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CORRECTION

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Correction: Vibrational dynamics and solvatochromism of the label SCN in various solvents and hemoglobin by time dependent IR and 2D-IR spectroscopy

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Correction for 'Vibrational dynamics and solvatochromism of the label SCN in various solvents and hemoglobin by time dependent IR and 2D-IR spectroscopy' by Luuk J. G. W. van Wilderen *et al.*, *Phys. Chem. Chem. Phys.*, 2014, **16**, 19643–19653.

We would like to point the reader to a mistake in our previous publication, which caused an error of a factor of $4\pi/3$ in the Stark tuning rate calculated from the Onsager reaction field model. The discussion and conclusions of the paper remain unaltered.

The Onsager field (in SI units) in our paper is correctly given by:

$$\vec{F}_{\text{Onsager}} = \frac{\overrightarrow{\mu_0}}{4\pi\varepsilon_0 a^3}\left[\frac{2(\varepsilon-1)(n^2+2)}{3(2\varepsilon+n^2)}\right]$$

In accordance with the previous literature,[1–3] a^3 was erroneously set equal to the volume V of the Onsager spherical cavity. Because a represents the Onsager spherical cavity radius, $a^3 = V{\cdot}3/(4\pi)$ has to be used instead. This has recently been pointed out by Bagchi and coworkers[4] and was mentioned before in the supplementary information of a previous publication.[5] For MeSCN, the Onsager spherical cavity volume is $V_{\text{MeSCN}} = \text{MW}/(\rho{\cdot}N_{\text{A}}) = 1.19 \times 10^{-28}$ m^3 and the cavity radius cubed becomes $a_{\text{MeSCN}}{}^3 = 2.8 \times 10^{-29}$ m^3. Correspondingly, the estimated Onsager field $\vec{F}_{\text{Onsager}}$ is a factor of $4\pi/3$ too low in our work as well as in the previous work of others.[1–3]

In Fig. 8 and Fig. S5 of the ESI, the Onsager solvent field on the X-axis therefore has to be multiplied by $4\pi/3$. The corrected figures are shown below. The slope of the line fitting the aprotic solvents in Fig. 8 and Fig. S5 (ESI) produces the Stark tuning rate, which accordingly was a factor of $4\pi/3$ too high in the previous publication and now becomes $|\Delta\vec{\mu}| = 1.7(4) \times 10^{-9}$ cm^{-1}/(V/m).

Note that the references in the captions to Fig. 8 and Fig. S5 (ESI) refer to the references in the original publication.

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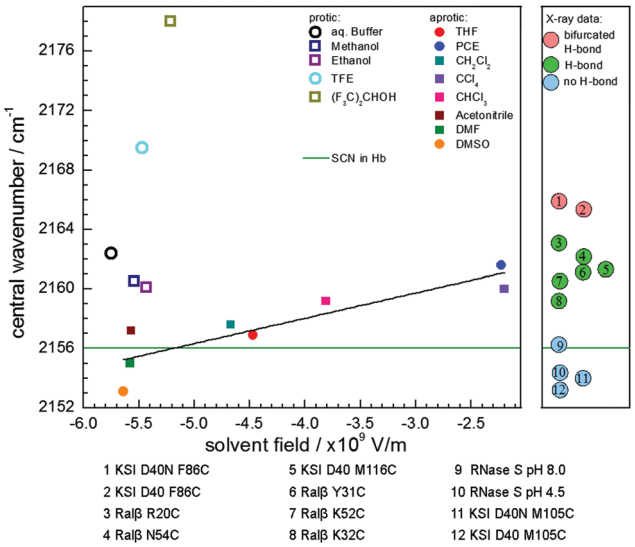
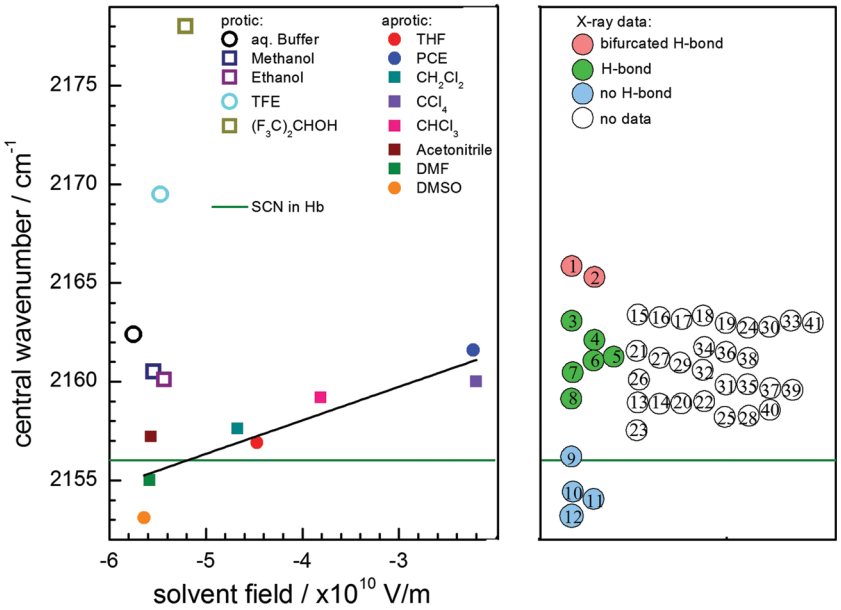


Fig. 8 Central wavenumber of the nitrile group in MeSCN in different solvents (left) and selected proteins (right). Left: Central wavenumber of MeSCN's nitrile group in protic (open symbols) and aprotic (solid symbols) solvents as a function of the calculated solvent field $\vec{F}_{\text{Onsager}}$. For aprotic solvents a linear fit (black line, R^2 = 0.76) is shown. The measured central wavenumber of SCN in Hb is depicted as a green line. The data points symbolized by circles are measured in this work, the data in squares are taken from ref. 38 with the exception of DMF (dimethylformamide), which has been taken from ref. 22. Right: Central wavenumber of thiocyanate incorporated into proteins for which the orientation is known from X-ray data (data points 1, 2, 5, 11 and 12 are taken from ref. 48; 3, 4, 6, 7 and 8 from ref. 21; and 9 and 10 from ref. 49). An additional figure with SCN central frequencies in proteins summarized from the literature is shown in Fig. S5 (ESI).



1 KSI D40N F86C
2 KSI D40 F86C
3 Ralβ R20C
4 Ralβ N54C
5 KSI D40 M116C
6 Ralβ Y31C
7 Ralβ K52C
8 Ralβ K32C
9 RNase S pH 8.0
10 RNase S pH 4.5
11 KSI D40N M105C
12 KSI D40 M105C
13 RC
14 hALR2
15 NTAIL S407C
16 NTAIL L498C
17 NTAIL S491C
18 NTAIL V517C
19 MBP F87C (buffer)
20 MBP F87C (DPC)
21 CM 15 L4C (buffer)
22 CM 15 L4C (DPC)
23 CM 15 L4C (E.coli lipids)
24 CM 15 I8C (buffer)
25 CM15 I8C (DPC)
26 CM 15 I8C (E.coli lipids)
27 CM 15 A10C (buffer)
28 CM 15 A10C (DPC)
29 CM 15 A10C (E.coli lipids)
30 CM 15 V14C (buffer)
31 CM 15 V14C (DPC)
32 CM 15 V14C (E.coli lipids)
33 Ralβ I18C
34 Ralβ N27C
35 Ralβ G28C
36 Ralβ N29C
37 Ralβ M30C
38 Ralβ S33C
39 KSI D40 M116C
40 KSI D40N L61C
41 DHFR

Fig. S5 Central wavenumber of the nitrile group of MeSCN in different solvents (left) and cyanylated cysteine in different proteins (right). Left: Central wavenumber of MeSCN's thiocyanate group in protic (open symbols) and aprotic (solid symbols) solvents as a function of the solvent field $\vec{F}_{Onsager}$. A linear fit (black line; $R^2 = 0.76$) of the central wavenumber as a function of the solvent field ($\tilde{\nu} = \tilde{\nu}_0 + |\Delta\vec{\mu}| \times \vec{F}_{Onsager}$) is shown, resulting in $\tilde{\nu}_0 = 2165(2)$ cm^{-1} and a Stark tuning rate of $|\Delta\vec{\mu}| = 1.7(4) \times 10^{-9}$ cm^{-1}/(V/m) for the aprotic solvents reported here together with those reported in previous publications. The measured central wavenumber of SCN in Hb is depicted by a green line. The data points symbolized by circles are measured in this work, the data in squares is taken from ref. 38 with the exception of DMF, which has been taken from ref. 22. Right: Central wavenumber of thiocyanate incorporated into proteins (data points 1, 2, 5, 11, 12, 39 and 40 are taken from ref. 48; 3, 4, 6, 7, 8 and 33 to 38 from ref. 21; 9 and 10 from ref. 49; 13 and 14 from ref. 15; 15 to 18 from ref. 2; 19 and 20 from ref. 39; 21 to 32 from ref. 57, and 41 from ref. 22. Note that our value of 2156 cm^{-1} is among the lowest reported so far.

Acknowledgements

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The Royal Society of Chemistry apologises for these errors and any consequent inconvenience to authors and readers.

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