# Polarized IR Spectroscopy and Transition Dipole Moment Determinations in Structural Studies

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The measurement of transition dipole orientation of IR active vibrations is known to be a very efficient tool for enhancing the reliability of vibrational assignments. Such information can be extracted from polarized IR spectra of oriented samples, i.e. from infrared linear dichroism (IR-LD) measurements. Spectral studies of oriented single crystals are met with a number of technical difficulties. In contrast, solute alignment in a nematic liquid crystal as anisotropic solvent has made the method applicable to a wide range of compounds. In this case the measured dichroic ratios (*R*i) of IR absorption bands can be converted to orientational parameters (*K*i) that can be used for the calculation of the absolute value of the angles that the transition moments (TMs) make with the preferred direction of molecular orientation called "long molecular axis". There is a sign ambiguity in this determination, that can be lifted by joint evaluation of experimental and theoretically predicted, calculated spectral parameters.

Several examples of the application of this approach will be given demonstrating its effectiveness in elucidating some details of band assignment and in making structural inferences in molecules with *planar* (Cs) symmetry [1-4]. Determination of the average orientation of such molecules and their experimental transition moment directions is facilitated by corrections introduced through comparison with quantum chemically calculated vibrational transition moments of two strong absorption bands. According to the accumulated evidence, TM directions calculated by DFT (B3LYP/6-31G* or higher level) for medium intense or stronger bands agree with experimental data within 5-10°, i.e. they are much more reliable than what can be anticipated from simple structural considerations.

Further improvement in performance of the method is expected from DFT calculations using the Integral Equation Formalism - Polarizable Continuum Model (IEF PCM) taking into account the effect of anisotropic medium on the solute molecules. This is being tested by asymmetric deuteration of naphthalene (1-D and 2-D-derivatives), where the *D*2h symmetry of the force field is retained and the observed and calculated changes in TM directions are due to the mass effects alone.

The proposed IR spectroscopic methodology may provide helpful reference data to increase the accuracy of determination of the direction of electronic transitions in a number of dye molecules used in liquid crystal display technology. Finally, other experimental IR-LD approaches encountered in spectroscopic literature (alignment of molecules in stretched polymers; alignment of crystallites in LC suspension; and alignment of biomolecules in helium nanodroplets by strong electric field) will be shortly described and characterized concerning their usefulness in studies of molecular structure.

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