

Vibrational Spectroscopies for large Quantum Number Transitions: NIR, NIR-VCD and Raman

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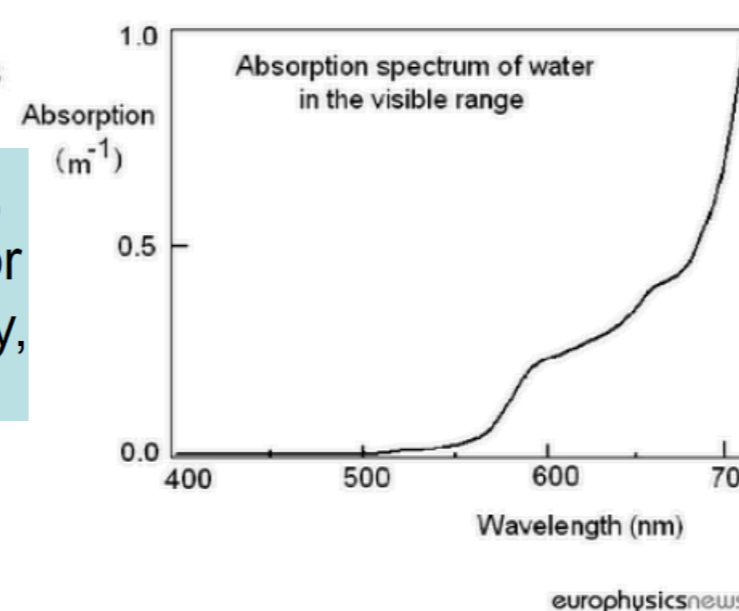
All Molecules possess vibrational transitions. Vibrational transitions produce absorption in the Infrared, but absorptions linger through the Near Infrared (NIR) and even the visible range, as long as there is enough substance or the path-length of travelling light is sufficiently long. Indeed one has OVERTONE and COMBINATION transitions there. They may be important to detect "dark" molecules in the universe, namely molecules electronic transitions in the far UV.

Blue skies, blue seas

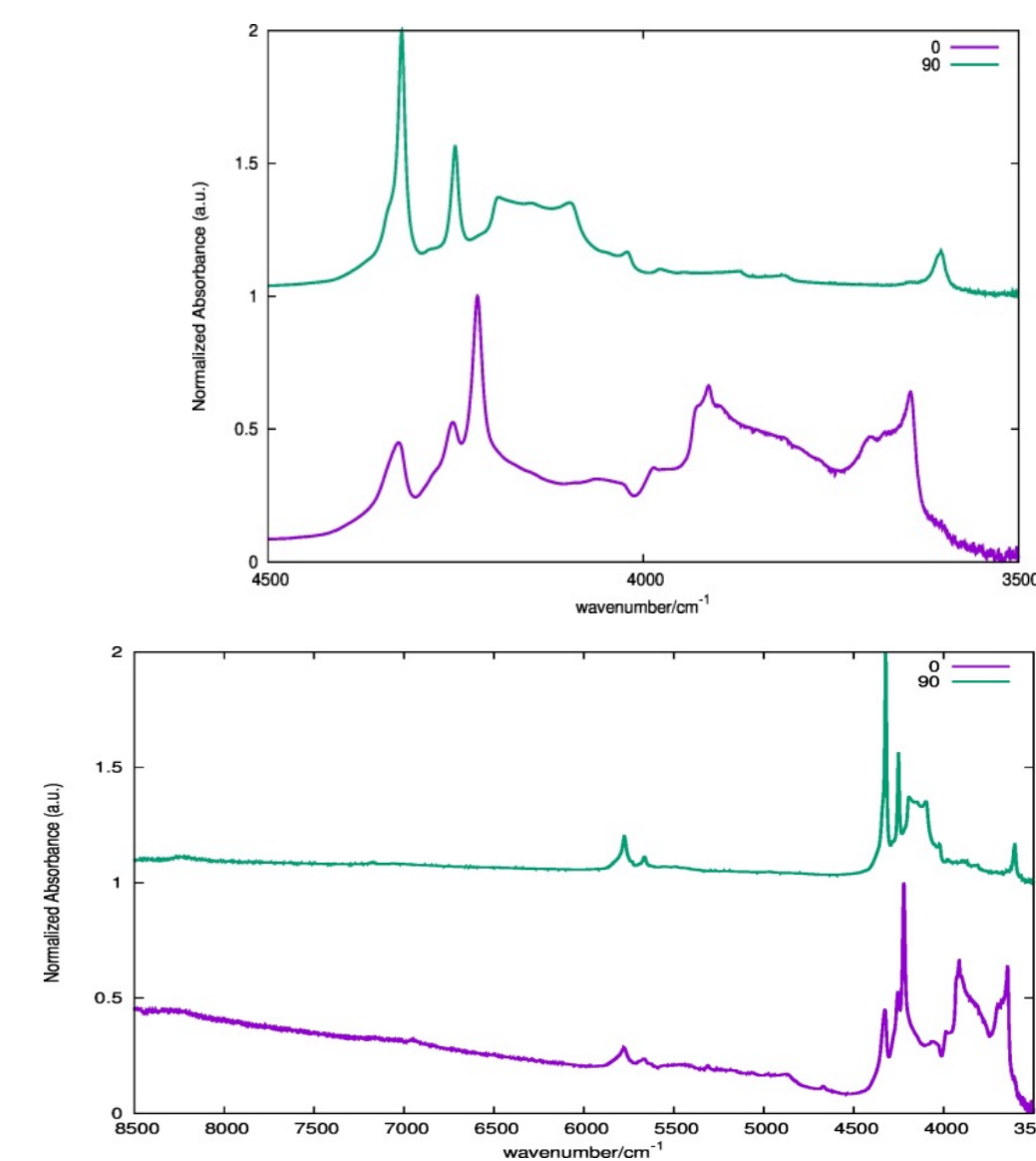
Why are overtones interesting?

L.J.F.(Jo) Hermans,
Leiden University - The Netherlands

...and Kjaergaard, in Otago, looked for pollutants in the sky, through NIR....

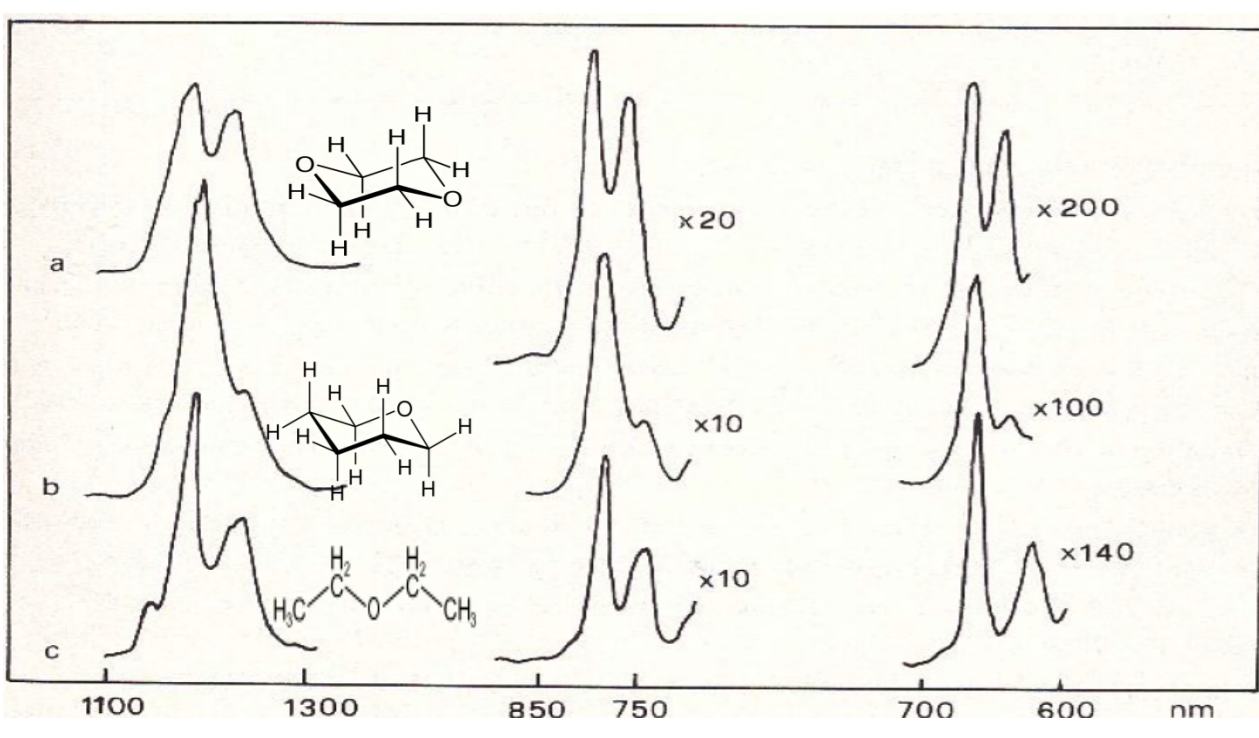


(Polyethylene)

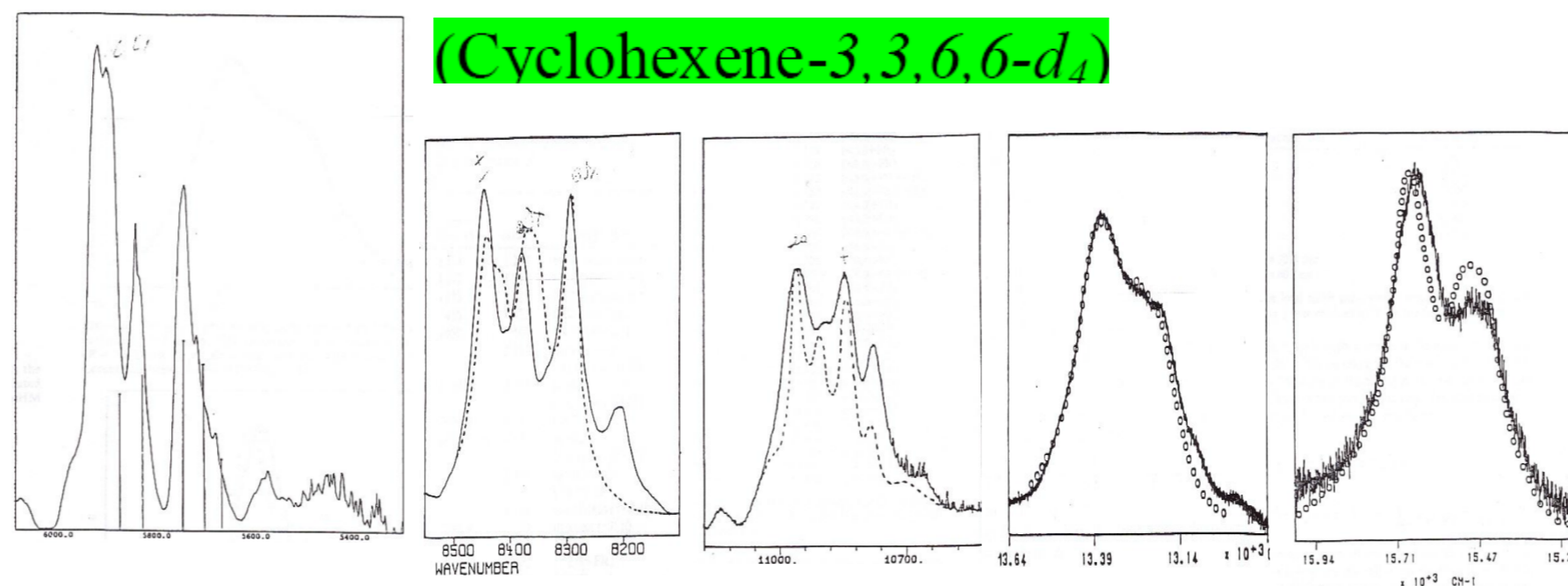


(Dioxane, Tetrahydropyran, and Diethyl Ether)

Examples of NIR Spectra



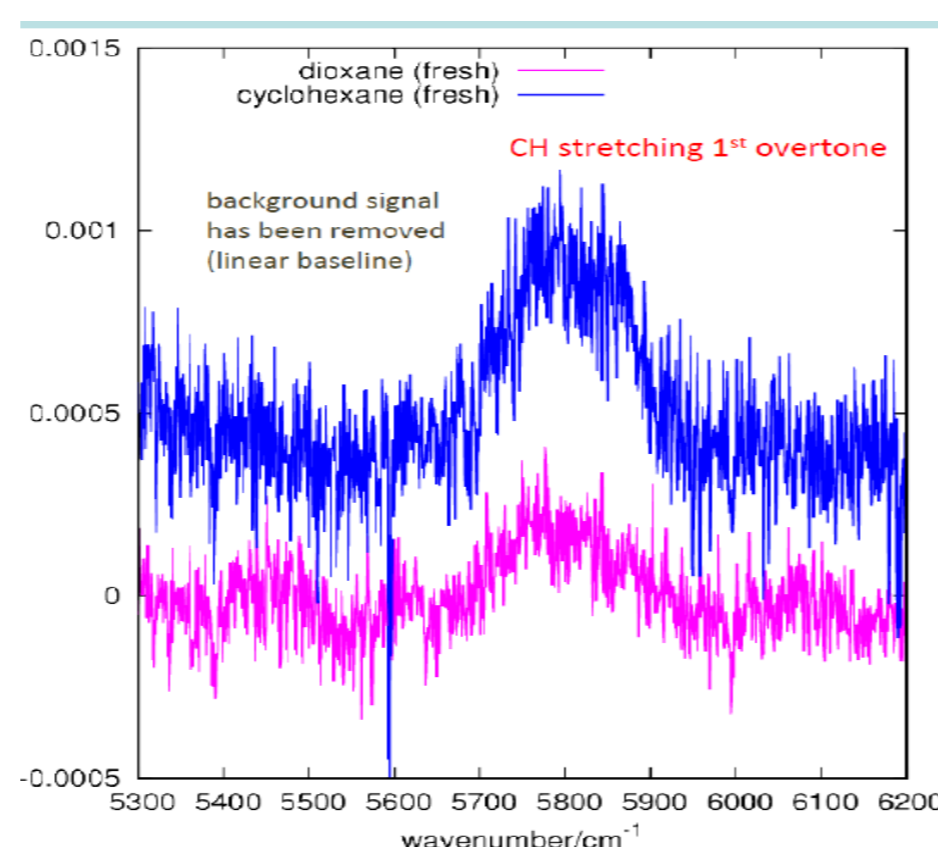
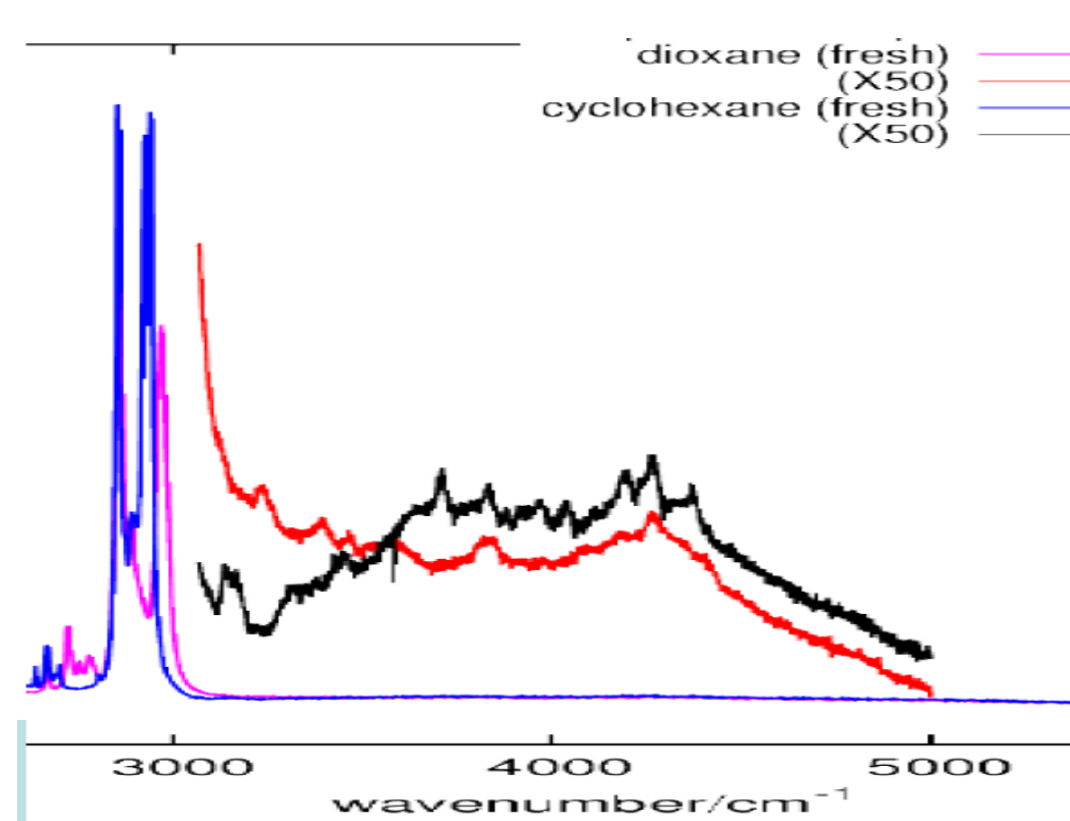
(Cyclohexene-3,3,6,6-d₂)



Spectra are easily interpreted in terms of **Local Modes**, since Mechanical Anharmonic effects prevail over Harmonic Couplings. One thus observes only symmetrically inequivalent XH-stretchings (mostly CH). However this is an approximation (see Cyclohexene case above) and Theoreticians are welcome to help.

Are other NIR (or Local Mode) Spectroscopies possible?

Overtone-Raman



Raman spectra of overtones and combinations (beyond Henry's neopentane) J. Chem. Phys. 79:2583-2589 1983

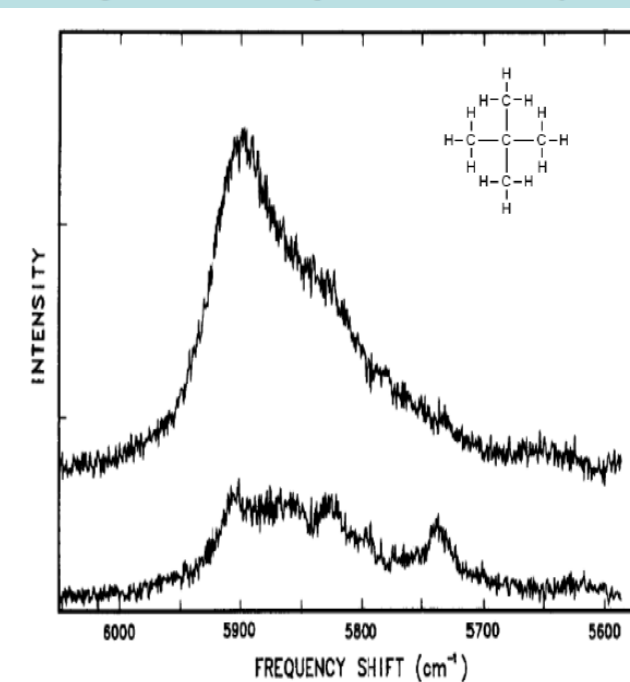


FIG. 2. Anisotropic (top) and isotropic (bottom) components of the Raman spectrum of liquid phase neopentane in the region of $\Delta\nu_{CH} = 2$. The spectrum was obtained with a spectral slit width of 4-5 cm^{-1} .

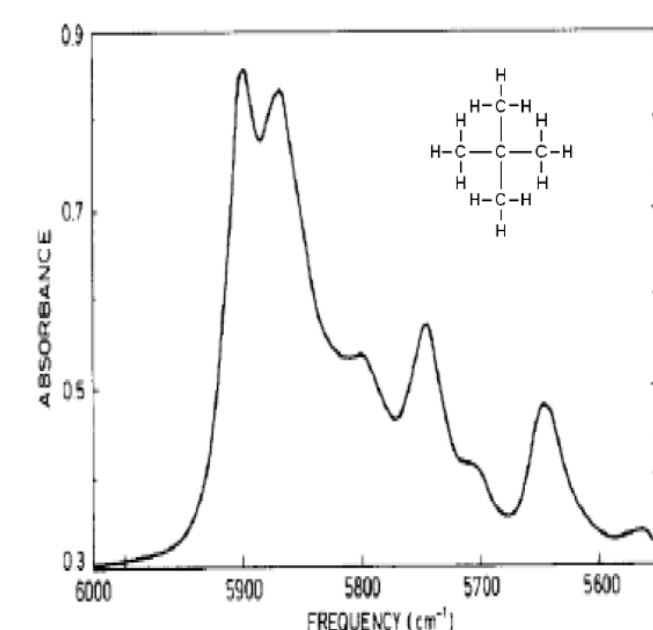
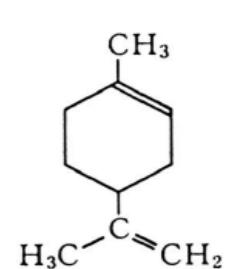


FIG. 3. Absorption spectrum of liquid phase neopentane in the $\Delta\nu_{CH} = 2$ region at 0,1 cm pathlength.

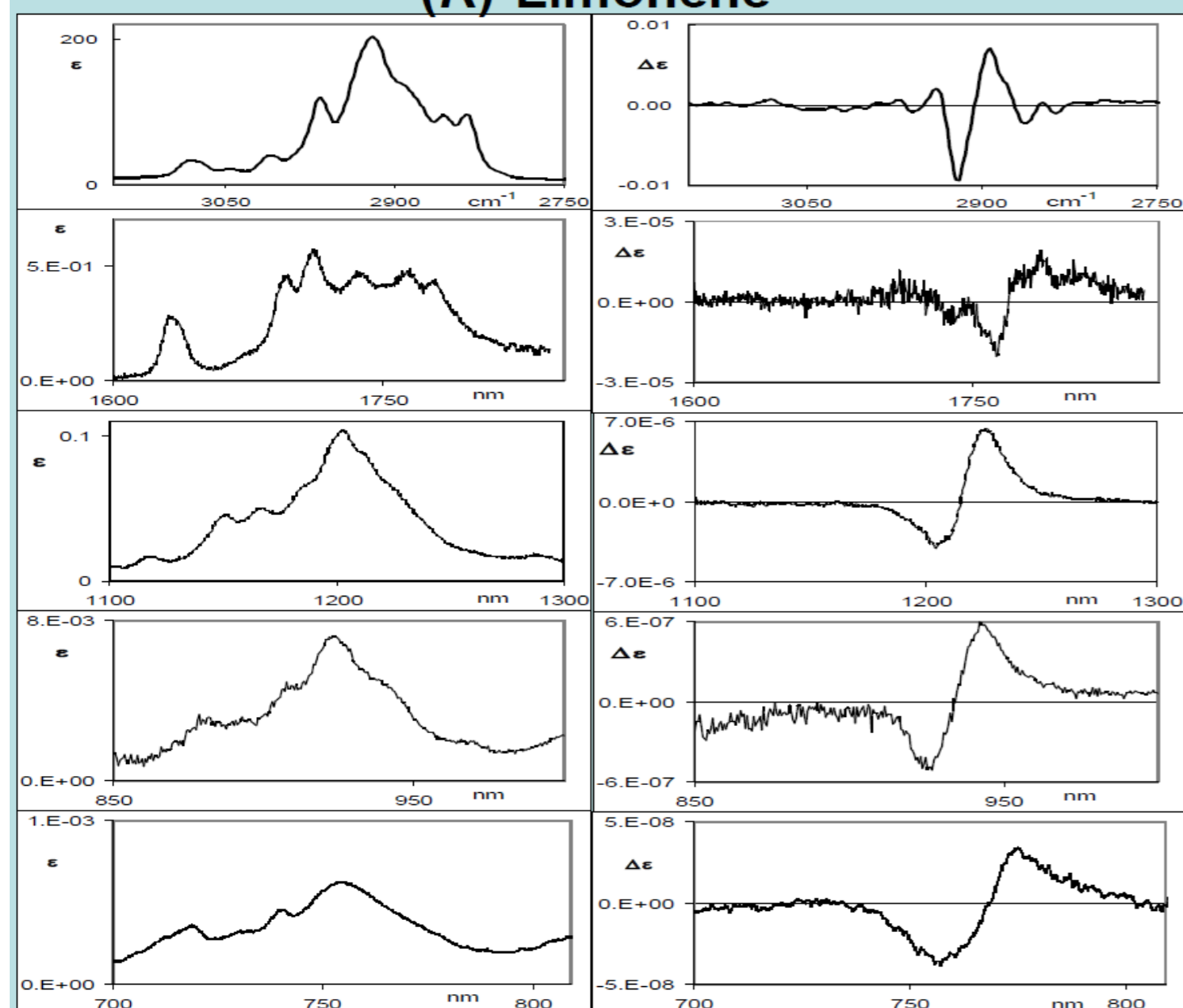
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NIR-VCD (permits to investigate right-handed (R) and left-handed (S) forms)

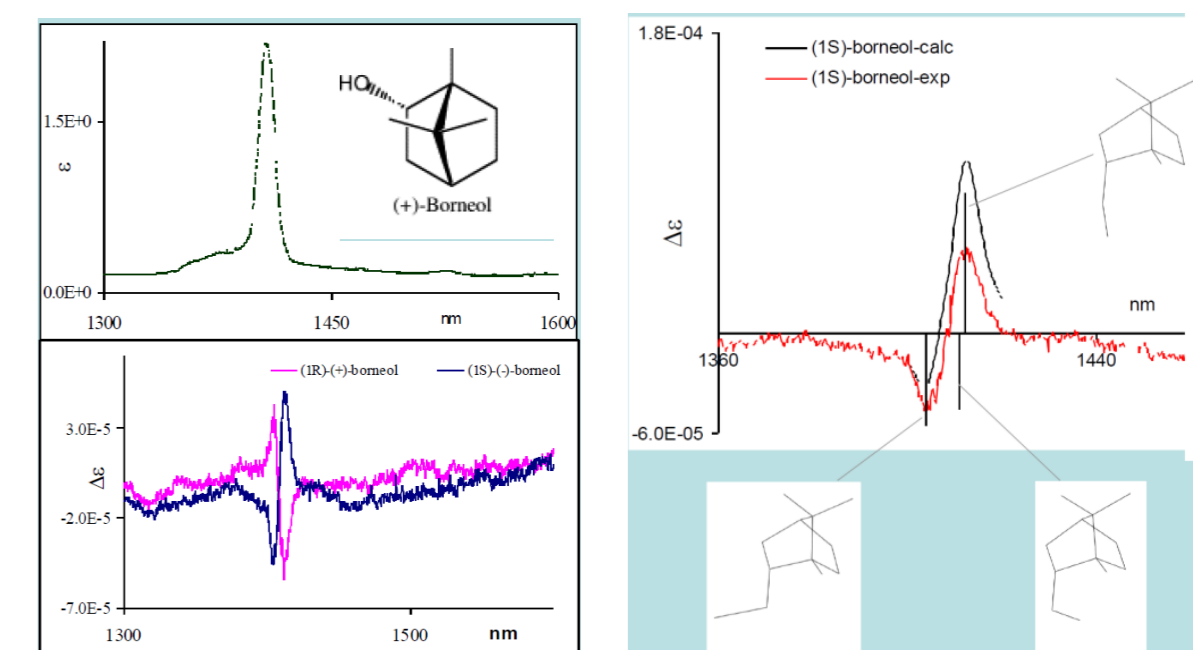
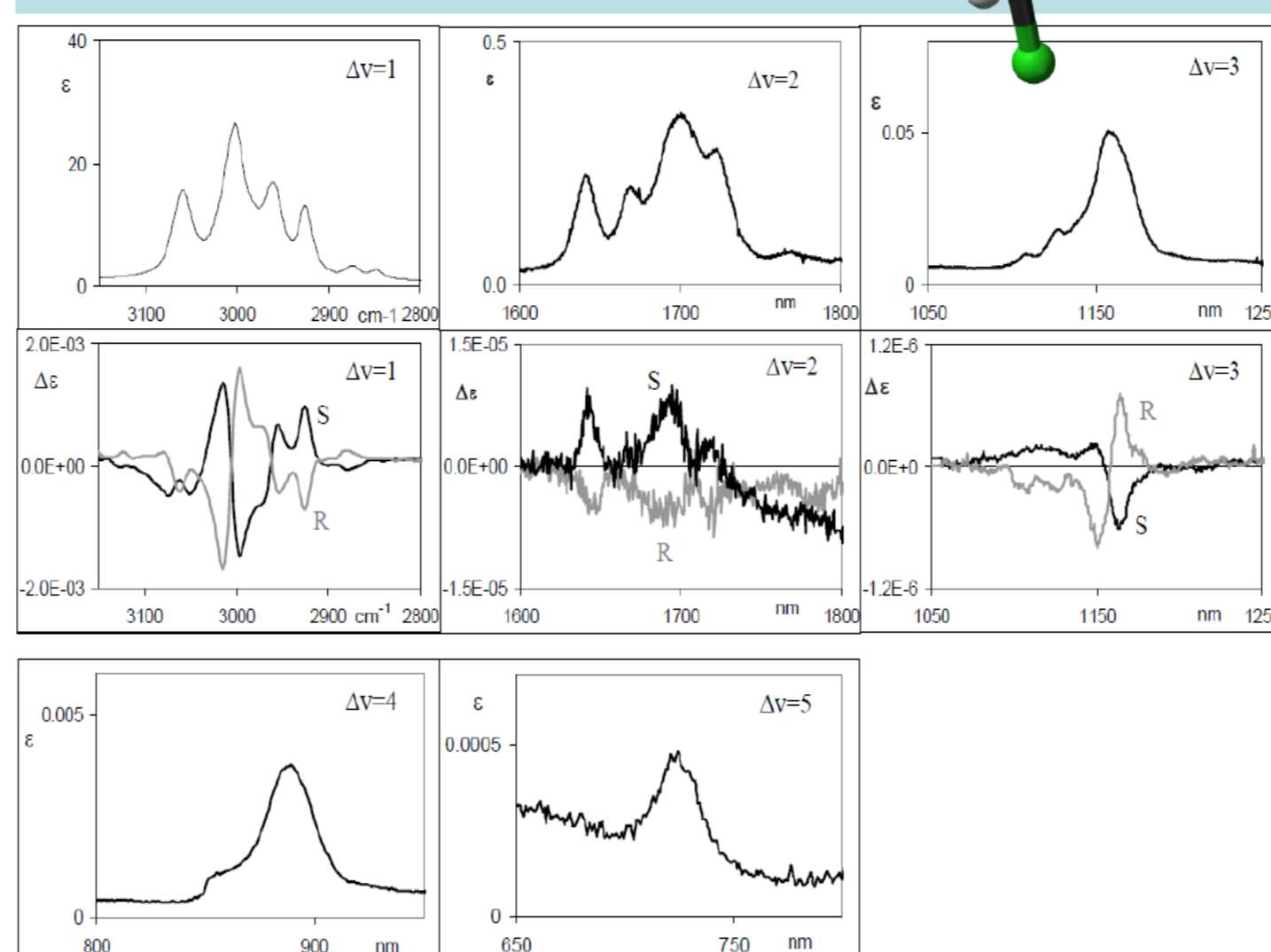
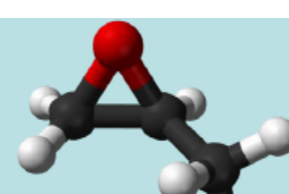
THE CASE OF *endo*-BORNEOL



(R)-Limonene



Epichlorohydrin



Butanediol at $\Delta\nu=2$ OH stretching

