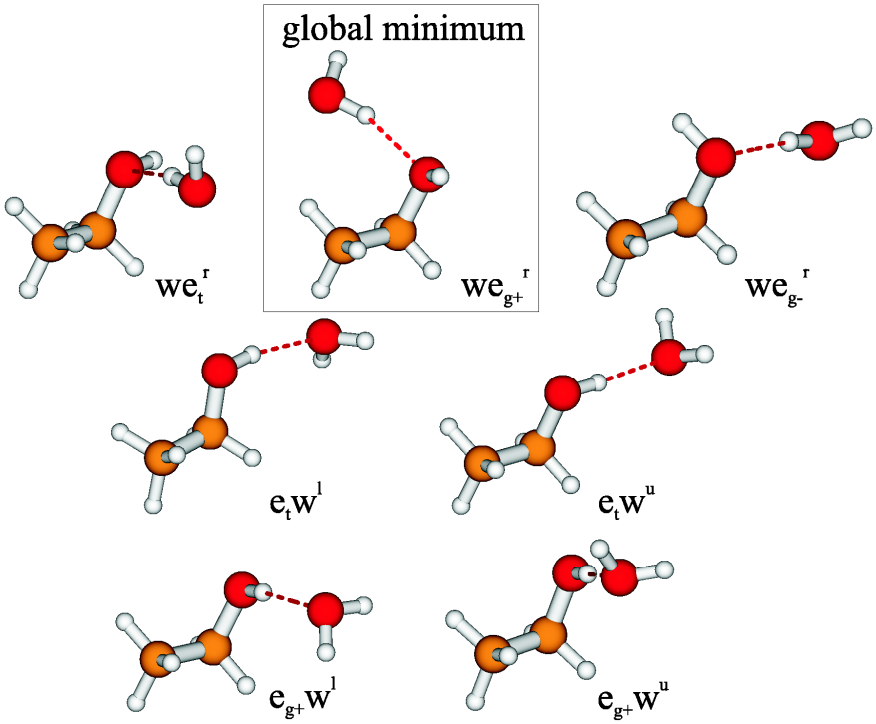
Raman spectroscopic evidence for the most stable water/ethanol dimer and for the negative mixing energy in cold water/ethanol trimers

Marija Nedić, Tobias N. Wassermann, Zhifeng Xue, Philipp Zielke, and Martin A. Suhm*

A) Enumeration of spectroscopically distinguishable water-ethanol dimers:

Ethanol can occur in the trans (e_t), gauche+ (e_{g+}) and gauche- (e_{g-}) conformation. When acting as a hydrogen bond acceptor, it can offer its right (r) or left (l) lone electron pair. The nomenclature used in the article always implies the enantiomer engaging the right lone pair. When water (w) acts as the acceptor, it may engage its upper (u) or lower (l) lone electron pair. This results in the following dimer possibilities, if we disregard water donor rotation around the hydrogen bond (2 achiral conformations and 3+2 chiral pairs, leading to a total of at most 7 spectrally distinguishable structures):

7 unique structures	mirror images
we_t^r	we_t^l
we_{g+}^r	we_{g-}^l
we_{g-}^r	we_{g+}^l
e_tw^u	-
e_tw^l	-
$e_{g+}w^u$	$e_{g-}w^u$
$e_{g+}w^l$	$e_{g-}w^l$



Detailed quantum-chemical results will be presented elsewhere, but we note that the zero-point energy corrected binding energy for we_{g+} is consistently higher by 10% than that for we_{g-} at the MP2/6-311++G(2d,p) and MP2/6-311G++(3df,2p) levels.

B) Observed band positions and uncertainties in Fig. 1 in cm^{-1}:

label	maximum	uncertainty
w	3694	±2
e_t	3678	±2
we_t, ee_t	3671	±3
e_{g+}	3661	±2
w	3658	±3
w	3649	±3
w	3621	±2
ww, w	3602	±3
we_t	3551	±2
we_{g+}	3548	±2
$e_{g+}e_{g+}$	3533	±2
www	3491	±4
eww	3427	±4
eew	3409	±4
eee	3386	±4

C) Experimental conditions in Fig. 1:

All shown spectra were measured by *c*lassical *un*r*e*stricted *R*aman spectroscop*y* in a supersonic *jet* (*curry-jet* technique; unrestricted stands for the universal applicability of classical spontaneous Raman scattering in contrast to stimulated or resonant techniques). In this experiment a frequency doubled continuous Nd:YVO_4 laser (532 nm, Coherent Verdi V18, *P*=18 W) was mildly focused (beam waist approx. 80 µm) on the zone of silence of a continuous supersonic jet expansion from a 4.0 mm x 0.15 mm slit nozzle into a vacuum chamber. The gas mixtures were prepared by bubbling He or He/Ar mixtures through thermostated saturators containing ethanol (99.5%) or water (p.a.), respectively, and collecting the mixtures in a 67 L stainless steel reservoir prior to expansion.

The chamber was evacuated by a 250 m^3/h Roots pump and a 100 m^3/h rotary vane pump. In all experiments the reservoir was initially filled to 1 bar with the gas mixtures of the given ethanol:water ratio. Due to flow limitations, the average stagnation pressure dropped down to approx. 0.5 bar in the course of the experiment with an average background pressure of approx. 2.5 mbar in the expansion chamber.

The scattered light was collected at 90° angle and collimated by a standard or camera lens. It was then focused on the entrance slit of a monochromator by an achromatic planoconvex lens and filtered with a Raman edge filter (L.O.T., Ø= 25 mm, OD 6.0, T > 90 %, 535.4 – 1200 nm). As detection device a back-illuminated liquid N_2 cooled CCD camera (PI Acton, Spec-10: 400B/LN, 1340x400 Pixel) was used. Cosmic ray signals were removed by the comparison of block-averaged spectra.

	Bottom spectrum (overview)	×6 inserts	×4 inserts					
Dimensions of vacuum chamber/ cm^3	22 x 14 x 14 (cylindrical)	60 x 60 x 40 (square footprint)	60 x 60 x 40 (square footprint)					
Distance of slit nozzle/ mm	1	3	2					
Objective	Edmund Optics E32-886 (Ø= 50 mm, f/3)	Nikon Nikkor (Ø= 50 mm, f/1.2)	Nikon Nikkor (Ø= 50 mm, f/1.2)					
Slit width/ μm	75	75	100					
Focussing lens	Edmund Optics L45-354 (Ø= 50 mm, f/7)	Edmund Optics L45-354 (Ø= 50 mm, f/7)	Newport PAC087AR.14 (Ø= 51 mm, f/4)					
Monochromator	McPherson 2051 (f= 1000 mm, f/8.7, 1200 gr/mm grating)	McPherson 2051 (f= 1000 mm, f/8.7, 1200 gr/mm grating)	McPherson 205f (f= 500 mm, f/3.2, 1800 gr/mm grating)					
			1:0	1:1	1:3	1:5	1:6	0:1
ϑ(ethanol)/ °C	-8	-8	-10	-8	-10	-21	-24	-
ϑ(water)/ °C	+9	+9	-	-4	+2	+6	+7	+3
Number of scans	5	6	6	6	6	12	12	6
Scan duration/ s	600	600	600	600	600	300	300	600