

1 **Water molecular structure underpins extreme desiccation tolerance of**
2 **the resurrection plant *Haberlea rhodopensis***

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20 **Table S1. Dehydration and subsequent rehydration of *Deinostigma eberhardtii* and**
 21 ***Haberlea rhodopensis*.** Sample timing and measured RWC content. Empty fields indicate
 22 times when measurements were not performed.

	Dehydration duration [h]	RWC [%]	Rehydration duration [h]	RWC [%]
<i>Deinostigma eberhardtii</i>	0	91.09	1	--
	1	71.13	2	--
	2	--	3	--
	3	45	6	--
	6	45.18	24	--
	24	43.75	48	83.35
	48	34.78	--	--
	72	22.58	--	--
	120	12.64	--	--
	168	9.11	--	--
	<i>Haberlea rhodopensis</i>	Dehydration duration [h]	RWC[%]	Rehydration duration [h]
0		93.37	1	56.48
1		72.6	2	56.12
2		57.19	3	55.63
3		36.19	6	67.13
6		24.85	24	90.65
24		13	48	90.75
48		12.85	--	--
72		12.85	--	--
120		12.85	--	--
168		12.85	--	--

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24 **Table S2. Assignments of the NIR vibrational absorption spectrum of water. ν_r , ν_1 ,**
 25 **ν_2 and ν_3 indicate rotational, symmetric stretching, bending and antisymmetric**
 26 **stretching mode of the water molecule, respectively. a , b are integers, ≥ 0 .**

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	ν_r	ν_1	ν_2	ν_3	Peak position	References
$a + b = 2$		$a\nu_1$	$+ \nu_2$	$+ b\nu_3$	1200 nm	
$a + b = 2$		$a\nu_1$	$+$	$b\nu_3$	1450 nm	1-7
$a + b = 1$		$a\nu_1$	$+ \nu_2$	$+ b\nu_3$	1930 nm	
$a + b = 1$	$\nu_r +$	$a\nu_1$	$+$	$b\nu_3$	1346 nm	8
$a + b = 1$	$\nu_r +$	$a\nu_1$	$+ \nu_2$	$+ b\nu_3$	1790 nm	

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29 **Table S3. Potential band assignments of important wavelengths in difference**
 30 **spectra (Fig.3) and PC1 loading vector (Fig.5).**

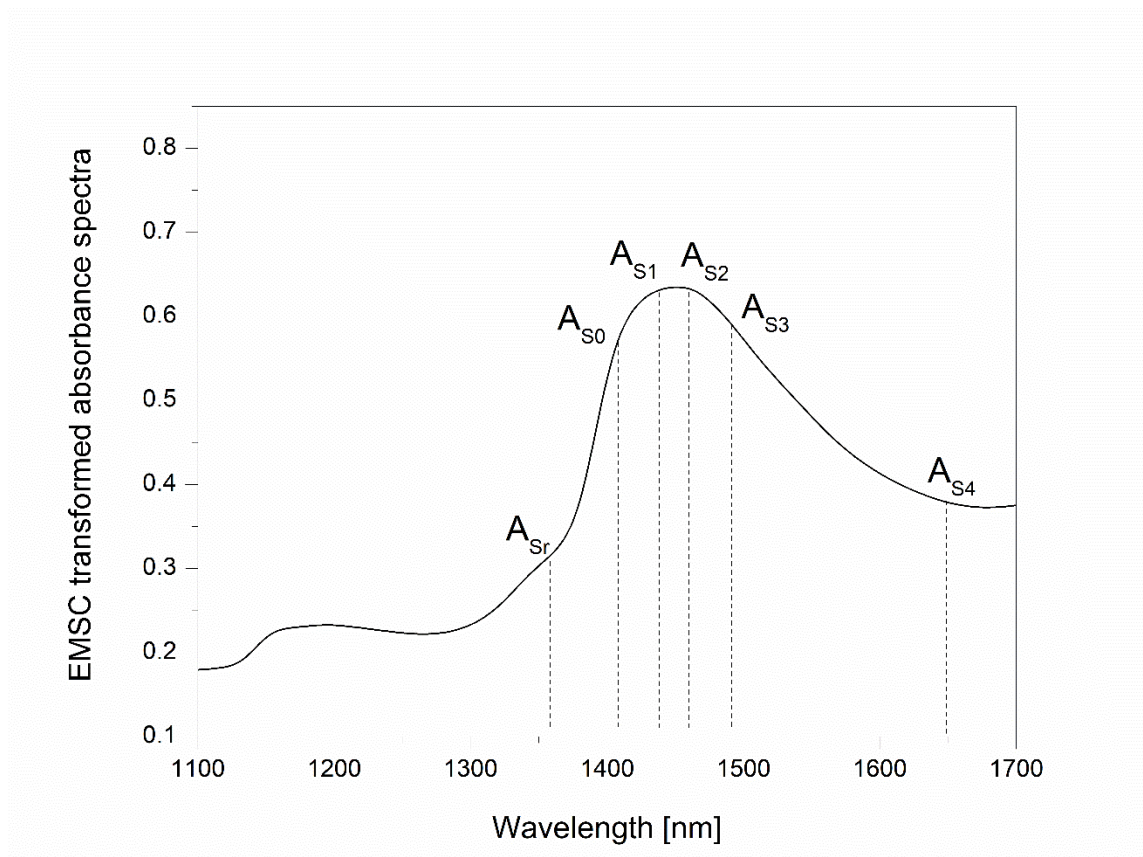
Wavelength	Potential assignments
1400 nm	Water confined in the local field of ions ⁹
1500 nm	1500nm - 1 st overtone of the NH stretching mode ^{3,7,10}
	1500nm - 1 st overtone of the OH stretching mode ^{3,7,10}
	1506nm – protonated water clusters [H ⁺ ·(H ₂ O) ₆] - H ₂ O in H ₅ O ₂ ⁺ asymmetric stretching, 1 st overt. ¹¹
1574nm	Associated O-H str., 1 st overtone (sugar) ^{12,13}
1704nm	C-H stretch, 1 st overtone (sugar) ^{12,13}
	1708nm- H-bonded OH stretching harmonic frequency of H ₉ O ₄ ⁺ , 1st overtone ¹⁴
1880nm	1876.2nm -OH stretch in fully hydrated hydronium, 1 st overtone ¹⁵
	1876.2nm protonated water clusters [H ⁺ ·(H ₂ O) ₄] - H ₃ O ⁺ asymmetric stretch, 1 st overtone ¹¹
	1880nm - C-H stretch ¹⁶
	1884nm free water molecules (without active H-bonds) ¹⁷
2016 nm	Dissociated O-H stretch + O-H bend. (sugar) ^{12,13}
	combination of amide A and amide III ^{6,17}
2130 nm	= C-H str. + C=C stretch (HC=CH) ^{6,12,13}
	2125nm C-H vibrations in isolated C=C bonds ⁶
	2080-2220nm –NH deformation ⁶
2226 nm	C-H str. + C=O str. (CHO) ^{12,13}
2284 nm	C-H str. + C-H bend. (CH ₃) ^{7,12,13}
2414 nm	O-H bend. 2 nd overt. (sugar) ^{12,13}

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32 **Table S4. Assignments of the water species in the present study based on previous**
 33 **studies.**

Water species	S_r	S_0	S_1	S_2	S_3	S_4	References
Wavelength [nm]	1351	1410	1439	1456	1506	1642	18
	1346	1411	1441	1462	1490	1650	19
	1346	1412	1440	1462	1490	1650	Present study

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36 **Figure S1. Relative absorbance as a measure of how each water species contributes**
37 **to the overall water molecular structure is calculated for each time point during**
38 **dehydration/rehydration cycle as a ration of the mean absorbance of particular**
39 **water species and the sum of mean absorbances of all 6 analyzed water species (S_r ,**
40 **S_0 , S_1 , S_2 , S_3 and S_4).**

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