Comparing Raman quantifications in water-ethanol-propanol mixtures – How much is it?

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Introduction

In the last year, students had the following task at our advanced lab exercise:
"In our current laboratory exercise research project, we will build a robust quantitative model of some chemical mixture. To do this both a calibration and a test data-set will be provided. On these data-sets several different approaches for building quantitative Raman models are tested and finally the accuracy and detection limits of the best model will be determined. Our goal is to demonstrate that even in the limited time available during a lab exercise it is possible to build a quantitative Raman model with sufficient confidence for real life applications."
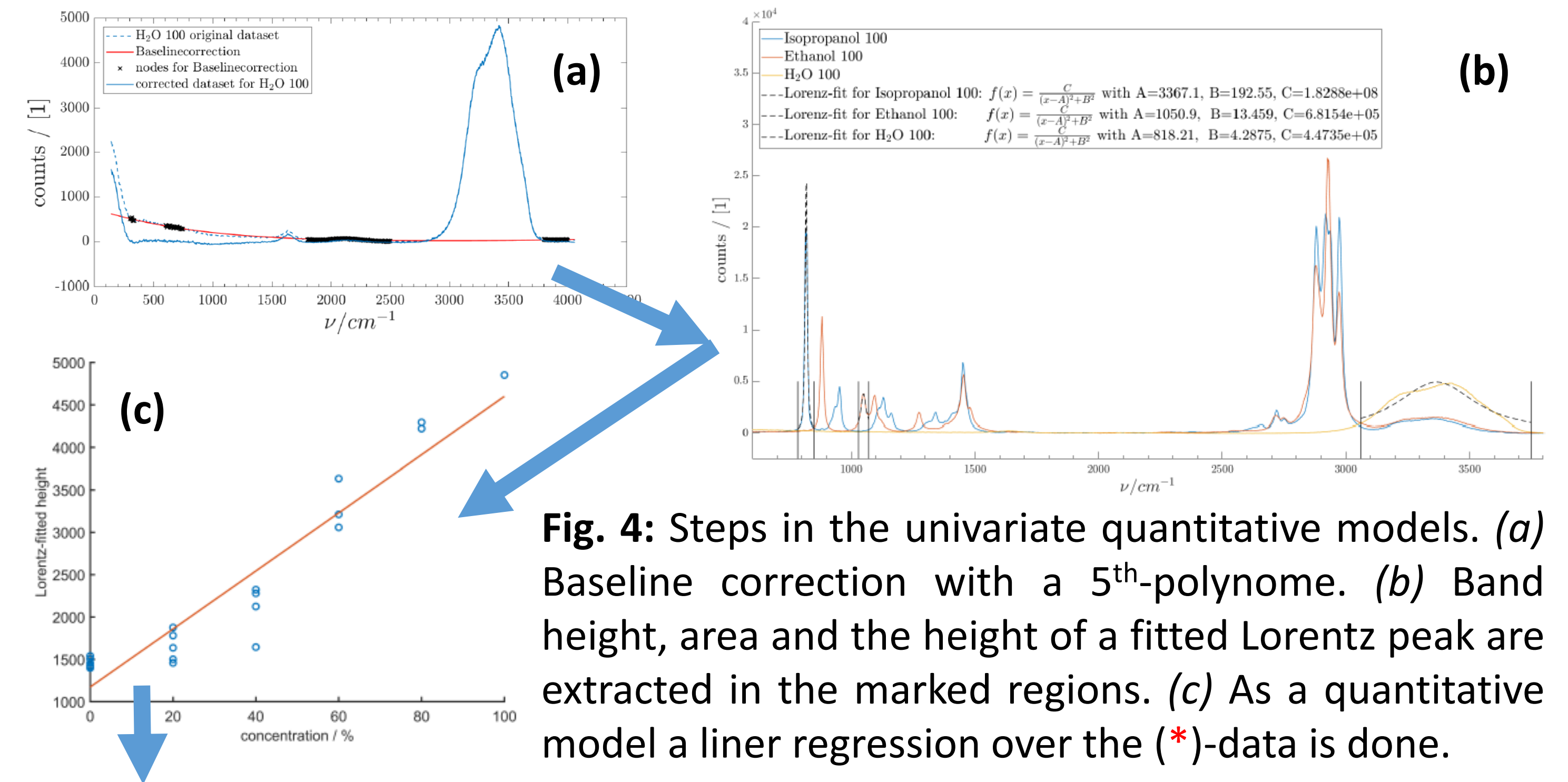
Please note that access to the Raman spectrometer was highly restricted for students during this lab exercise due to the COVID pandemic. Therefore, there is a strong focus on optimizing data treatment rather than measurement in this work.

Raw Data – Raman spectra and Parameter space
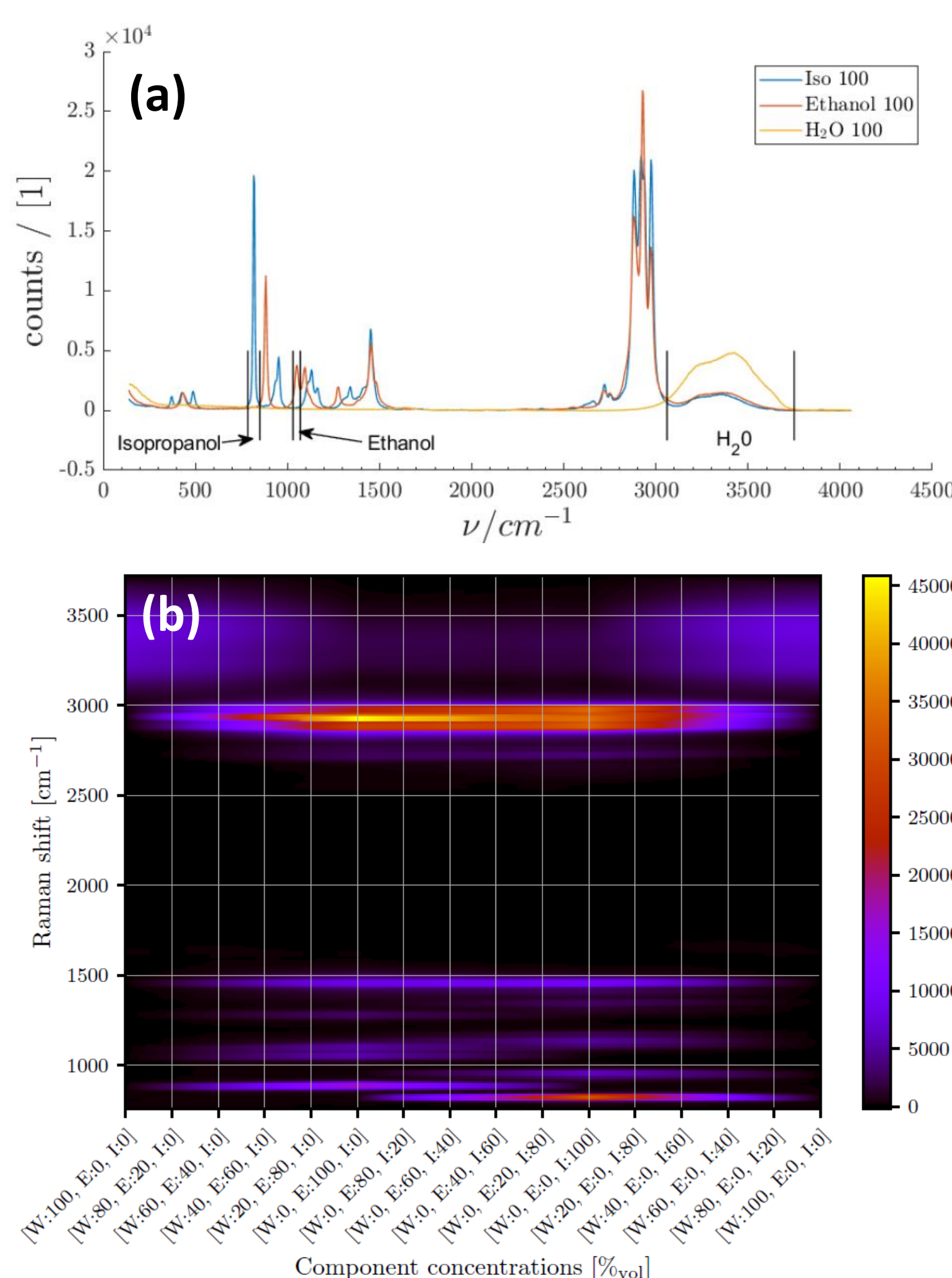
Fig. 1: *(a)* Pure component spectra; the bands critical for univariate evaluation are marked. *(b)* Raman intensity along the edges of the mixture diagram in (c). *(c)* Mixture diagram of H_2O-EtOH-PrOH; a 20%-step-grid of calibration data (*) and 14 random mixtures of test data (o) were measured.
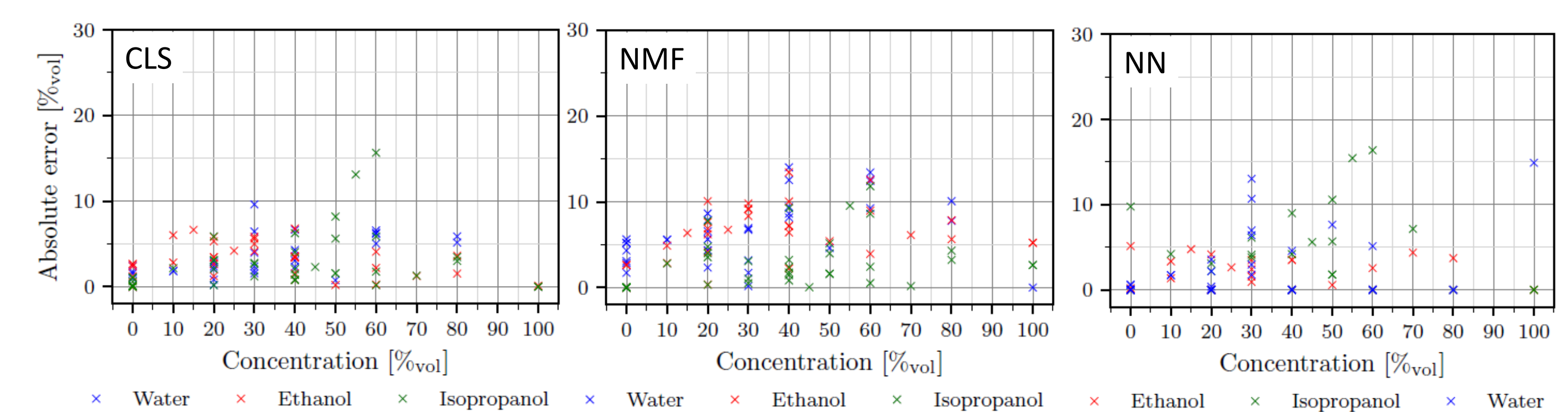
Measurement approaches – Dish vs Capillary
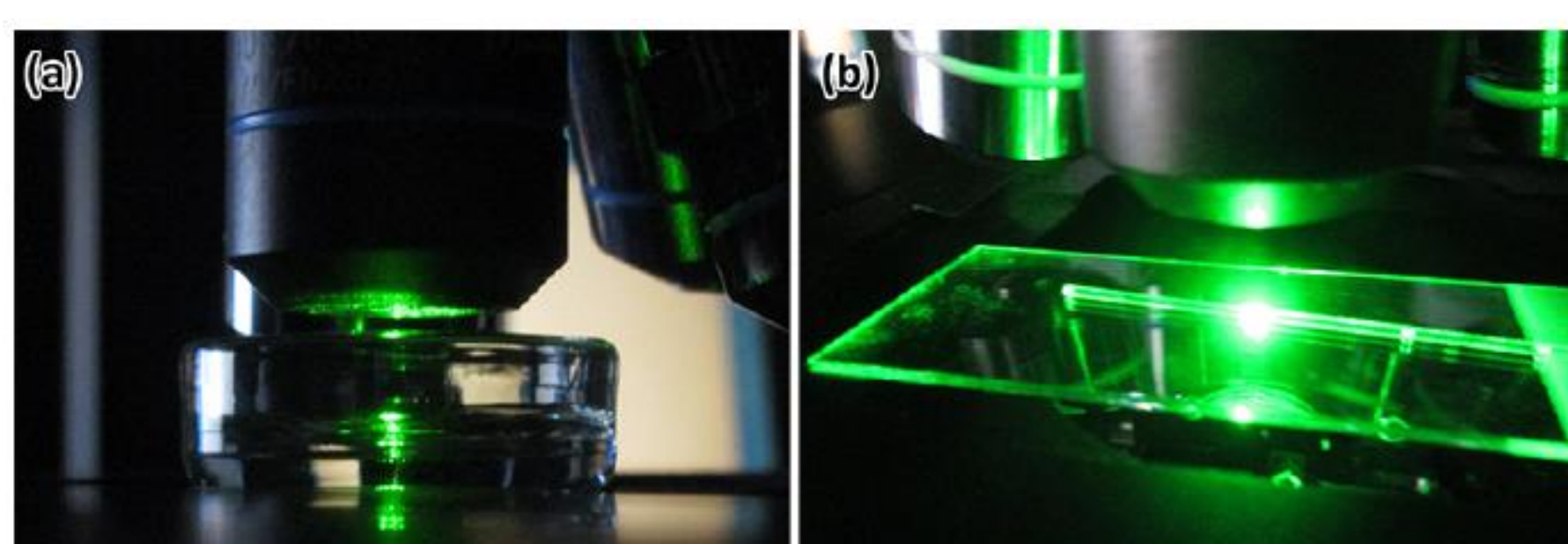
Fig. 2: Both measuring in a small dish *(a)* and a capillary *(b)* were tested. The dish provides a large volume of liquid, whereas the capillary a well defined volume.
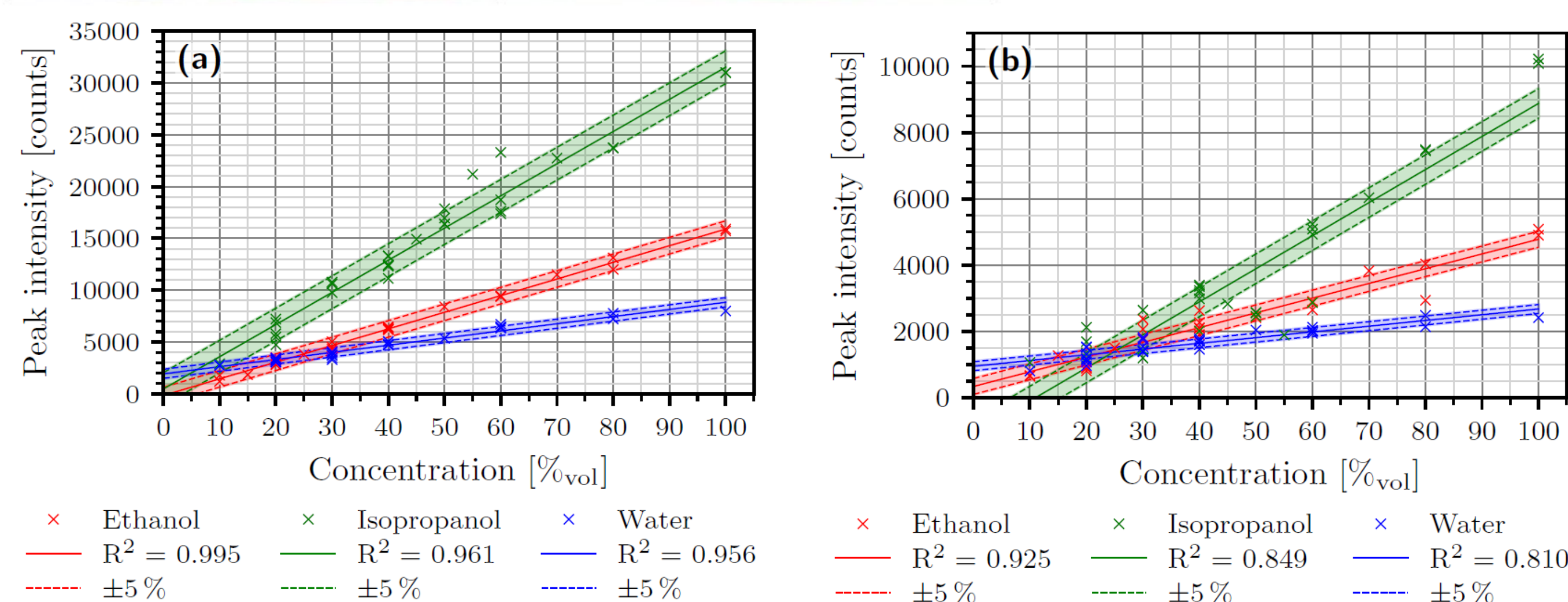
Fig. 3: As an example the calibration curves (including the test data points) using the univariate band height method are shown for the dish *(a)* and capillary *(b)* setup. Better fits and more accurate predictions are achieved with the dish setup. This has been qualitatively reproduced with the CLS, NMF and NN approaches leading to the conclusion that the dish setup is superior.

Univariate approaches – band height, area & fits

Fig. 4: Steps in the univariate quantitative models. *(a)* Baseline correction with a 5th-polynome. *(b)* Band height, area and the height of a fitted Lorentz peak are extracted in the marked regions. *(c)* As a quantitative model a liner regression over the (*)-data is done.

Table 1: Accuracy of the models from Fig 4. tested using the (o)-data. $\left(P = \sum_{i \in H,E,P} \sqrt{\left(C_i^{model} - C_i^{real}\right)^2} \right)$

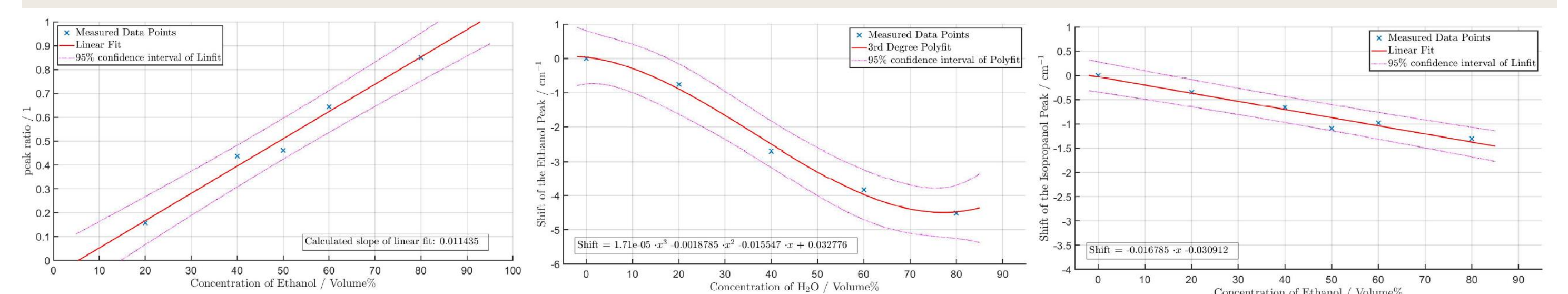| Method	Err_{max}^{EtOH} /%	Err_{mean}^{EtOH} /%	Err_{max}^{PrOH} /%	Err_{mean}^{PrOH} /%	$Err_{max}^{H_2O}$ /%	$Err_{max}^{H_2O}$ /%	P-value/%
Height	14.8	7 ± 5	18.0	8 ± 7	12.9	6 ± 4	13 ± 6
Area	14.3	7 ± 4	22.3	10 ± 9	12.7	5 ± 4	13 ± 9
Lorentz-fit	13.8	6 ± 5	26.8	9 ± 9	13.9	6 ± 5	15 ± 8

Multivariate approaches – CLS, NMF, NN

Fig. 5: Error plots of the multivariate approaches for the quantification, including both datasets (*,o). The best results were accomplished by Common least square fit (*CLS*), which is a weighted fit of pure component spectra. The machine learning approaches Non-Negative Matrix Factorization (*NMF*) and Neural Networks (*NN*) achieved acceptable results but do not beat the univariate approaches.

Special approach – high-resolution, shifts and intensity

Fig. 6: As a special approach the position dependents of the EtOH [1,2] and PrOH [3] bands in H_2O was used to created a quantitative model. For this special high-resolution measurements of the 885 cm^{-1} (EtOH) and 820 cm^{-1} (PrOH) were made. The relative band intensity (left) is used to determine the relative concentration of EtOH-PrOH, where as the band shift of EtOH (middle) corrected for the influence of PrOH (right) is used to determine the H_2O concentration.

Table 2: Results of 4 test measurements to asses the accuracy of the band shift method. Surprisingly, large errors are found for EtOH and PrOH, but not H_2O.

Modelled concentrations			Actual concentrations		
H2O /%	PrOH /%	EtOH /%	H2O /%	PrOH /%	EtOH /%
26	16	58	20	20	60
26	50	24	20	40	40
35	28	37	40	20	40
36	55	9	40	40	20

Acknowledgements

Reference

[1] Li, F., Men, Z., Li, S., Wang, S., Li, Z., & Sun, C. (2018). Study of hydrogen bonding in ethanol-water binary solutions by Raman spectroscopy. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, *189*, 621-624.

[2] Dolenko, T. A., Burikov, S. A., Dolenko, S. A., Efitorov, A. O., Plastinin, I. V., Yuzhakov, V. I., & Patsaeva, S. V. (2015). Raman spectroscopy of water–ethanol solutions: the estimation of hydrogen bonding energy and the appearance of clathrate-like structures in solutions. *The Journal of Physical Chemistry A*, *119*(44), 10806-10815.

[3] Alavi, S., Takeya, S., Ohmura, R., Woo, T. K., & Ripmeester, J. A. (2010). Hydrogen-bonding alcohol-water interactions in binary ethanol, 1-propanol, and 2-propanol+ methane structure II clathrate hydrates. *The Journal of chemical physics*, *133*(7), 074505.

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