

## ORD

ORD has been for years a rather neglected technique. The practical taking over of CD versus ORD can be traced at the end of the sixties; it was not casual that ORD/CD manufacturers such as JASCO and Cary switched to CD only machines when introducing second generation units (like the J-40 and the Cary 61).

Since that time ORD has been limited to sugar/polysaccharides, i.e. to samples with no chromophore in the UV-VIS range, even so often sample derivatization had been a way to use more conveniently the CD technique. Other typical ORD customers have been for a while the pharmaceutical industries or university departments, which for  $\alpha$  was synonymous of chirality.

As a matter of fact while both techniques are giving the same sort of information (since spectra can be converted each-other by Kramers-Kronig), but real ORD machines were more expensive than *equivalent* CD spectrometers and low UV penetration was somehow limited by the need of the second, crossed, polarizer.

But ORD still have a unique facility versus CD: it can see far away where chromophores absorb in the vacuum UV not accessible by conventional spectrometers<sup>1</sup>.

With the recent progresses of computational methods, the *ab initio* prediction of optical rotation (OR) is nowadays possible. A simple criterion (presence of low-lying, intense Cotton effects which dominate the OR at 589 nm in sign and magnitude) has been proposed<sup>2</sup> to *a priori* decide when a small basis set calculation is reliable: in this way also the absolute configuration of large molecule (up to 60 atoms) can be assigned by *ab initio* calculating the OR (with the complementary help of the relevant CD spectra).

A very comprehensive review on OR as a tool in determining absolute configuration has been recently published by Polavarapu<sup>3</sup>.

For these sort of jobs the ideal experimental data would be OR measured in gas phase, where solute-solute interactions are avoided. This is typically not easy since pathlength of commercial ORD spectrometers or polarimeters is limited to 10 or 20cm in the best of the cases. To bypass the limitation new experimental set-ups as Cavity Ring Down Polarimetry (CRDP)<sup>4,5</sup> have been successfully applied (for instrumental funs also previous papers on cavity techniques are interesting<sup>6,7</sup>).

CRDP technique is however still very specialized and it's hard to foresee a wide diffusion. In addition the change of analytical wavelength calls for the addition (and the alignment) of different (and expensive) components.

Since comparison between calculated and experimental data carried out on several wavelengths provide more information than a comparison carried out at a single wavelength leading to a more safe configurational assignment, the possibility of a renaissance of optical rotatory dispersion is here, even if limited by the relative cell short path and/or solution phase measurements.

In the opposite direction it's also possible to foresee the development of more sensitive, but still simple, polarimeters running at a fixed or at a few wavelengths from a laser source, but incorporating long path gas cells (in the meter range) and sensitive detection systems based on HPLC/OR detectors.

A sensitivity enhancement of two order of magnitudes versus conventional polarimeters or ORD spectropolarimeters should be easy to achieve at a moderate cost.

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<sup>1</sup> Meguro H. et al. *Poster P54 at CD2001*, Sendai (Jp), 2001

<sup>2</sup> Giorgio, E.; Minichino, C.; Viglione, R.G.; Zanasi, R.; Rosini, C., *J. Org. Chem.*, 68, 2003, 5186

<sup>3</sup> Polavarapu P.L., *Chirality*, 14, 2002, 788

<sup>4</sup> Muller T., Wiberg K.B., Vaccaro P.H., *J. Phys. Chem. A*, 104, 2000, 5959

<sup>5</sup> Muller T., Wiberg K.B., Vaccaro P.H., Cheeseman J.R., Frisch M.J., *J. Opt. Soc. Am. B*, 19, 2002, 125

<sup>6</sup> Engeln R., Berden G., Peeters R., Meijer G., *Rev. Sci. Instrum.*, 69, 1998, 3763

<sup>7</sup> Le Grand Y., Medjaou M., Le Floch A., Naour R., *Appl. Phys. Lett.*, 51, 1987, 1574