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Article

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Strong Isotope Effect in the Vibrational Response of the Hydration Shells of Hydrophobic Ions

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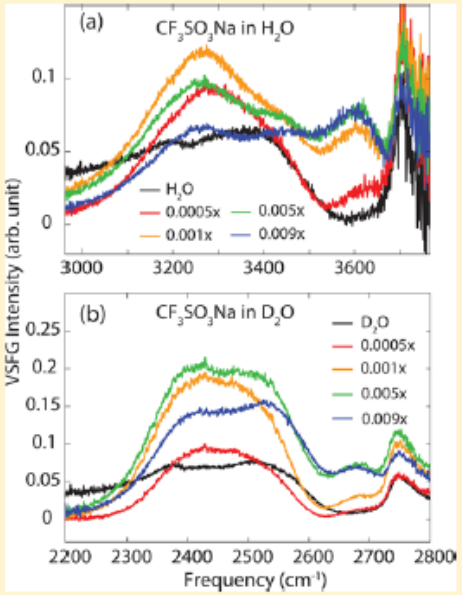
Supporting Information

ABSTRACT: We have studied the properties of water molecules at the surface of salt solutions containing hydrophobic anions like triflate ($CF_3SO_3^-$), ethanesulfonate ($C_2H_5SO_3^-$), and butanesulfonate ($C_4H_9SO_3^-$) using vibrational sum-frequency generation (VSFG) spectroscopy. The VSFG spectra reveal a surprisingly strong isotope effect in the intra- and intermolecular mixing of the water molecules contained in the hydration shells of the hydrophobic anions. The O−H stretch vibrations of H_2O molecules in the hydration shell are strongly mixed, whereas the O−D stretch vibrations of hydrating D_2O molecules are decoupled. This isotope effect is not observed for other ions like perchlorate (ClO_4^-), and can be explained from the structure of the hydration shells of the hydrophobic ions.



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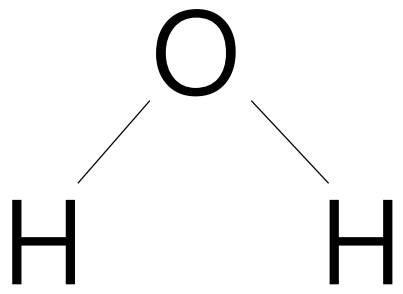
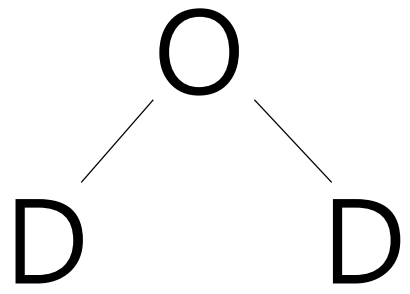
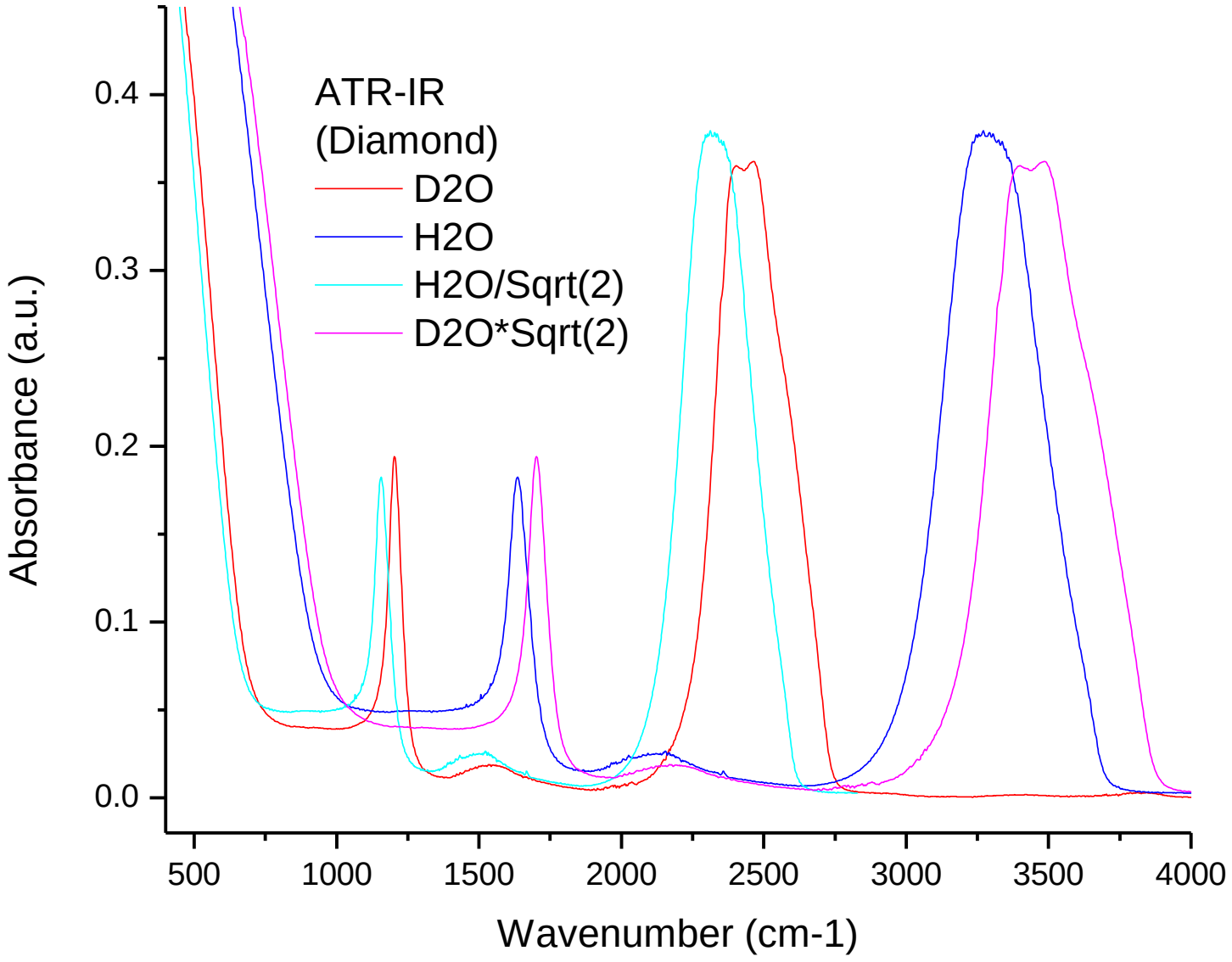
Properties[9]	D_2O (Heavy water)	HDO (Semiheavy water)	H_2O (Light water)
Freezing point	3.82 °C (38.9 °F) (276.97 K)	2.04 °C (35.7 °F) (275.19 K)	0.0 °C (32 °F) (273.15 K)
Boiling point	101.4 °C (214.5 °F) (374.55 K)	100.7 °C (213.3 °F) (373.85 K)	100.0 °C (212 °F) (373.15 K)
Density at STP (g/mL)	1.1056	1.054	0.9982
Temp. of maximum density	11.6 °C		3.98 °C[10]
Dynamic viscosity (at 20 °C, mPa·s)	1.2467	1.1248	1.0016
Surface tension (at 25 °C, N/m)	0.07187	0.07193	0.07198
Heat of fusion (kJ/mol)	6.132	6.227	6.00678
Heat of vaporisation (kJ/mol)	41.521		40.657
pH (at 25 °C)	7.43 (sometimes "pD")	7.266 (sometimes "pHD")	6.9996
Refractive index (at 20 °C, 0.5893 μm)[11]	1.32844		1.33335

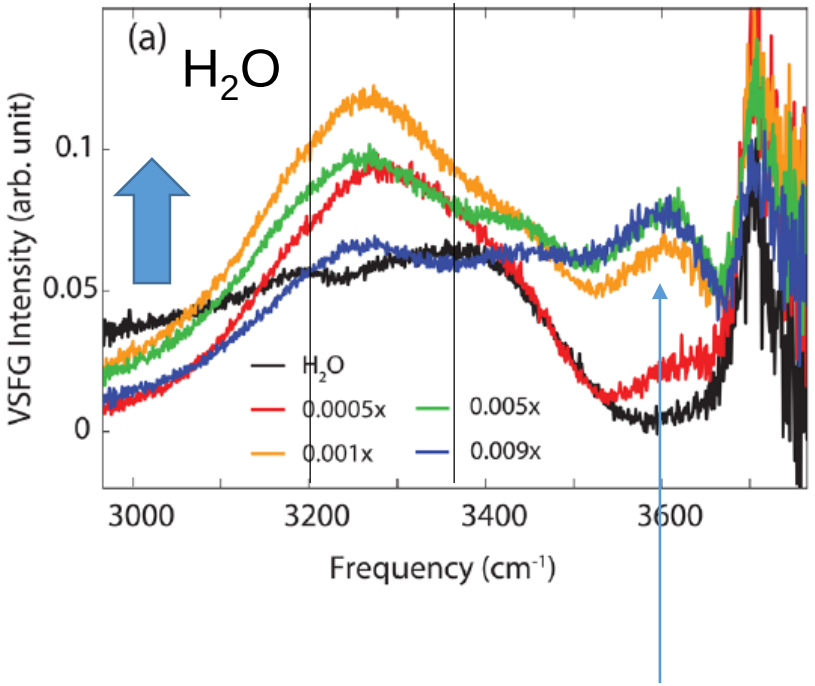


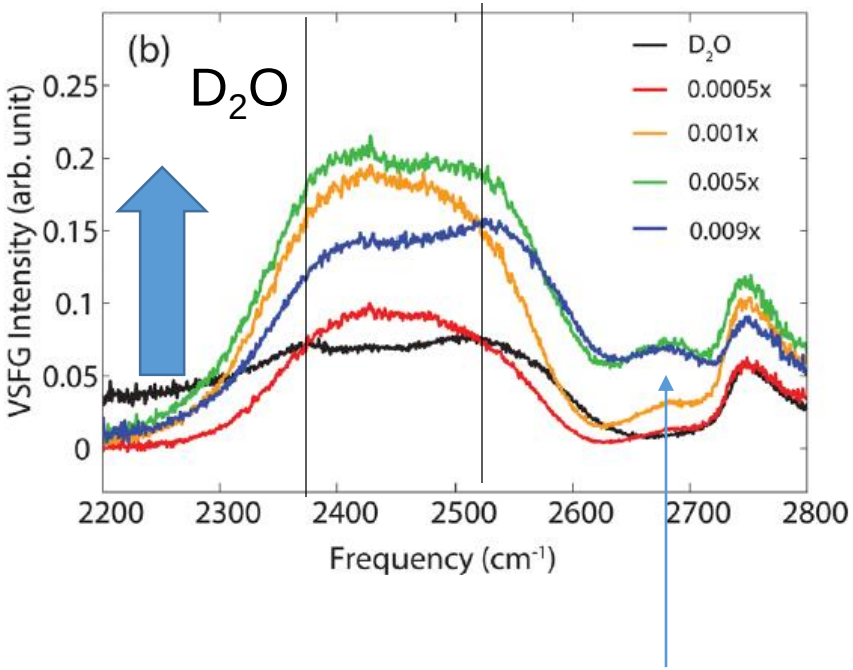


$$\omega \sim \sqrt{\frac{k}{m}}$$



Sodium triflate ($NaCF_3SO_3$)

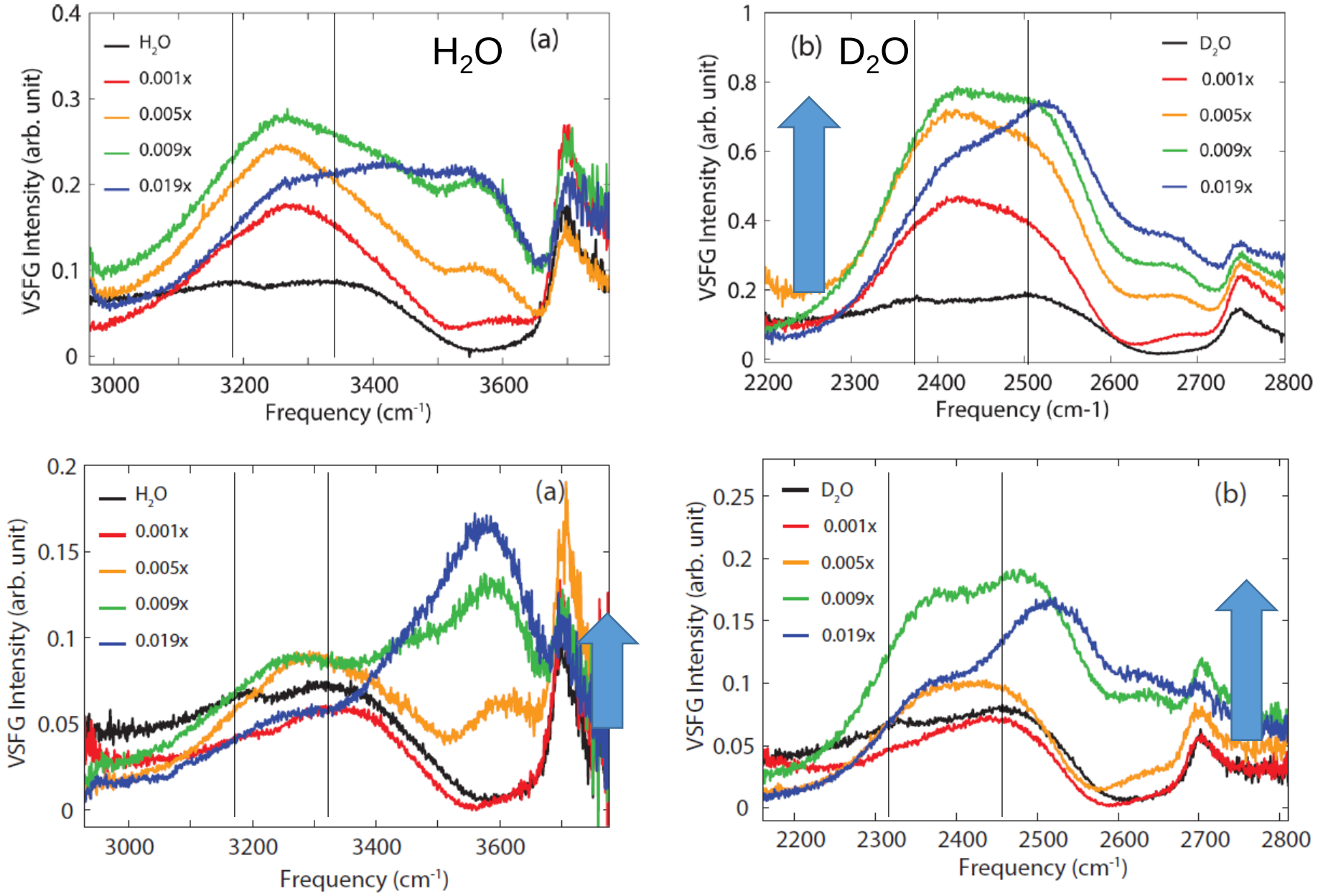




Weak hydrogen bond
$SO_3^- \cdots H_2O$

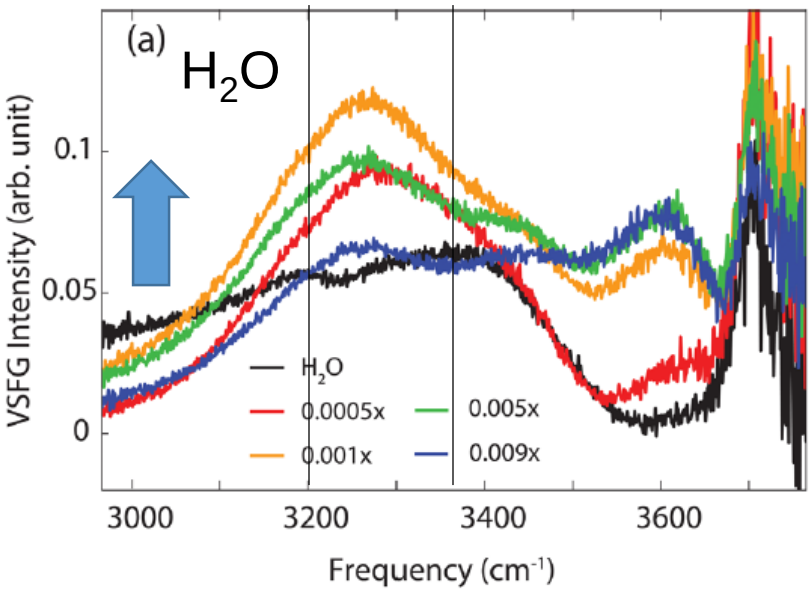
Weak hydrogen bond
$SO_3^- \cdots D_2O$

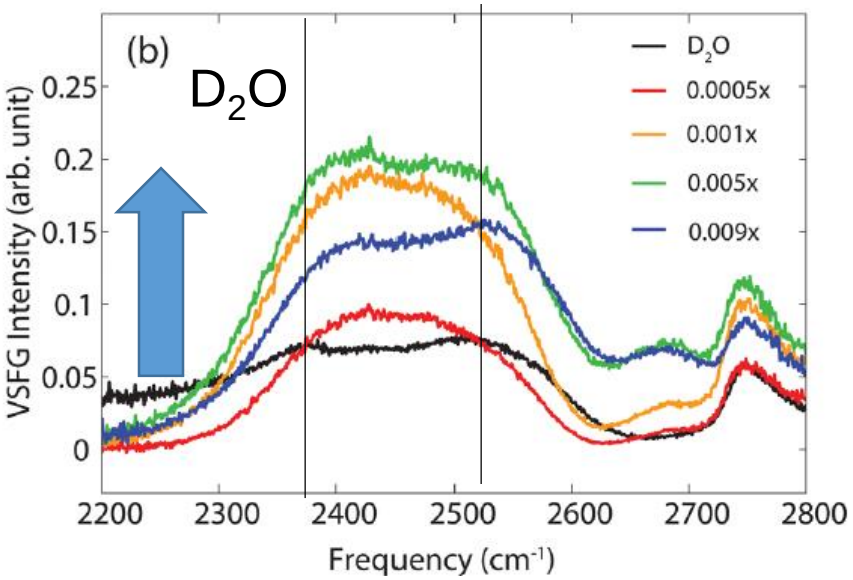
Sodium butanesulfonate ($NaC_4H_9SO_3$)

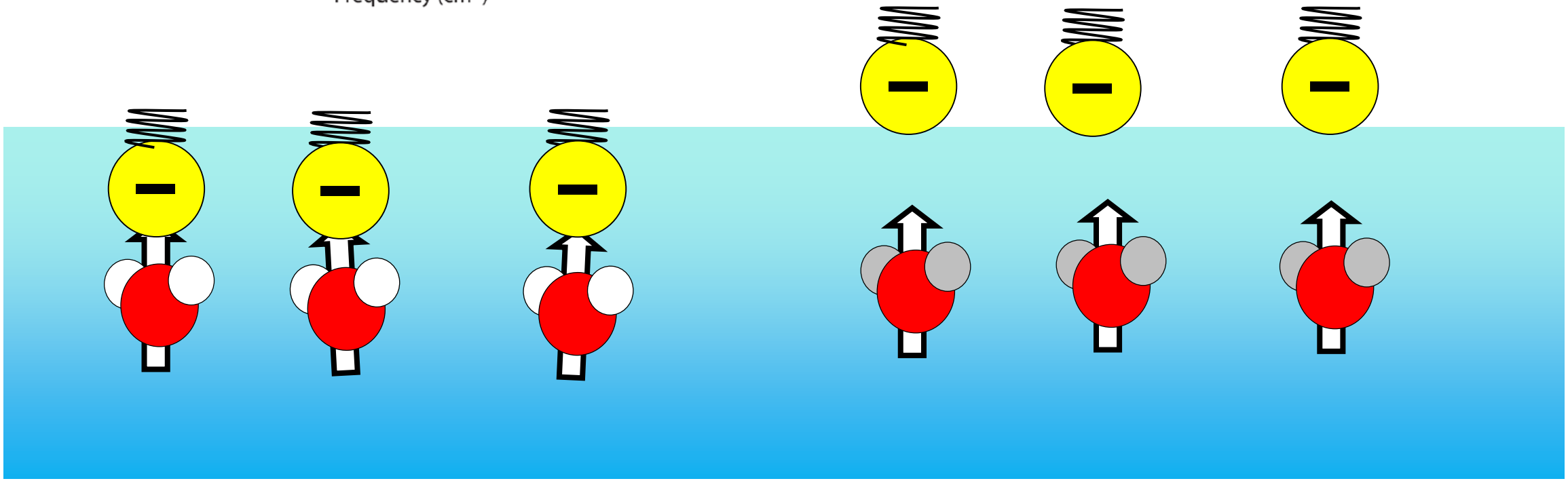


Sodium ethanesulfonate ($NaC_2H_5SO_3$)

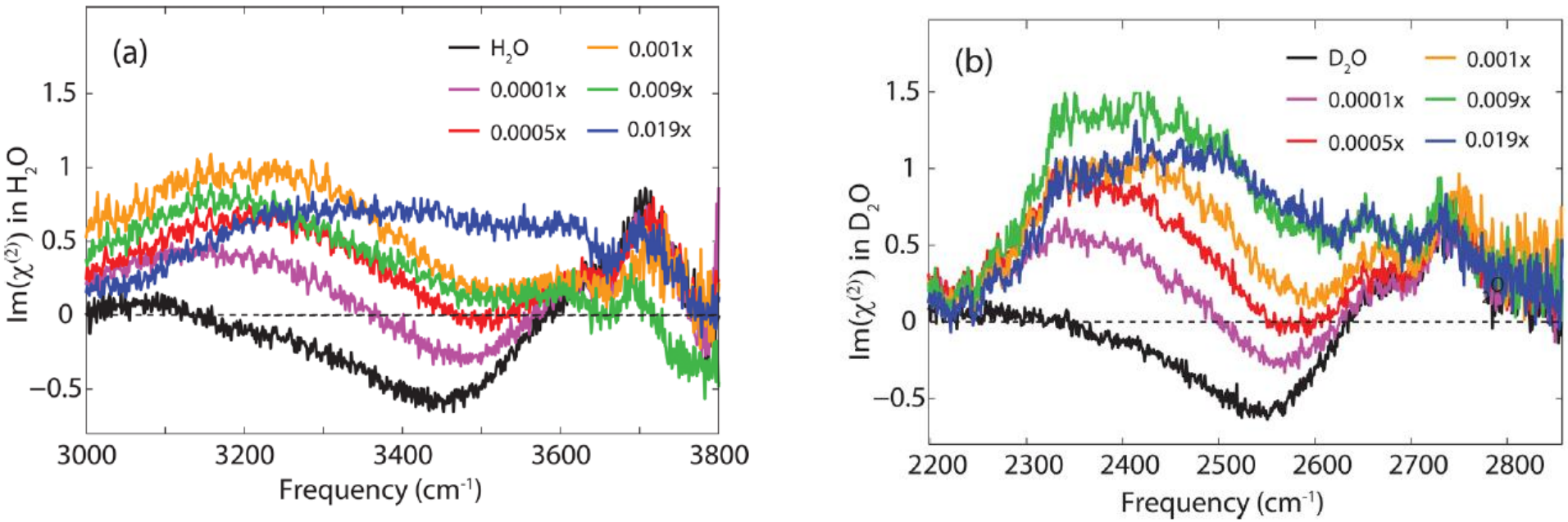
Sodium triflate ($NaCF_3SO_3$)





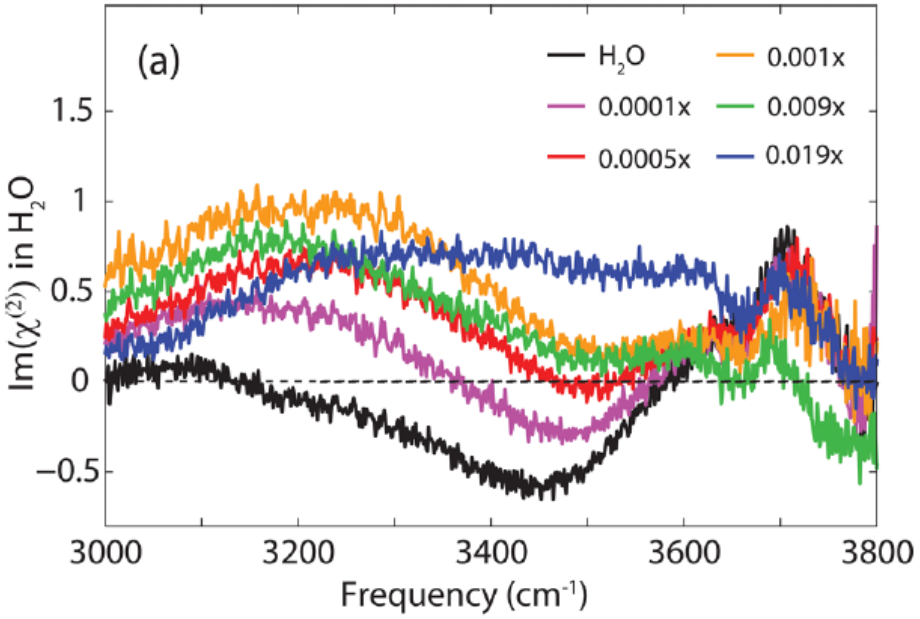


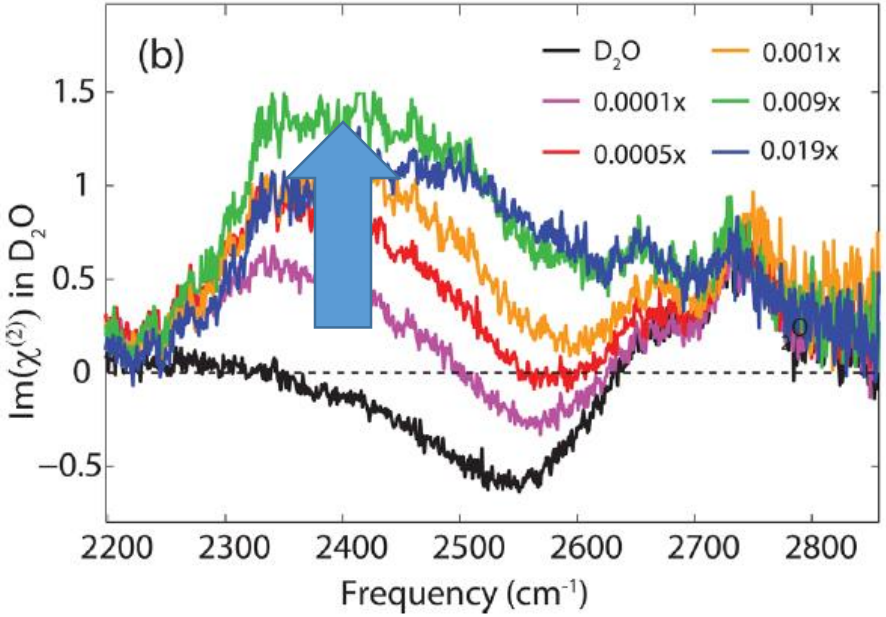
Phase measurement for Sodium triflate ($NaCF_3SO_3$)



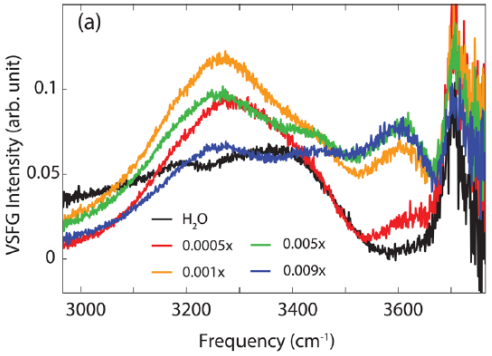
Surface propensity of triflate is same for H_2O and D_2O

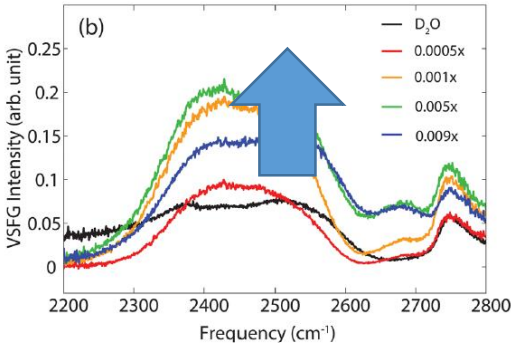
Phase measurement for Sodium triflate ($NaCF_3SO_3$)



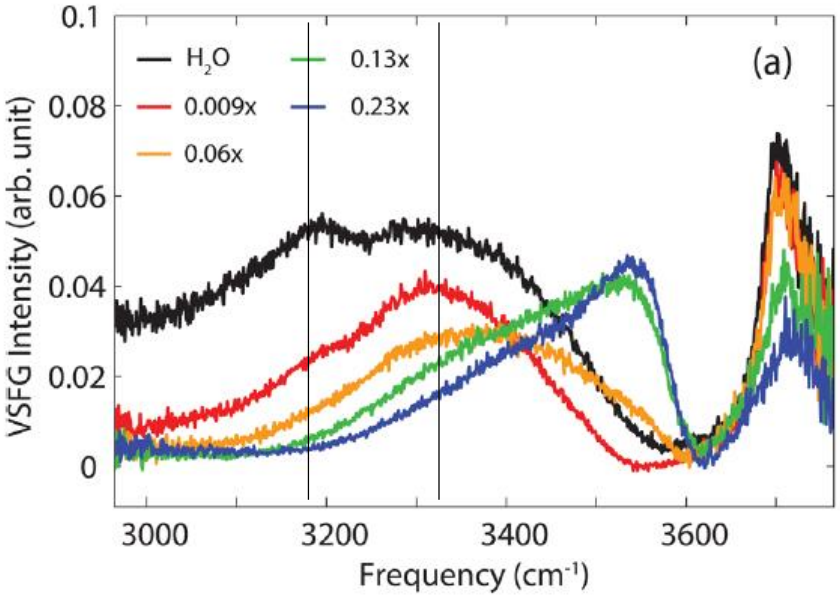


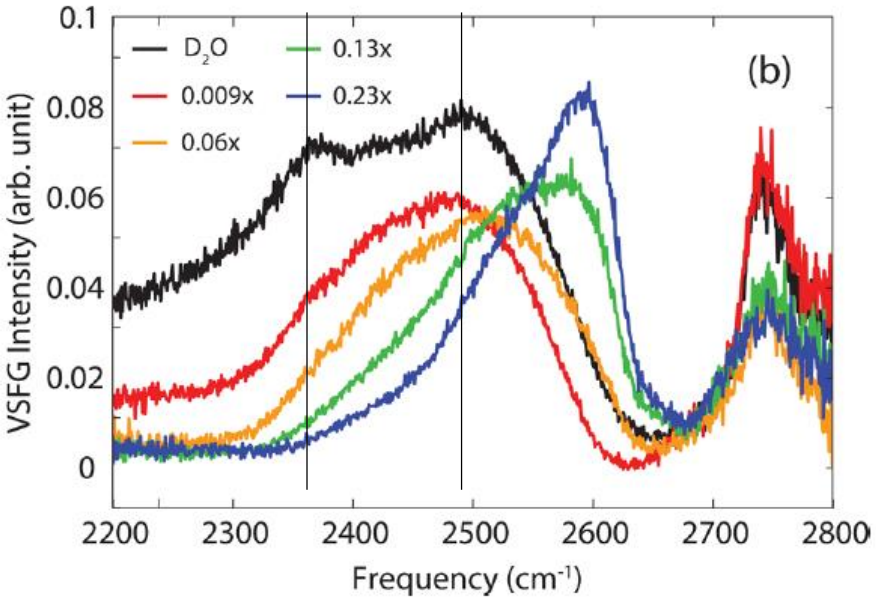
Surface propensity of triflate is same for H_2O and D_2O
Amplitude is more enhanced for D_2O





Sodium perchlorate ($NaClO_4$)





FT-IR for Sodium triflate ($NaCF_3SO_3$)