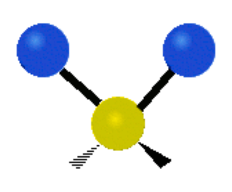
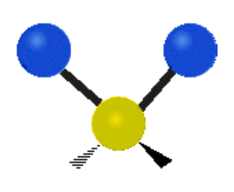
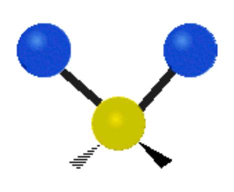
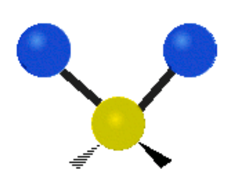
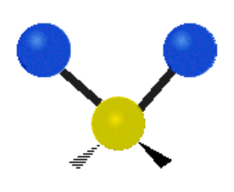
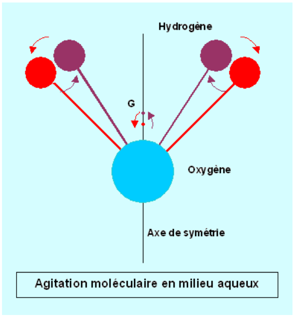
Vibrational circular dichroism

Vibrational circular dichroism (VCD) spectroscopy is basically circular dichroism spectroscopy in the infrared and near infrared ranges[1] . Because VCD is sensitive to the mutual orientation of distinct groups in a molecule, it provides three-dimensional structural information. Thus, it is a powerful technique as VCD spectra of enantiomers can be simulated using *ab initio* calculations, thereby allowing the identification of absolute configurations of small molecules in solution from VCD spectra. Among such quantum computations of VCD spectra resulting from the chiral properties of small organic molecules are those based on density functional theory (DFT) and gauge-invariant atomic orbitals (GIAO). As a simple example of the experimental results that were obtained by VCD are the spectral data obtained within the carbon-hydrogen (C-H) stretching region of 21 amino acids in heavy water solutions. Measurements of vibrational optical activity (VOA) have thus numerous applications, not only for small molecules, but also for large and complex biopolymers such as muscle proteins (myosin, for example) and DNA.

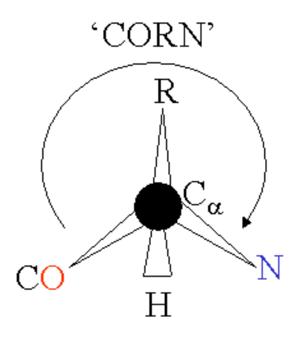
Vibrational modes

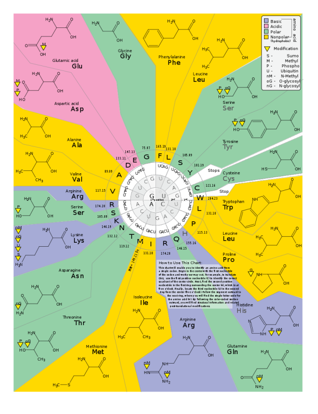







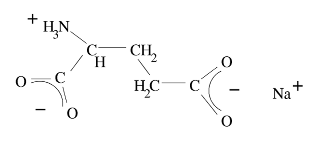
VCD of peptides and proteins

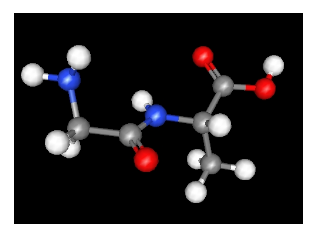
Extensive VCD studies have been reported for both polypeptides and several proteins in solution[2] [3] [4] ; several recent reviews were also compiled[5] [6] [7] [8] . An extensive but not comprehensive VCD publications list is also provided in the "References" section. The published reports over the last 22 years have established VCD as a powerful technique with improved results over those previously obtained by visible/UV circular dichroism (CD) or optical rotatory dispersion (ORD) for proteins and nucleic acids.

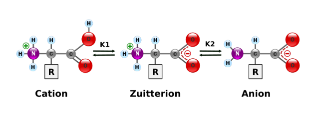
Amino acid and polypeptide structures

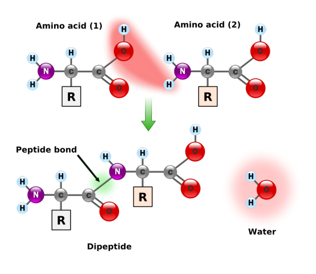


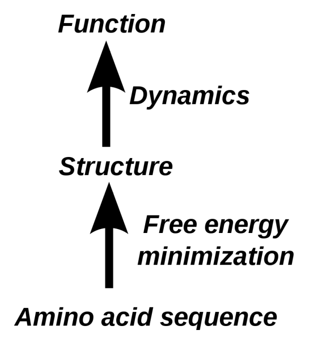


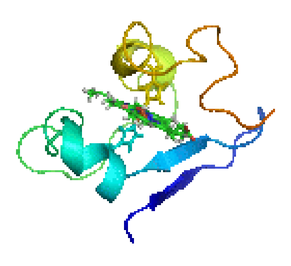


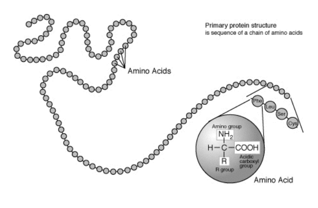


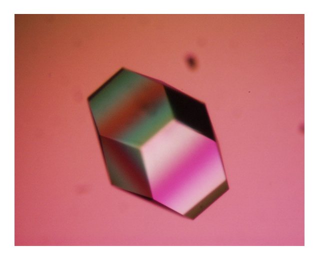


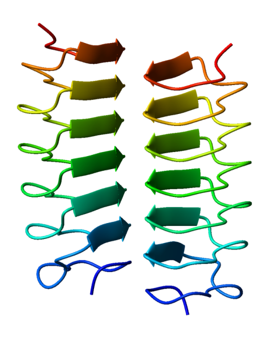


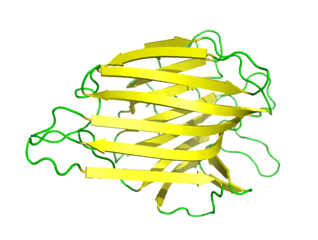


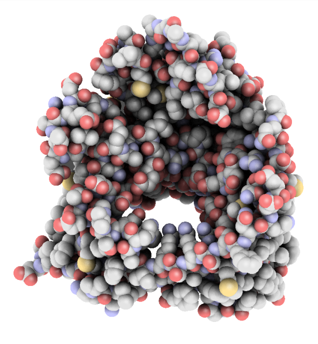


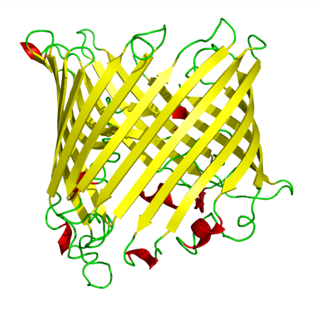


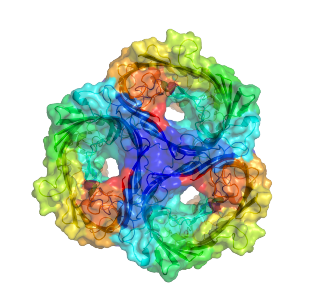


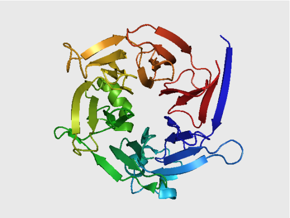


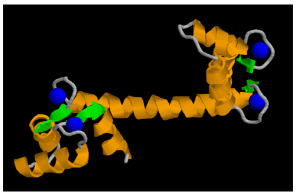


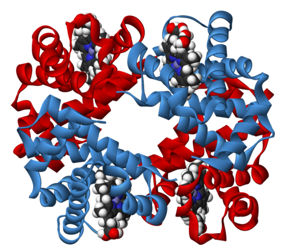


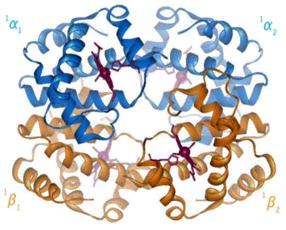


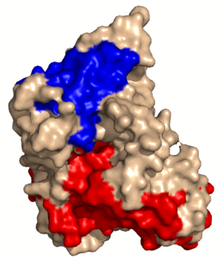


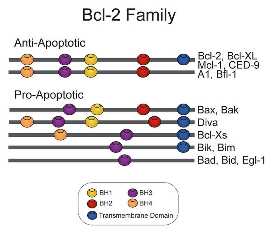


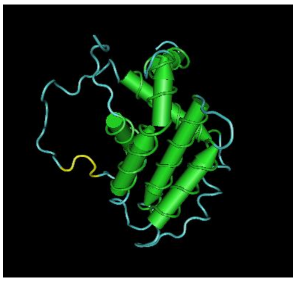


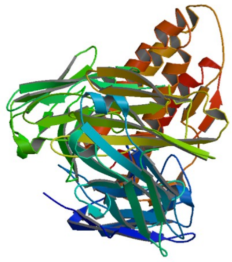


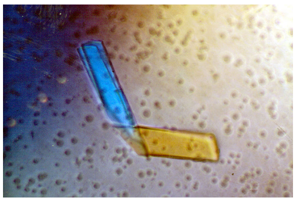


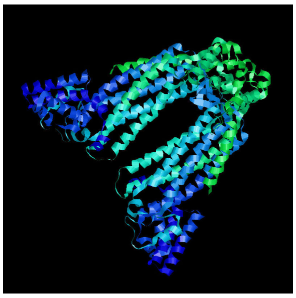










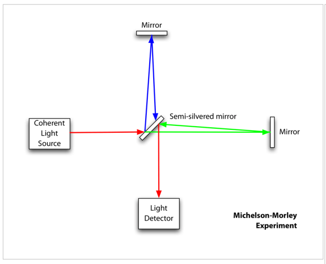


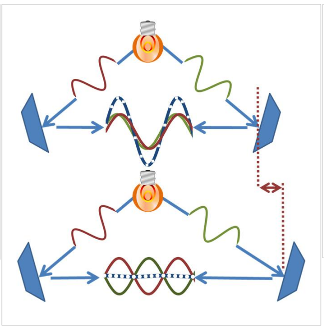
VCD of nucleic acids

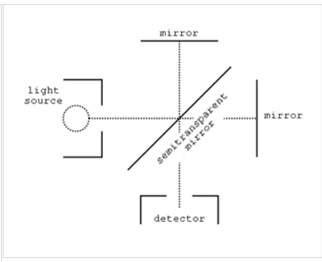
VCD spectra of nucleotides, synthetic polynucleotides and several nucleic acids, including DNA, have been reported and assigned in terms of the type and number of helices present in A- , B-, and Z- DNA.

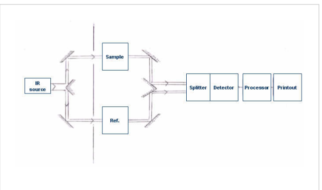
VCD Instrumentation

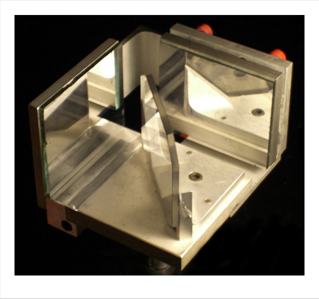
For biopolymers such as proteins and nucleic acids, the difference in absorbance between the levo- and dextro- configurations is five orders of magnitude smaller than the corresonding (unpolarized) absorbance. Therefore, VCD of biopolymers requires the use of very sensitive, specially built instrumentation as well as time-averaging over relatively long intervals of time even with such sensitive VCD spectrometers. Most CD instruments produce left- and right- circularly polarized light which is then either sine-wave or square-wave modulated, with subsequent phase-sensitive detection and lock-in amplification of the detected signal. In the case of FT-VCD, a photo-elastic modulator (PEM) is employed in conjunction with an FT-IR interferometer set-up. An example is that of a Bomem model MB-100 FT-IR interferometer equipped with additional polarizing optics/ accessories needed for recording VCD spectra. A parallel beam emerges through a side port of the interferometer which passes first through a wire grid linear polarizer and then through an octagonal-shaped ZnSe crystal PEM which modulates the polarized beam at a fixed, lower frequency such as 37.5 kHz. A mechanically stressed crystal such as ZnSe exhibits birefringence when stressed by an adjacent piezoelectric transducer. The linear polarizer is positioned close to, and at 45 degrees, with respect to the ZnSe crystal axis. The polarized radiation focused onto the detector is doubly modulated, both by the PEM and by the interferometer setup. A very low noise detector, such as MCT (HgCdTe), is also selected for the VCD signal phase-sensitive detection. Quasi-complete commercial FT-VCD instruments are also available from a few manufacturers but these are quite expensive and also have to be still considered as being at the prototype stage. To prevent detector saturation an appropriate, long wave pass filter is placed before the very low noise MCT detector, which allows only radiation below 1750 cm^{-1} to reach the MCT detector; the latter however measures radiation only down to 750 cm^{-1}. FT-VCD spectra accumulation of the selected sample solution is then carried out, digitized and stored by an in-line computer. Published reviews that compare various VCD methods are also available.[9] [10]

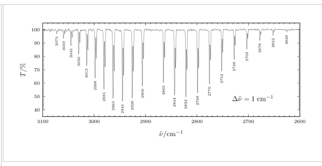


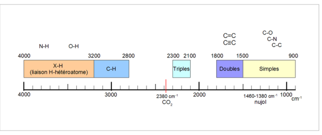


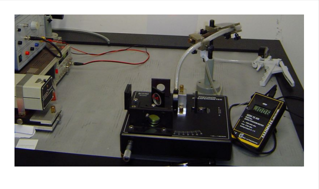


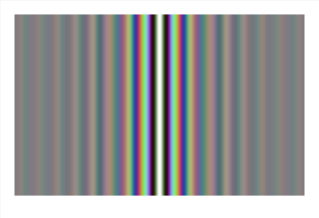


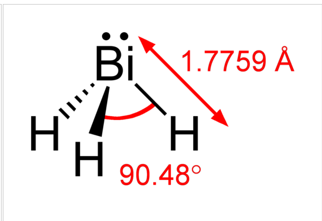












Magnetic VCD

VCD spectra have also been reported in the presence of an applied external magnetic field[11] . This method can enhance the VCD spectral resolution for small molecules[12] [13] [14] [15] [16] .

Raman optical activity (ROA)

ROA is a technique complementary to VCD especially useful in the 50--1600 cm^{-1} spectral region; it is considered as the technique of choice for determining optical activity for photon energies less then 600 cm^{-1}.

Notes

[1] http://planetphysics.org/?op=getobj;from=objects;id=410 Principles of IR and NIR Spectroscopy

[2] *"Vibrational Circular Dichroism of Polypeptides XII. Re-evaluation of the Fourier Transform Vibrational Circular Dichroism of Poly-gamma-Benzyl-L-Glutamate," P. Malon, R. Kobrinskaya, T. A. Keiderling, Biopolymers 27, 733-746 (1988).

[3] *"Vibrational Circular Dichroism of Biopolymers," T. A. Keiderling, S. C. Yasui, U. Narayanan, A. Annamalai, P. Malon, R. Kobrinskaya, L. Yang, in *Spectroscopy of Biological Molecules New Advances* ed. E. D. Schmid, F. W. Schneider, F. Siebert, p. 73-76 (1988).

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[9] "Polarization Modulation Fourier Transform Infrared Spectroscopy with Digital SignalProcessing: Comparison of Vibrational Circular Dichroism Methods." Jovencio Hilario, DavidDrapcho, Raul Curbelo, Timothy A. Keiderling, Applied Spectroscopy 55, 1435-1447(2001)--

[10] "Vibrational circular dichroism of biopolymers. Summary of methods and applications.", Timothy A. Keiderling, Jan Kubelka, Jovencio Hilario, in *Vibrational spectroscopy of polymers and biological systems*, Ed. Mark Braiman, Vasilis Gregoriou, Taylor&Francis, Atlanta (CRC Press, Boca Raton, FL) (2006) pp. 253-324 (originally written in 2000, updated in 2003)

[11] "Observation of Magnetic Vibrational Circular Dichroism," T. A. Keiderling, Journal of Chemical Physics, 75, 3639-41 (1981).

[12] "Vibrational Spectral Assignment and Enhanced Resolution Using Magnetic Vibrational Circular Dichroism," T. R. Devine and T. A. Keiderling, *Spectrochimica Acta*, 43A, 627-629 (1987).

[13] "Magnetic Vibrational Circular Dichroism with an FTIR" P. V. Croatto, R. K. Yoo, T. A. Keiderling, SPIE Proceedings 1145 (7th International Conference on FTS, ed. D. G. Cameron) 152-153 (1989).

[14] "Direct Measurement of the Rotational g-Value in the Ground State of Acetylene by Magnetic Vibrational Circular Dichroism." C. N. Tam and T. A. Keiderling, Chemical Physics Letters, 243, 55-58 (1995).

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See also

- Circular dichroism
- Birefringence
- Optical rotatory dispersion
- IR spectroscopy
- Polarization
- Proteins
- Nucleic Acids
- DNA
- Molecular models of DNA
- DNA structure
- Protein structure
- Amino acids
- Density functional theory
- Quantum chemistry
- Raman optical activity (ROA)

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