within harmonic approximation **m=n±1** but anharmonic terms will break this rule.

The Orca output have results like, where the T**2 is the
intensity.

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IR SPECTRUM
```

```
Mode freq (cm**-1) T**2        TX          TY          TZ
-------------------------------------------------------------
6:   1278.77       6.157280  ( -2.481387 -0.000010 -0.000287)
7:   1395.78      29.682711  ( -0.000003 -5.448182 -0.004815)
8:   1765.08       4.180497  ( 0.000537 -0.022003 2.044508)
9:   2100.53       8.550050  ( 0.000080 0.011990 2.924022)
10:  3498.72       1.843422  ( 0.001027 -0.178764 -1.345907)
11:  3646.23      19.778426  ( 0.000035 4.446922 -0.057577)
```

There are also utility program that will make a file **Test-Freq-H2CO.ir.dat** that will contain the spectra.

orca_mapspc Test-Freq-H2CO.out ir -w50

Raman intensities

The electric field is time dependent $E(t) = E_0 \sin 2\pi\upsilon t$. This external electric field will pull the electrons and ions on different directions and the dipole moment of the molecule will change: $\mu(t) = \mu_0 + \alpha \cdot E(t)$ here the α is the polarization of the molecule. Now also this change of the dipole moment with respect of the vibration can be measured.

$$\alpha(t) = \alpha_0 + \frac{\partial \alpha}{\partial x} x$$

$$\mu_{nm} = ... + E(d\alpha/dx)\int \varphi_n^*(x) x \varphi_m(x) dx + ...$$

The output form the Raman spectrum calculations:

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```

```
RAMAN SPECTRUM
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Mode freq (cm**-1) Activity Depolarization
----------------------------------------------------
 6:  1278.77       0.007349 0.749649
 7:  1395.78       3.020010 0.749997
 8:  1765.08      16.366586 0.708084
 9:  2100.53       6.696490 0.075444
10: 3498.72       38.650431 0.186962
11: 3646.23       24.528483 0.748312
```

Compare the intensities (T**2 and Activity) of the same modes.
Again a file for spectra can be made with orca_mapspc
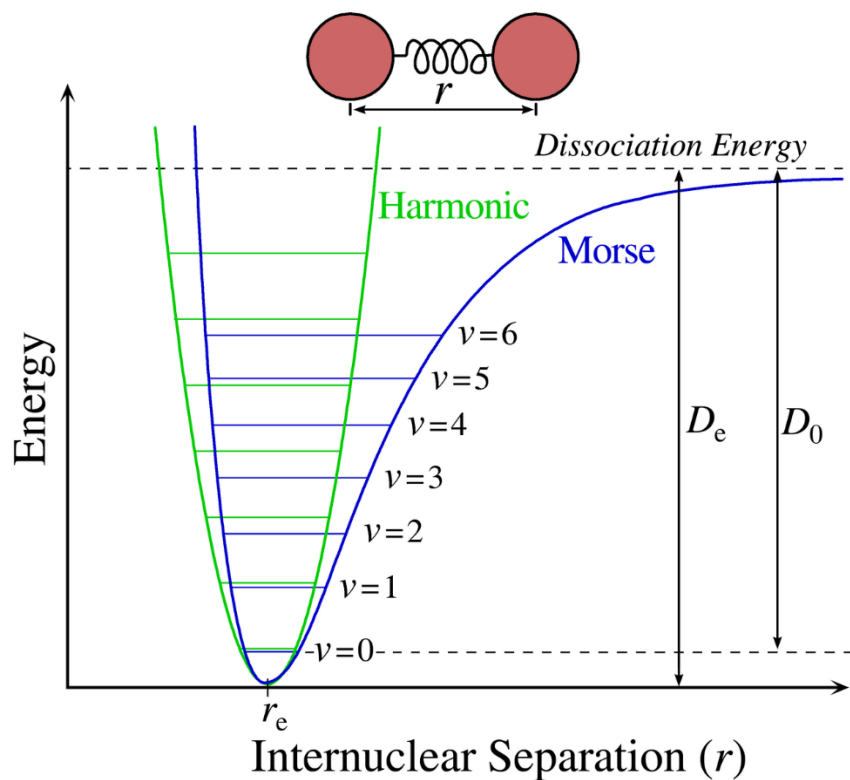
orca_mapspc Test-Freq-H2CO.out raman -w50

Anharmonic effects

The anharmonic potential can be taken into account by fitting
the scanned potential to the Morse potential

$$V(r) = D_e[(1 - \exp(-a(r - r_0)))^2 - 1] = D_e[\exp(-2a(r - r_0)) - 2\exp(-a(r - r_0))]$$

Where D is the dissociation energy.

The energies of the Morse potential are

$$E_n = \hbar\omega\left(n+\frac{1}{2}\right) - \frac{\left[\hbar\omega\left(n+\frac{1}{2}\right)\right]^2}{4D} = \hbar\omega\left(n+\frac{1}{2}\right) - \hbar\omega\chi\left(n+\frac{1}{2}\right)^2$$

The Morse potential fit can be done to all the vibrational modes.

Orca will have an automatic method for anharmonic analysis, VPT2. The VPT2 is based on multidimensional polynomial fit up to power 4. It should be used for anharmonic analysis of small molecules (search 'anharmonic' form the manual). The VPT2 is not reliable for larger molecules.

The output for water:

```
Fundamental transition
-------------------------------------------
Mode[i] w[i] [1/cm]  v[i] [1/cm]  Diff [1/cm]
-------------------------------------------
   1        1570.09       1539.77       -30.33
   2        3692.68       3521.43      -171.25
   3        3805.77       3616.78      -188.99
-------------------------------------------
```

w is the harmonic frequency and v the anharmonic. Note that the
difference is rather large so the anharmonicity really matters.

Benzene


```
HIT-NO=1237 |SCORE=  (  )|SDBS-NO=898    |IR-NIDA-63541 : LIQUID FILM
BENZENE

C6H6
```

3091	42	1393	84
3072	49	1176	86
3036	27	1038	49
1961	77	674	4
1815	70		
1528	81		
1479	20		
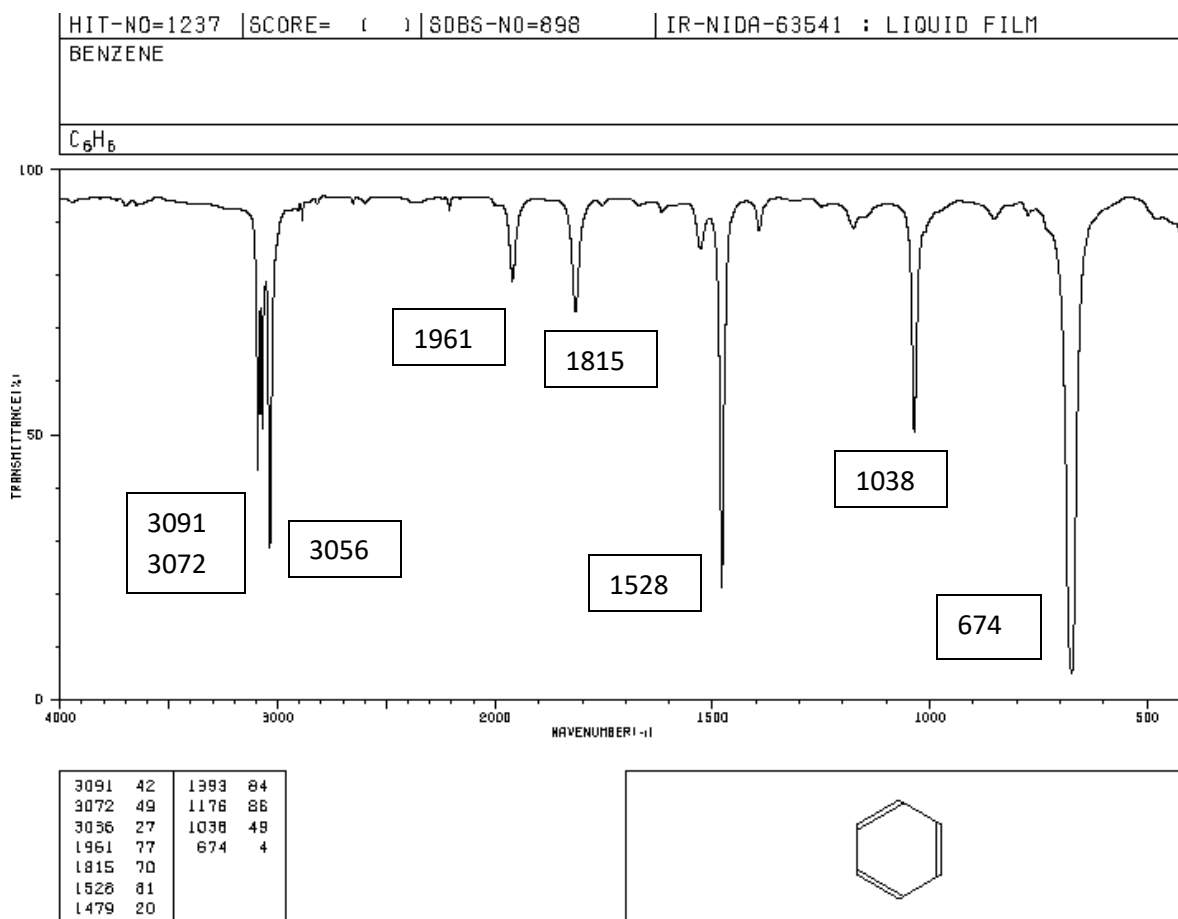
above is the IR spectrum from

[AIST:Spectral Database for Organic Compounds,SDBS](#) (PBE, TZVP, DFT-GGA model, with def2-QZVPP basis gave 2-6 cm^-1 smaller freq) of benzene and below the computed frequencies. See the PBE0 values in the boxes. Check the agreement. Is something missing? Note that the computations gives only the harmonic frequencies.

```
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IR SPECTRUM
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 Mode      freq (cm**-1)    T**2
-----------------------------------
  6:          379.60      0.013169
  7:          386.56      0.000533
  8:          602.74      0.000002
  9:          603.12      0.000001
 10:          659.08    113.720837
 11:          666.30      0.000060
 12:          826.21      0.000041
 13:          827.44      0.000007
 14:          913.28      0.011906
 15:          913.45      0.025175
 16:          957.83      0.000073
 17:          993.32      0.001346
 18:          994.83      0.000001
 19:         1035.47      6.566432
 20:         1035.97      6.608068
 21:         1146.16      0.000286
 22:         1166.30      0.000016
 23:         1166.45      0.000013
 24:         1334.31      0.000000
 25:         1342.01      0.001605
 26:         1467.15      7.401818
 27:         1467.48      7.714655
 28:         1590.62      0.000013
 29:         1590.94      0.000014
 30:         3092.82      0.078992
 31:         3101.31      0.000217
 32:         3103.25      0.000185
 33:         3116.58     33.056128
 34:         3118.19     34.252047
 35:         3127.49      0.000024
```

| 659 (calc. harm)   exp: 674 |
| 689 (PBE0, harm) |

| 1036 (calc. harm)   exp: 1038 |
| 1070 (PBE0, harm) |

| 1467 (calc. harm)   exp: 1528 |
| 1520 (PBE0, harm) |

| 3117 (calc. harm)   exp: 3056- 3091 |
| 3207 (PBE0, harm) |

The experimental peaks at 1961 and 1815 cm^-1 are not
fundamental modes of benzene molecule. The 1961 could be an
overtone of 1038 mode (double excitation) and 1815 could be
combination of 1038 and 674 (but this do not match very well).

Vibrations of solid systems

The vibrational analysis can also be done on solid systems.

NMR spectra

The molecules NMR spectra can be computed. The theory behind it
is complex I do not go into it. ORCA have excellent tools for
NMR calculations but the interpretation of the results needs
some understanding of NMR. The calculations are easy, you just
add NMR keyword to the commend line. Typically you should first
optimize the molecules structure. In NMR calculations you should
use rather large basis because we need a description of the
electron density at the nucleus - TZVPP is a good one. (See
below)

From Orca manual

Let us consider an example - propionic acid (CH_3CH_2COOH). In databases like the AIST
(http://sdbs.db.aist.go.jp) the ^{13}C spectrum in $CDCl_3$ can be found. The chemical shifts are given
as δ_1 = 8.9 ppm, δ_2 = 27.6 ppm, δ_3 = 181.5 ppm. While intuition already tells us that the carbon
of the carboxylic acid group should be shielded the least and hence shifted to lower fields
(larger δ values), let's look at what calculations at the HF, BP86 and B3LYP level of theory using
the SVP and the TZVPP basis sets yield:

method	σ_1	σ_2	σ_3
HF/SVP	191.7	176.6	23.7
HF/TZVPP	183.5	167.1	9.7
B86/SVP	181.9	165.8	26.5
B86/TZVPP	174.7	155.5	7.6
B3LYP/SVP	181.8	165.8	22.9
B3LYP/TZVPP	173.9	155.0	2.9

Looking at these results, we can observe several things - the dramatic effect of using too small
basis sets, which yields differences of more than 10 ppm. Second, the results obviously change
a lot upon inclusion of electron correlation by DFT and are functional dependent. Last, these
values have nothing in common with the experimental ones (they change in the wrong order),

as the calculation yields absolute shielding like in the table above, but the experimental ones are relative shifts, in this case relative to TMS.

In order to obtain the relative shifts, we calculate the shielding σ_{TMS} of the standard molecule (TMS HF/TZVPP: 194.1 ppm, BP86/TZVPP: 184.8 ppm, B3LYP/TZVPP: 184.3 ppm) and by using $\delta mol = \sigma_{ref} - \sigma_{mol}$ we can evaluate the relative chemical shieldings (in ppm) and directly compare to experiment:

method	δ_1	δ_2	δ_3
HF/TZVPP	10.6	27.0	184.4
B86/TZVPP	10.1	29.3	177.2
B3LYP/TZVPP	10.4	29.3	181.4
Exp.	8.9	27.6	181.5