The Circular Dichroism of (R)-(+)-Ethan[2H]ol

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The vacuum ultraviolet CD of (R)-(+)-ethan[2H]ol in the first excited state shows a relatively large positive CD signal.

The information that can be deduced from CD measurements is of importance. When the electronic excited state of a chromophore is well known and defined, the sign of the CD signal can be correlated with the absolute configuration. In cases where the molecular structure and conformation are known, the sign of the CD signal can help in assigning and characterizing the excited state. Alcohols and the hydroxy chromophores have attracted much attention, even prior to the extension of CD measurements into the vacuum UV (VUV). Various theories have been applied to calculate the
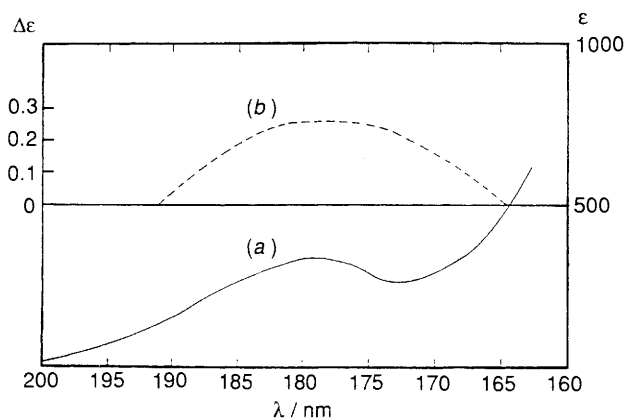
Fig. 1 (a) Absorption spectrum and (b) CD of (R)-(+)-ethan[^{2}H]ol in the gas phase. The spectral resolution is 16 Å.

$[\alpha]_D$ of (S)-(+)-butan-2-ol,[1-5] which is the smallest chiral alcohol exclusive of isotopic substitution.

The first results describing the CD spectra of alcohols were reported by Kirk et al.[6] who measured the spectra of hydroxy steroids and terpenes in hexane solution. For many compounds it was possible to predict the CD using a sector rule which was derived empirically.[6] Texter and Stevens[7] studied the CD spectra of ten alcohols in hexane solution, and followed their experiments with random-phase calculations using a time-dependent Hartree theory, considering only the first excited state. The CD of the first transition (ca. 56000 cm^{-1}; 178 nm) was calculated as a function of hydroxy rotation about the CO bond, by coupling the zero-order transition moments of this state to the backbone CC and CH bond density of states. This coupling is dominated energetically by electric-dipole, magnetic-dipole interaction terms ($\mu_e\mu_m$-coupling mechanism), and the electric-dipole of the first excited state could account for the sector rule formulated by Kirk et al.[6]

The nature of the first excited state of alcohols is a subject of debate.[10] There is agreement that the transition originates at a nonbonding 2p orbital at oxygen atom, but it has been suggested that it terminates at either a 3s Rydberg[10] or a valence σ^*,[8] with a conjugate 3s/σ^* as a compromise.[7]

Snyder and Johnson[8] measured the gas phase VUV CD of (S)-(+)-butan-2-ol, and observed three CD bands: a broad positive diffuse band centred at ca. 56000 cm^{-1}, a second positive, stronger band at 64000 cm^{-1}, and a third, negative band, at 67000 cm^{-1}. The CD of (S)-butan-2-ol was later measured in both water and hexafluoropropan-2-ol solution;[9] the CD spectrum of 1-borneol has also been measured in gas and liquid phases.[9]

Semiempirical[7,8] and ab initio I calculations[11] accounted for the sign of the first excited state of various alcohols but failed to reproduce the CD sign of the third band of (S)-(+)-butan-2-ol. Gottarelli and Samori have reviewed the early literature on the CD of alcohols.[12]

In this study we report the CD spectrum of (R)-(+)-ethan[^{2}H]ol in the gas phase.†

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† The instrument for the VUV CD measurements has been described previously.[13] The vapour pressure of the (R)-(+)-ethan[^{2}H]ol was measured using a Wallace and Tiernan manometer. An 11 cm optical cell was used. (R)-(+)-Ethan[^{2}H]ol was synthesized by an adaptation of the enzyme equilibration method of Simon[14,15] using ethanol in D$_2$O with catalytic amounts of yeast alcohol dehydrogenase, NADH and porcine heart diaphorase. The initial product (8.8 g) was dried over molecular sieves and refractionated. It contained less than 0.5% D$_2$O–HOD (GLC) and 3–1% of CH$_3$CH$_2$OD (by 400 MHz NMR analysis, CDCl$_3$ solvent): $\alpha_D{}^{20}$ + 0.199 (neat l = 1.000), $[\alpha]_D{}^{20}$ + 0.257 ± 0.003 (neat, density d^{20} 0.791); lit. $[\alpha]_D{}^{20}$ + 0.29 (neat),[14] $[\alpha]_D{}^{20}$ − 0.28 ± 0.02 (neat) for the enantiomer.[15]

The absorption and CD spectra of (R)-(+)-ethanol[^{2}H]ol are in Fig. 1. The value of ε (molar absorption coefficient) and the position of the absorption maximum correspond to those reported for C$_2$H$_5$OH.[10] A positive CD signal was observed, yielding a $\Delta\varepsilon/\varepsilon$ of 6.0 × 10^{-4}. This is relatively large for a chiral molecule whose chirality is due to a D–H substitution, especially for a flexible aliphatic system. A similar $\Delta\varepsilon/\varepsilon$ value was reported for the first CD band for (S)-(+)-butan-2-ol. The absorption and CD do not provide any additional information on the nature of the first excited state. The ORD of various [1-^{2}H]neopentyl derivatives (Bu^{t}CHDX) has been studied.[16] (R)-Derivatives with X = OH, F, Cl, Br or I gave plain negative ORD curves at λ>300 nm. It is also significant that (R)-(−)-butan-1-[^{2}H]ol and (R)-(−)-propan-1-[^{2}H]ol show the same sign. However, these are opposite in sign to the configurationally related (R)-(+)-ethan[^{2}H]ol. Clearly, this apparent anomaly required further investigation. Whether this opposite behaviour can be related to the disignate behaviour that deuterium atoms reveal in many chromophores[17] is not clear. The positive CD signs of the first excited state of (S)-(+)-butan-2-ol[8] and (R)-(+)-ethan[^{2}H]ol indicate that they should be compared. This is difficult because each molecule has various conformations whose contribution to the CD is unknown. However, for (S)-(+)-butan-2-ol the rotatory strength of the important conformers was also calculated,[11] and one conformation is similar to that of anti-(R)-ethan-[^{2}H]ol, the most stable conformer,[18] and presumably the one responsible for its positive sign. However, this comparison (which would have yielded a consignate behaviour for the deuterium atom and ethyl group) can be queried because this conformer, despite its relatively large positive CD, is not the most stable conformer for (S)-(+)-butan-2-ol, and it is not clear whether it is responsible for the positive sign.

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