

Ultrafast Conformational Dynamics of (R) - 1,1'-Bi-2-naphthol Measured with Time-Resolved Circular Dichroism

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Circular dichroism (CD) is known to be a sensitive probe of molecular conformations. The idea of using CD in a pump-probe configuration in order to study the dynamics of structural changes occurring in molecules or in biomolecules is therefore quite natural [1]. In this context, we have recently developed a new technique which allows measurements of time-resolved CD in a user-friendly and artefact-free way. We will present and apply it to the study of the conformational dynamics of the excited state of 1,1'-Bi-2-naphthol.

CD can be obtained either with modulated circular polarizations or through ellipticity measurements. To get rid of the artefacts induced by the first technique, we have developed the second one which only involves non-modulated, linearly-polarized beams. The sample is placed between crossed polarizer and analyzer. The probe ellipticity is measured through a Babinet-Soleil compensator (BS) by recording the transmitted intensity (the "PM" signal) as a function of the BS retardation. A mechanical chopper is inserted on the pump optical path and a lock-in amplifier allows us to measure the modulated part of the PM signal (the "LI" signal). When measuring simultaneously the PM and the LI signals for small BS retardations, we obtain two parabolas [2]. Comparing both quadratic coefficients of the PM and LI parabolas directly yields the change in absorption whereas the shift between the LI and PM parabolas yields the change in CD (see figure 1d,e).

Experiments have been performed in the UV to investigate the dihedral angle changes in photoexcited (R)-1,1'-Bi-2-naphthol. Pump pulses are obtained after frequency tripling the output of a 150 fs, 1 kHz Titanium-Sapphire laser. Pulse energy is about 200 nJ. A tunable probe was obtained through several stages of optical parametric amplification. Results for two solvents are given in figure 1c ($c = 2.2 \cdot 10^{-4}$ M) for a probe wavelength of 237 nm. The pump-induced CD is plotted as a function of the pump-probe delay. The dots are obtained for Ethanol whereas the squares are for Ethylene Glycol. Pump-induced absorption changes are plotted in figure 1b. It is important to note that the absorption change is the same for both solvents and that there is no noticeable dynamics on the 400 psec timescale. On the contrary, we observe a quite different behaviour for the CD curves: a large difference is obtained for the two solvents and a 100 psec dynamics is measured for Ethanol. These differences prove that we observe true changes in the molecule conformation and not just an electronic relaxation or a reorientation effect. These conformational changes are clearly solvent dependent: the higher the viscosity, the longer the relaxation time. We assign this dynamics to a dihedral angle variation [3, 4].

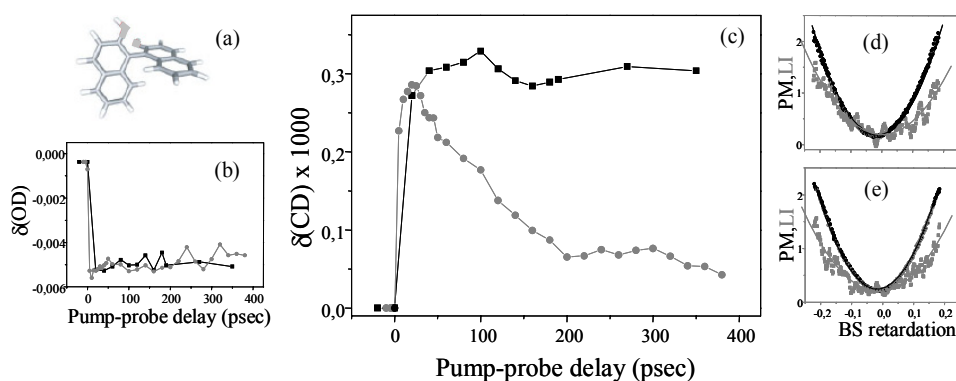


Fig. 1: (a) Structure of 1,1'-Bi-2-naphthol. (b,c) Time-resolved absorption and CD of 1,1'-Bi-2-naphthol in Ethanol (dots) and in Ethylene Glycol (squares). (d,e) Raw PM and LI parabolas at delays 40 and 375 psec in Ethanol.

We have also performed this experiment at 245 nm where we observe induced absorption. In that case, we observe the onset of a CD signal. The rise time is about 25 ± 10 psec in Cyclohexane (a value in agreement with previous estimations performed in 1,1'-Binaphthyl [3, 4]) whereas it is 80 ± 20 psec in Ethanol. This difference is attributed to the formation of hydrogen bonds between the hydroxy groups and the solvent in the latter case.

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