UNIVERSITY OF COPENHAGEN
FACULTY OF SCIENCE

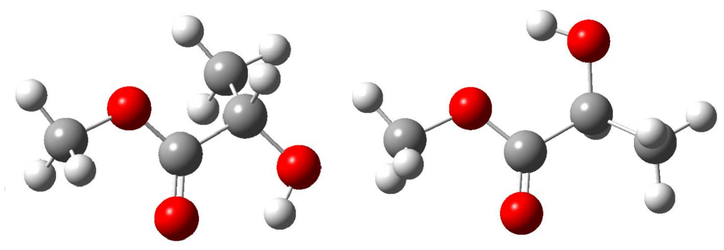
# Intramolecular Hydrogen Bonding in Methyl Lactate

Jens H. Wallberg, Sidsel D. Schrøder, Zeina Maroun, and Henrik G. Kjaergaard

Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark

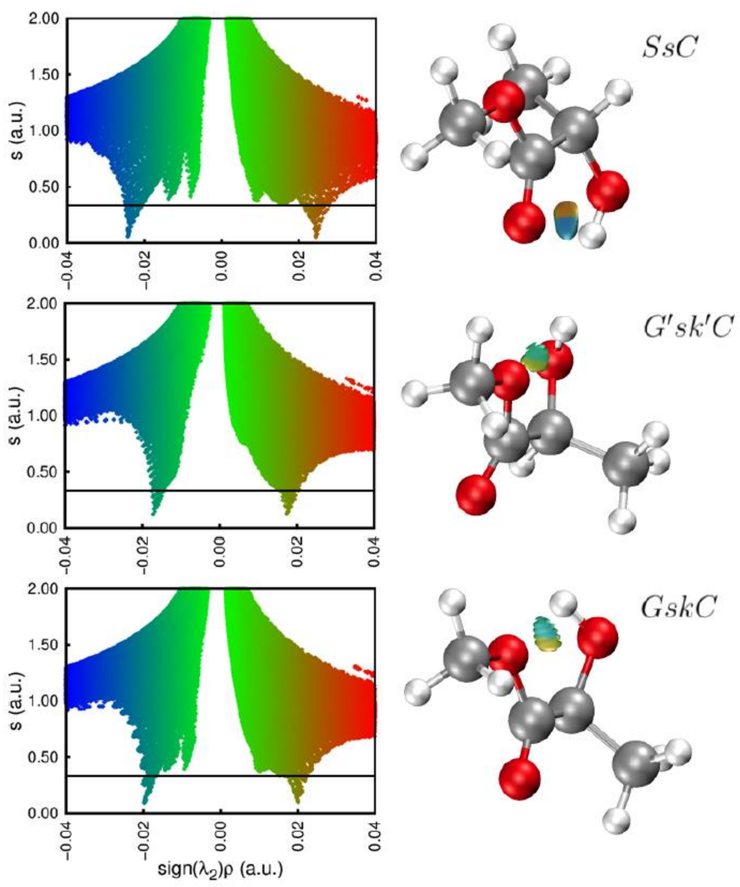
## Different types of hydrogen bonds

Competition between different types of hydrogen bonds is important. Methyl lactate (ML) has the ability to form either a OH···O=C or a OH···$O_{divalent}$ hydrogen bond - both involving the same types of atoms. Thus it can be used to investigate the factors, besides atom type, which may influence hydrogen bond strengths.



## Calculations

Our conformer search found three conformers (named *SsC*, *G'sk'C* and *GskC*, respectively) with abundancies above 1%. The *SsC* conformer is the most abundant with a Boltzmann distribution of 97%. Structurally, all three conformers seem to possess an intramolecular O-H···O hydrogen bond.

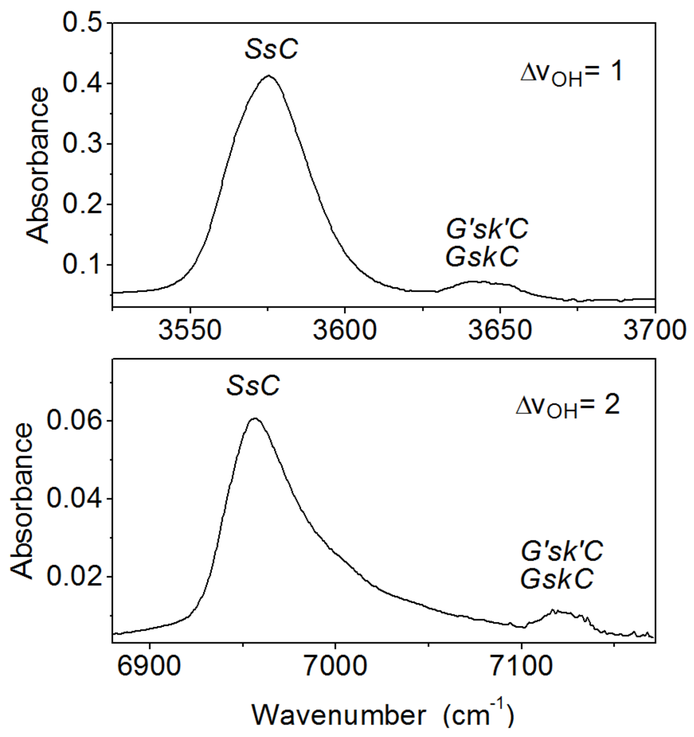



The NCI analysis above clearly show intramolecular hydrogen bond interactions in the three conformers and suggest that the strongest hydrogen bond is found in the *SsC* conformer as indicated by the position of the trough in the 2D NCI plot.

The NBO analysis confirms this as it predicts a higher stabilization energy for the *SsC* ($E^{(2)}$=12.9 kJ/mol) than for the *G'sk'C*/*GskC* ($E^{(2)}$=2.0 / 3.9 kJ/mol) conformers.

## FTIR of OH bands

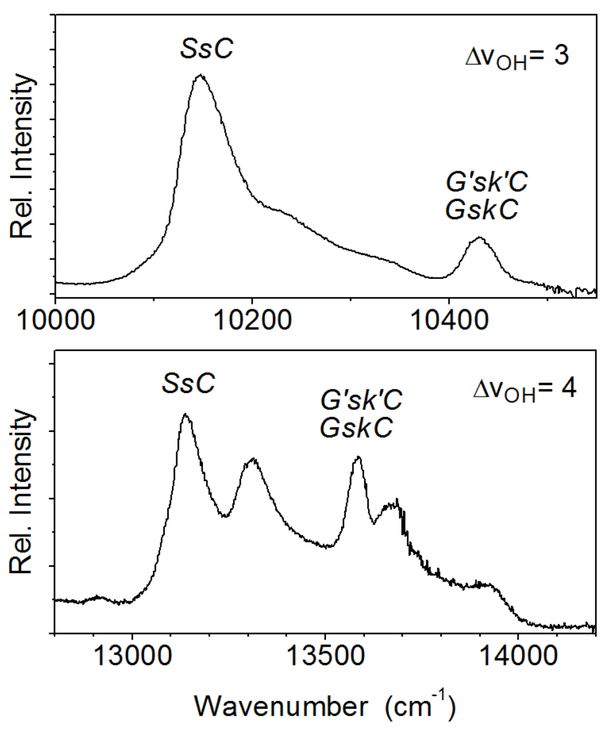
The $\Delta v_{OH}$=1-2 transitions of gas phase ML were recorded with FTIR.
In both regions the band for the *SsC* conformer is red-shifted with respect to the *G'sk'C*/*GskC* conformers indicating a stronger hydrogen bond in *SsC*.




## ICL-PAS of OH bands

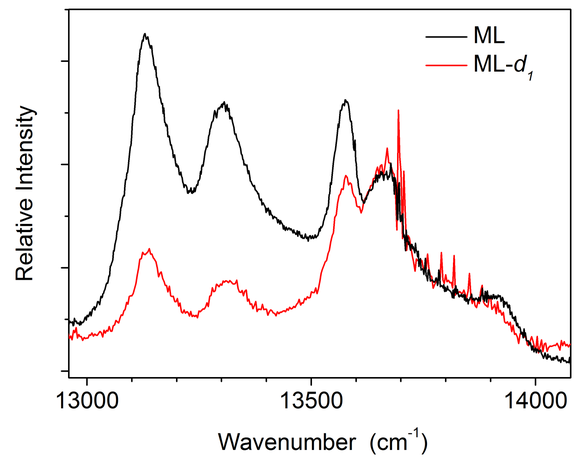
The weak $\Delta v_{OH}$=3-4 transitions of gas phase ML were recorded using the sensitive intracavity laser photoacoustic spectroscopy (ICL-PAS) technique.

These spectra confirm the trend seen in the FTIR spectra. However, the $\Delta v_{OH}$=4 spectrum is more complicated due to overlapping with $\Delta v_{CH}$=5 transitions. Assignments in this region required further experiments as shown to the right.



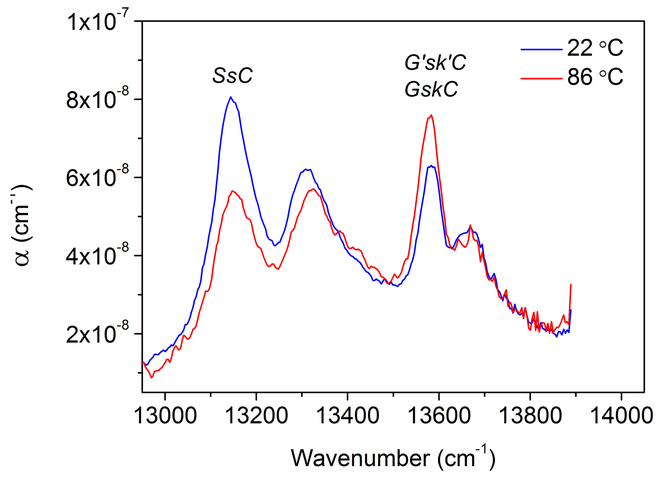

## Isotopic substitution study

The ICL-PAS spectrum of the $\Delta v_{OH}$=4 region of partially deuterated ML (ML-$d_1$) is shown along with the spectrum of undeuterated ML. Deuteration should make all OH bands disappear. However, complete deuteration was not possible and the ML-$d_1$ spectra still contain bands from the OH-stretching in ML, albeit at reduced intensity.




## Temperature study with CRD

The temperature dependence of the $\Delta v_{OH}$=4 region of ML was examined by recording a cavity ring-down (CRD) spectrum at two different temperatures. One band increases in intensity with temperature and one band decreases due to changing population of the different conformers facilitating the final assignment of bands.




## Conclusion

The intramolecular hydrogen bond in ML was observed to be stronger in the *SsC* conformer than in the *GskC*/*G'sk'C* conformers indicating that carbonyl oxygen is a better hydrogen bond acceptor than ester oxygen.

## Acknowledgements

Jay Kroll and Veronica Vaida are acknowledged for their valuable contribution to this project.

## Reference

S. D. Schrøder, J. H. Wallberg, J. A. Kroll, Z. Maroun, V. Vaida, and H. G. Kjaergaard, *J. Phys. Chem. A,* **2015**, in press,
DOI: 10.1021/acs.jpca.5b04812