Experimental Determination of Molecular Structure

For the inorganic chemist probably the most important tool for determining the structure of molecules is X-ray crystallography.

Very basically, in **X-ray crystallography** a small crystal (0.1 - 0.3 mm on a side) is glued to the end of a thin glass fiber. A beam of X-rays is then directed at the crystal. When the X-rays strike the crystal, the electrons, particularly the core electrons, diffract them. Since the molecules are aligned in a regular fashion, a regular pattern of reflections develops. A mobile detector measures the positions of these reflections and their relative intensities. Using a computer, these data produce an "electron density map" that is a relief map of the electron density of the molecule. Since heavier atoms tend to have more core electrons, they will diffract better and have higher peaks in the electron density map. (One way to visualize this is to imagine a ball-and-stick model of a molecule suspended above a sheet of paper with a light directly above the model. The shadows that appear on the paper are the atoms. If larger atoms cast more intense shadows, you'd have a fairly good simulation of an electron density map.) Since you should already know the elemental composition of your compound and have some guess as to what it looks like, you then assign the peaks on the basis of their height and separation. After the assignments are made a 3-D image projected onto a sheet of paper is done by the computer. As late as the 1950's one could get a Ph.D. by doing the structure of a *single* fairly simple molecule. Today, because of computers, a much more difficult molecule can be solved in a matter of hours by an undergraduate student.

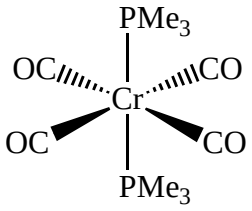
Electron Diffraction – This method is similar to X-ray diffraction except that it can be done in either the gas or solid phases with a beam of electrons that scatter off the molecular electrons (hence like X-ray structures, large atoms scatter better than smaller ones). Its advantages involve much smaller sample sizes and for very low melting substances much easier sample handling. *Drawbacks* – For gas phase samples, it must maintain its structure in the gas phase. The accuracy of atom location is ordinarily lower than that of X-ray diffraction.

Neutron Diffraction – This method is also similar to X-ray crystallography except that a beam of neutrons scatters off the nuclei. *Advantages* - Since all nuclei are of similar size, all can be found with comparable accuracy. This is particularly useful if the location of hydrogen atoms is desired. Neutron diffraction generally gives more accurate bond lengths and angles since the location of the atoms is known with better precision. *Disadvantages* - need a bigger crystal (1-2 mm on a side) and a source of neutrons (a nuclear reactor).

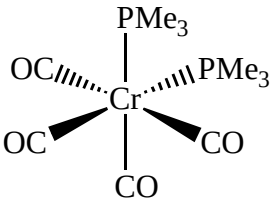
Other Structural Determination Methods

The major ones include IR, Raman, and NMR spectroscopies. All of these techniques yield structural information that can reject a particular structure proposal, so a combination of these techniques usually is required to demonstrate a structure. Other methods, such as electron spin (paramagnetic) resonance (ESR/EPR) spectroscopy and mass spectrometry can provide structural information, but they are less common for varying reasons.

IR and Raman spectroscopies provide information relating to what functional groups are present in a molecule and information on the symmetry of the molecule. Two isomers of a molecule can frequently be distinguished on the basis of IR or Raman spectroscopy. An example of this would be distinguishing between the *cis*- and *trans*- isomers of $Cr(CO)_4(PMe_3)_2$:

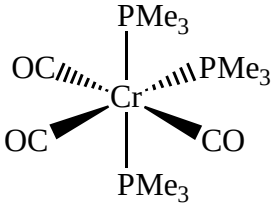


trans - 1 CO stretch in the IR

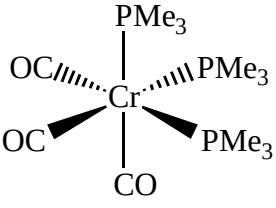


cis - 2 CO stretches in the IR

NMR - Most of you are used to thinking only in terms of ^{1}H and ^{13}C NMR, however most elements have magnetically active nuclei in sufficient natural abundance that NMR can be performed conveniently on them (e.g. ^{19}F, ^{15}N, ^{31}P, ^{55}Fe, etc.). Consider a molecule with the formula $Cr(CO)_3(PMe_3)_3$. It has two possible structures *meridonal* (*mer*) or *facial* (*fac*):



mer



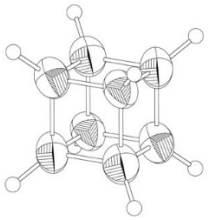
fac

The three phosphines in the facial isomer are equivalent and so a ^{31}P NMR of it would produce a singlet, while the meridional isomer has two different phosphines (by symmetry) and would generate two singlets with an intensity ratio of 2:1. (One isotope of chromium (10% abundance) has spin = $^{3}/_{2}$. This would yield sets of quartets centered about the singlets. The intensities would be quite small because of the splitting, however.)

Speeds of the Various Methods

The time scale of an instrument is largely controlled by the wavelength of the radiation used. Recall that $c = \lambda\nu$ for electromagnetic radiation. Thus, as the wavelength (λ) of the radiation is increased, the frequency (ν) decreases. Since frequency has units of s^{-1}, the time required for a wave cycle to pass a given point is $^{1}/_{\nu}$. For any wavelength of light, the interaction time for that light is the time it takes for one complete wave cycle to interact with the molecule being studied. If a process occurs more rapidly than $^{1}/_{\nu}$ (i.e. the rotation, inversion, etc. occurs many times before the wave cycle interacts with the molecule), then all that is seen in the spectrometer output is the average of the processes occurring (analogous to a camera taking a photograph at a slow shutter speed). If on the other hand, that process occurs much more slowly that $^{1}/_{\nu}$, then the process is "frozen out" (analogous to taking a photograph at high shutter speed).

The three diffraction methods have interaction times of about 10^{-18} sec, since X-rays have a frequency of about 10^{18} sec. That is, any motion that requires more than 10^{-18} sec is frozen out and this includes molecular vibrations. However, since it is not possible to measure the position of an atom with a single photon, many such measurements are taken over time. The result is that a collection of measurements showing the position of each atom at a variety of times is produced. Thermal ellipsoids are one way of graphically displaying this information. There is a certain probability (say 50%) of finding the respective atomic cores inside the thermal ellipsoids at any given time, t.



Crystal structure of cubane
There are thermal ellipsoids for carbon, but hydrogen atoms are not experimentally determined.

IR, Raman, and UV-visible spectroscopy are on the *ca.* 10^{-14} sec time scale. These methods give you averaged molecular vibrations because vibration is faster than this time scale. This much faster than intramolecular rearrangements and so a "snap-shot" view of the molecule is obtained.

NMR has a time scale of 0.1 - 10^{-6} sec, depending on the NMR magnet and the nucleus under study. Many intramolecular motions (such as bond rotations) or rearrangements (such as fluxional processes) are faster than this time scale. If the rearrangement is faster, then the spectrum reflects the average atomic arrangement. If it is slower, then the spectrum is of the molecule with the arrangement frozen out. By varying the temperature, the rate of rearrangement can be changed and sometimes this molecular motion can have its rate affected sufficiently to cause both the average and frozen out spectra to be observed (at different temperatures). From this, a rate constant can be determined for the rearrangement.

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