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## **Supporting Information**

Comment on "Local, solvation pressures and conformational changes in ethylenediamine aqueous solutions probed using Raman spectroscopy" by M. Caceres, A. Lobato, N. J. Mendoza, L. J. Bonales, and V. G. Baonza, *Phys. Chem. Chem. Phys.*, 2016, 18, 26192

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A. Conformer energies, 0W modelling (including the Gaussian94 problem)

B. Conformer energies, 4W modelling

<u>A. Conformer energies, 0W modelling</u>. The data in Table 1 is plotted below, in Fig. S1. All five models with Gaussian09 show 7 low-lying conformers. The Gaussian94 data of Ref. 4 does not (the high curve in Fig. S1). This Gaussian94 data arose from an older version of PCM called DPCM, which was more prone to inaccuracy. In our further exploration of the problem (Table S1), we tested the various ways still in Gaussian09 for curing the problem of escaped charge (of solute into the continuum), with the ICOMP (charge compensation) flag. Note the unfortunate combination of DPCM with UAHFx1.2 radii, which produces an imbalance in escaped charge between TTT and TGP conformers (particularly bad for the TTT isomer), leading to large variances in the energy difference with ICOMP choice. As the table shows, this problem is essentially eliminated by the IEFPCM model that has been the default in Gaussian since 1998.



Fig. S1. Relative energies of ethylenediamine conformers, 0W modelling (Table 1 data).

Table S1: The gauche-trans energy gap E(TTT)-E(TGP) (kcal mol<sup>-1</sup>), MP2/6-31G(d,p), using gas-phase MP2/6-31G(d,p) geometries

		IEFPCM	DPCM	DPCM	ref. 4
ICOMP	meaning	uahfx1.2	uahfx1.2	bondix1.2	(G94)
0	no compensation	-0.1	-0.6	-0.1	
1	uniform charge density	-0.1	-1.5	-0.2	
3	e-density weighting	-0.1	-3.7	-0.2	
4	effective charges	n/a	2.4	0.1	2.5
	escaped charge, TTT		0.60	0.35	
	escaped charge, TGP		0.16	0.35	

<u>B. Conformer energies, 4W modelling.</u> The 29 clusters have energies plotted in Fig. S2 and tabulated in Table S2, and structures shown in Fig. S3. The energies can be fit (rms error 1.42 kcal mol<sup>-1</sup>) to the following equation:

$$E = 30.63 - 7.58 n_{OH-N} - 4.45 n_{OH-O} - 0.99 n_{NH-O} + 1.39 n_{as} + 2.29 n_{ps}$$

where { $n_{\text{OH-N}}$ ,  $n_{\text{OH-O}}$ ,  $n_{\text{NH-O}}$ } are the number of such hydrogen bonds in the structure, { $n_{\text{as}}$ } is the number of angle strains due to an HOH molecule in an H-bonded ring having two H-bonds to its two H atoms (0 or 1), and { $n_{\text{ps}}$ } is the number of nitrogen lone-pair strains (0, except 1 in the G'GG' conformer). The particularly strong OH-N interaction is apparent (7.58 kcal mol<sup>-1</sup>).

However, note that this function employs no effects from the conformer of ethylenediamine itself (other than separating out the high-energy G'GG' conformer); such effects are too small to be discernible in this sample over this wide energy range. Other limitations include the selection of only 29 possibilities, the neglect of H-bonding with the rest of the solution, and the neglect of temperature and entropy effects. Interestingly, the lowest trans conformer here, TTG (in TTG230), differs from the lowest trans conformer in 0W modelling (TTT), and the lowest gauche conformer here, GGP (in GGP231tri), differs from the lowest gauche conformer in 0W modelling (TGP), but this may be an artefact of the number of water molecules employed. Probably from this data one should simply note that the lowest gauche and lowest trans structures are only 1.1 kcal mol<sup>-1</sup> apart, still close enough (given the limitations of 4W modelling) to prevent the ruling out of either gauche or trans conformers.



Fig. S2: Relative energies of conformers, 4W modelling (Table S1 data). Efit is the fitted function (Eq. 1).



Fig. S3: Optimized structures of conformers of ethylenediamine with 4 explicit waters (4W).

	E (au)	<i>en</i> conformers	E <sub>fit</sub>	<i>E</i> <sub>fit</sub> E <sub>B3LYP</sub> Hydrogen bonds				S	Strai ns	
Nameª			kcal/m ol	kcal/m ol	OH- N	OH- O	NH- O	Tot al	НОН	GG' G
GGP231t ri	- 496.308 39	G'G'G	1.10	0.0	2	3	1	6	0	0
TTG230	- 496.306 71	TTG	2.09	1.1	2	3	0	5	0	0
PGP231	- 496.305 53	GG'G	3.39	1.8	2	3	1	6	0	1
GTG230	- 496.303 28	GTG	2.09	3.2	2	3	0	5	0	0
GGP231s tr	- 496.303 26	G'G'G	2.49	3.2	2	3	1	6	1	0
TGP221	- 496.302 62	TGG'	5.56	3.6	2	2	1	5	0	0
PGP230	- 496.302 50	GG'G	4.38	3.7	2	3	0	5	0	1
TGT220	- 496.301 69	TG'T	6.55	4.2	2	2	0	4	0	0
GTG221	- 496.299 42	GTG	5.56	5.6	2	2	1	5	0	0
PGP231s tr	- 496.299 13	G'GG'	4.78	5.8	2	3	1	6	1	1
TTT220	- 496.297 10	ттт	6.55	7.1	2	2	0	4	0	0
TGP132tr i	- 496.296 78	TGG'	7.70	7.3	1	3	2	6	0	0
TTT211	- 496.295 53	ттт	10.01	8.1	2	1	1	4	0	0
TGP212s qu	- 496.295 08	TG'G	9.02	8.3	2	1	2	5	0	0
GTP211	- 496.293 98	GTG'	10.01	9.0	2	1	1	4	0	0
GTP122	- 496.293 81	GTG'	12.15	9.1	1	2	2	5	0	0

Table S2: Energies of conformers (B3LYP/6-31+G(d)/SCRF+4W optimizations).

GTP220	- 496.292 57	GTG'	6.55	9.9	2	2	0	4	0	0
TGP212tr i	- 496.291 99	TG'G	9.02	10.3	2	1	2	5	0	0
GGP122	- 496.291 30	G'G'G	12.15	10.7	1	2	2	5	0	0
GTG211	- 496.289 74	G'TG'	10.01	11.7	2	1	1	4	0	0
TGP122tr i	- 496.289 70	TGG'	12.15	11.7	1	2	2	5	0	0
TTT202	- 496.288 86	ТТТ	13.48	12.3	2	0	2	4	0	0
GTP122	- 496.287 95	GTG'	13.54	12.8	1	2	2	5	1	0
PGP211s qu	- 496.286 80	GG'G	12.30	13.5	2	1	1	4	0	1
GGP113t ri	- 496.285 60	G'G'G	15.61	14.3	1	1	3	5	0	0
PGG032	- 496.283 50	GG'G'	16.67	15.6	0	3	2	5	1	0
PTG021	- 496.277 22	G'TG	20.73	19.6	0	2	1	3	0	0
GGP012	- 496.270 80	G'G'G	24.19	23.6	0	1	2	3	0	0
PTG000	- 496.259 00	GTG'	30.63	31.0	0	0	0	0	0	0

<sup>a</sup> Notation: P = G' of Fig 1/Table 1; the three numbers (for example "113") indicate number of OH-N, OH-O and NH-O hydrogen bonds respectively; tri = presence of H-bonded triangle "ONN" unit; squ = presence of H-bonded square "NOON" unit; str = presence of an angle-strained H<sub>2</sub>O molecule.