PCCP

ROYAL SOCIETY OF CHEMISTRY

COMMENT

View Article Online
View Journal | View Issue

Check for updates

Cite this: *Phys. Chem. Chem. Phys.*, 2020, **22**, 7119

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

A. A. Mukadam, N. P. Aravindakshan and A. L. L. East *

Received 5th December 2019,
Accepted 13th March 2020

DOI: 10.1039/c9cp06589j

rsc.li/pccp

Liquid ethylenediamine contains both *trans* and *gauche* conformers, but there are conflicting claims in the literature that the relative abundance of *gauche* conformers is either completely quenched (*J. Mol. Struct.*, 1999, **482**, 639–646) or enhanced (*Phys. Chem. Chem. Phys.*, 2016, **18**, 26192–26198) in 1 M aqueous solutions. Density-functional-theory spectra predictions are employed here to resolve the conflict. In both the 1999 and 2016 reports, the effects seen were misinterpreted, and are instead due to loss of direct amine–amine H-bond interaction upon dilution, which appears to be complete at ~0.66 mole fraction of water. Both *trans* and *gauche* conformers of ethylenediamine are concluded to be present, in both liquid and aqueous phases, with as yet no solid evidence for a shift in conformer ratio.

1. Introduction

We recently uncovered confusion in the literature regarding the prevailing conformer(s) of ethylenediamine (ethane-1,2-diamine) in aqueous solutions, and wish to clarify the matter.

In the 1970s, Omura and Shimanouchi published three papers on their use of vibrational spectroscopy to interpret the *trans vs. gauche* backbone (φ_{NCCN}) possibilities for ethylenediamine. They first presented an infrared spectrum (concentration 55 wt% ≈ 6–9 M, pH = 13.6) and assigned the backbone to be *gauche* due to the preponderance of peaks from 1300–1500 cm^{-1} (only 4 would be predicted from a *trans* conformer).[1] However, two years later, the same authors presented a Raman spectrum (concentration 6 M, pH = 13.6) and concluded that both *gauche* and *trans* conformers are present, due to peaks at 475 cm^{-1} (assigned to *trans*) and 340 cm^{-1} (assigned to *gauche*).[2] They also concluded that both conformers also exist in cyclohexane solution and in the pure liquid state.[3]

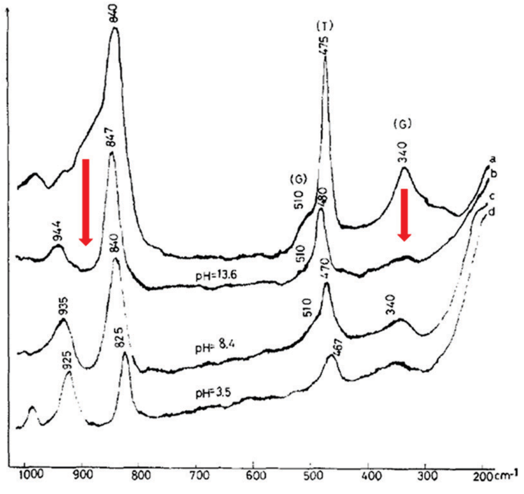
In 1999, Batista de Carvalho *et al.*[4] reported higher-resolution Raman spectra, of the pure liquid and 1 M aqueous solution, noting the near disappearance of the peak at 340 (as well as the one at 880 cm^{-1}, and perhaps 980 and 1080 cm^{-1} as well) upon dilution to 1 M rather than 6–9 M. Assigning all 4 of these peaks to the *gauche* conformer, they concluded that dilution from the liquid state shifts the *trans*/*gauche* ratio to predominantly *trans*.

In 2016, Cáceres *et al.*[5] reported Raman spectra at thirty different aqueous concentrations, focusing in particular on the C–H and N–H stretch frequencies (2500–3500 cm^{-1}) which all shift gradually to higher frequency (up 8 to 20 cm^{-1}) during dilution down to 1 M. The N–H stretch frequencies showed an abnormal slope change at 0.6 mole fraction amine. To explain the change in blue-shift rate during dilution, they concluded that dilution shifts the *trans*/*gauche* ratio *towards gauche* during dilution. (They erroneously stated that Batista de Carvalho *et al.* had also concluded this, adding to the confusion.)

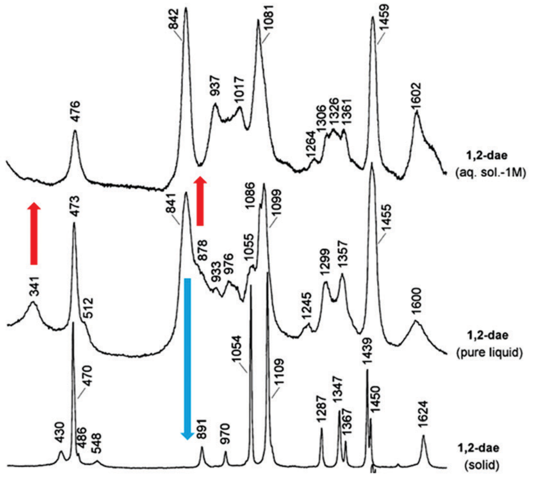
We present a reanalysis of these previously published Raman spectra (reproduced here, Fig. 1), with the valuable benefit of new density functional theory predictions of Raman spectra of various conformers. As we will show, both the 1999 and 2016 reports made errors in interpretation: the disappearing peaks and the abnormal NH-stretch slope change are due to loss of interamine interactions. *gauche* and *trans* conformers are present, not only in the liquid, but also down to 1 M aqueous concentrations, with as yet no discernible shift in relative abundance.

Department of Chemistry and Biochemistry, University of Regina, Regina, SK S4S 0A2, Canada. E-mail: allan.east@uregina.ca

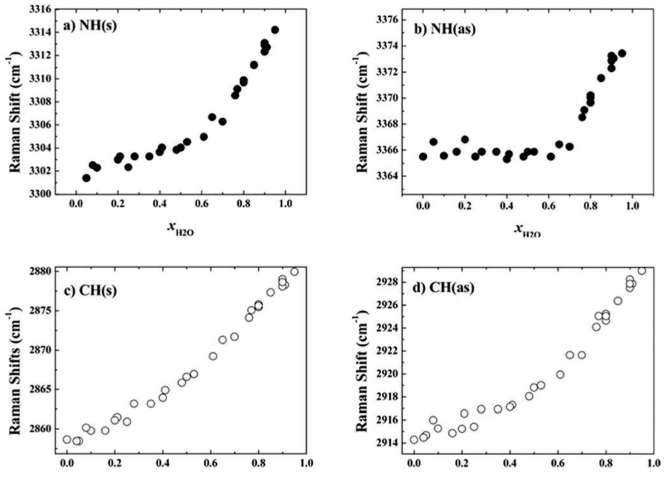
† Electronic supplementary information (ESI) available: Plots of Table 1 data, and results of the 4W conformer computations. See DOI: 10.1039/c9cp06589j



1975, Omura and Shimanouchi



1999, Batista de Carvalho et al.



2016, Cáceres et al.

Fig. 1 Raman spectra of ethylenediamine in condensed phases. (a) Omura and Shimanouchi.[1] (permission: Elsevier) (b) Batista de Carvalho *et al.*[4] (permission: Elsevier) (c) Cáceres *et al.*[5] (permission: PCCP Owner Societies). The added red arrows show the disappearing peaks at 341 and 878 cm^{-1} upon diluting the liquid, while the blue arrow in (b) shows the disappearing peak at 841 cm^{-1} upon freezing the liquid.

2. Methods

All computations used Gaussian09,[6] the basis set 6-31+G(d), and the default continuum solvation model (IEFPCM with the dielectric constant of water).[7] The electronic structure methods (ESMs) tested for relative conformer energies were B3LYP,[8,9] M06-2X,[10] and the *ab initio* method MP2.[11] Predicted Raman spectra used the M06-2X/6-31+G(d)/IEFPCM level of theory, which reproduces the known spectrum of crystalline ethylenediamine (bottom spectrum of Fig. 1b) very well.

To determine possible intermolecular amine–amine structures, simulations of H-bonded dimers were done using Vienna Ab initio Simulation Package (VASP) software,[12,13] with its potpawGGA plane-wave basis sets,[14,15] PW91 level of density-functional theory[16] with an added Grimme-style van der Waals (vdW) attractive potential for the forces,[17] standard precision (PREC = NORMAL), ENMAX = 400 eV, isotope-averaged masses, a Nosé thermostat for canonical-ensemble (*NVT*) conditions[18] with 40 fs thermal oscillations (SMASS = 0), and a Verlet velocity algorithm.[19] Visualization of simulation movies and their further analysis were done with VMD software.[20]

3. Results

3.1. Conformer energies

First, we updated the quantum-chemistry conformation energies that Batista de Carvalho *et al.* had calculated and published with their spectra in 1999,[4] optimizing the same 10 different conformers (Fig. 2) of ethylenediamine, but at 5 different levels of theory (see Table 1). The current best predictions (B3LYP, MP2, and M06-2X in 2nd–4th columns) predict 7 conformers within 0.8 kcal mol^{-1} of each other, including a mix of "*gauche*" (*gauche*-NCCN) and "*trans*" (*trans*-NCCN) ones. The 1999 predictions using Gaussian94 (7th column) gave only two low-lying *gauche* conformers, adversely affected by the "escaped charge" problem of early continuum models[21–23] (see ESI†).

This Table 1 data, from ordinary continuum modelling, does not incorporate effects due to strong hydrogen bonds (H-bonds) between solute and solvent, which could conceivably affect relative conformer energies. Therefore, conformer energies were also obtained with 4W semicontinuum modelling (4 explicit water molecules inside the continuum with the solute ethylenediamine molecule). Twenty-nine different clusters of ethylenediamine·4W (16 *gauche* and 13 *trans* cases) were optimized (B3LYP/6-31+G(d)/SCRF), but the resulting conformer energies (Table S2 and Fig. S2, S3 of ESI,† for those who are interested) were not terribly helpful. The great variety of the number of explicit H-bonds in the clusters caused an unrealistic and greatly expanded energy range (30 kcal mol^{-1}) of relative energies, obscuring the fine differences in energy of the conformers. (A proper explicit-solvation study of relative conformer energies would require many more waters and thousands of optimized structures.)

Thus, even today, *ab initio* conformer-energy predictions are not accurate enough to determine which conformers should be dominant in liquid *vs.* aqueous systems. Comparison of predicted

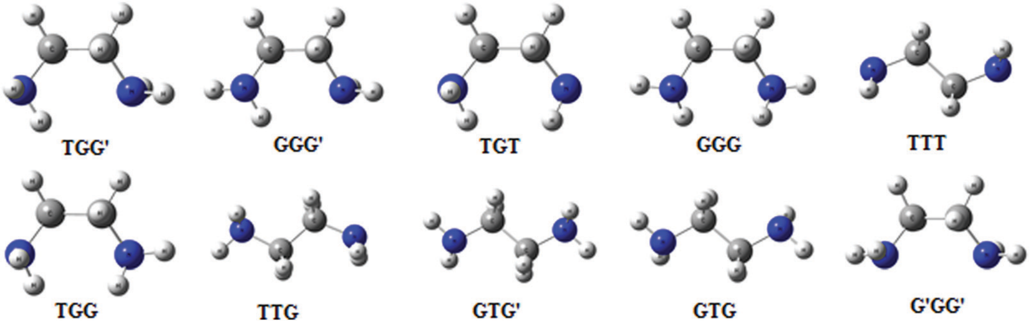


Fig. 2 Optimized structures of ethylenediamine conformers. The labels {T,G,G′} mean dihedral angles of ≈{180°,+60°,−60°} for $\varphi_{\text{LP-N-C-C}}$, $\varphi_{\text{N-C-C-N}}$, $\varphi_{\text{C-C-N-LP}}$, where LP means lone pair of electrons.

Table 1 Relative energies (kcal mol^{-1}) of ethylenediamine conformers, 0W optimizations[a]

Conformers[b]	$E_{\text{B3LYP/6-31+G(d) SCRF}}$[c]	$E_{\text{M06-2X/6-31+G(d) SCRF}}$[c]	$E_{\text{MP2/6-31+G(d) SCRF}}$[c]	$E_{\text{MP2/6-31G(d,p) SCRF}}$[c]	$E_{\text{MP2/6-31G(d,p) SCRF}}$[d]	$E_{\text{MP2/6-31G(d,p) SCRF G94}}$[e]
TGG′	0.00	0.00	0.00	0.00	0.00	0.00
GGG′	0.20	0.10	0.01	0.37	0.47	0.75
TGT	0.01	0.18	0.25	0.23	−0.32	2.52
TTT	−0.12	0.41	0.29	0.28	−0.12	2.51
GGG	0.57	0.48	0.28	1.01	0.90	1.87
TGG	0.37	0.43	0.40	0.78	0.43	1.76
TTG	0.32	0.75	0.61	1.00	0.69	2.10
GTG′	0.72	1.07	0.88	1.62	1.41	3.31
GTG	0.75	1.10	0.91	1.59	1.37	2.71
G′GG′	2.04	2.26	2.21	2.65	2.51	4.89

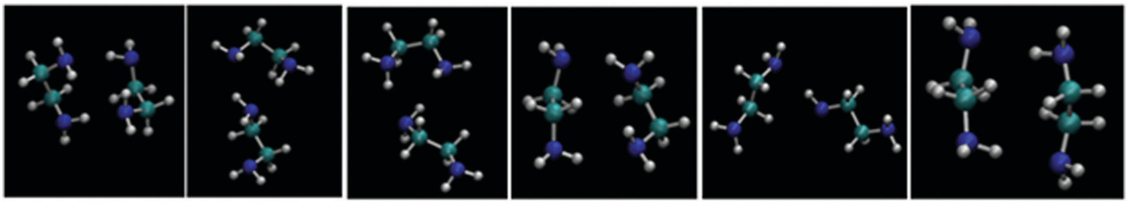
[a] 0W = no explicit water molecules added. [b] See Fig. 2. [c] IEFPCM with UFFx1.1 radii (the Gaussian09 default). [d] IEFPCM with UAHFx1.2 radii. [e] From ref. 4; a DPCM model that was soon thereafter deprecated. See ESI for details.

Raman spectra to the measured ones would thus be of value to settle the question.

3.2. Intermonomer simulations

We hypothesized that the Raman peaks that disappear upon aqueous dilution were due to what we shall call triangle intermonomer structures. The idea came to us during ethylenediamine·4W cluster study, where we commonly observed optimized structures featuring both ends of a *gauche* ethylenediamine molecule hydrogen-bonding to a common water molecule (an NNO-triangle structure). The visual resemblance to a bidentate ligand of a transition metal atom was striking. To explore the possibility of an analogous NNN-triangle structure in liquid ethylenediamine, we performed 9 trials of cold (100 K) simulations of two separated gas-phase ethylenediamine molecules, to probe how they might H-bond to each other. Two molecules were simulated (see Methods) in a cubic box (16 × 16 × 16 Å^3), at nine different starting geometries: *gauche–gauche* (3 trials), *gauche–trans* (3 trials) and *trans–trans* (3 trials). All the nine simulations were started with the two molecules 4 Å apart at a temperature of 100 K, and continued to 20 000 timesteps (1 timestep = 1 fs); Fig. 3 shows the resulting structures. The intermolecular N–H distances involved in the structure formation in the first 2 trials are plotted *versus* time (Fig. 4) to demonstrate the timescale of formation and persistence of the structures formed.

While the *trans–trans* simulations most commonly formed "linear" structures featuring a single H-bond, the *gauche–gauche* and *gauche–trans* simulations most commonly formed an NNN-triangle intermonomer structure. Since an exhaustive search of intermonomer conformers in the liquid would require excessive simulation time, we report these nine results as support that these NNN-triangle intermonomer structures might be present in the liquid.



Trial 1: GG square
Trials 2 and 3: GG triangle
Trials 4 and 5: GT triangle
Trial 6: GT square
Trials 7 and 9: TT linear
Trial 8: TT square

Fig. 3 Snapshots of structures observed in 20 ps simulations (4 Å initial separation, *T* = 100 K).

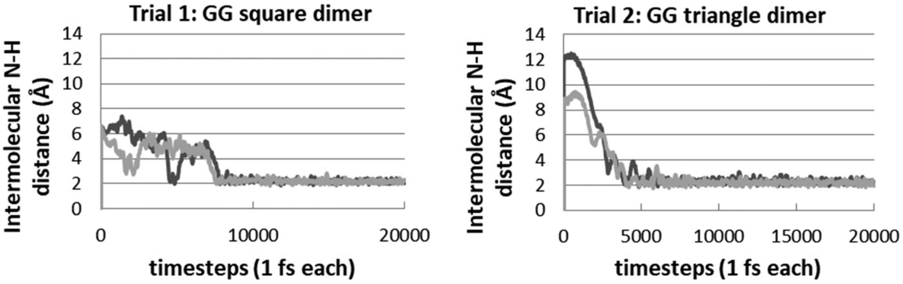


Fig. 4 The N–H distances *versus* time of the first 2 trials, demonstrating the formation and persistence of the two resulting structures.

Gubskaya and Kusalik in 2004 reported empirical molecular mechanics simulations of both liquid[24] and aqueous[25] ethylenediamine, and while equilibration of the *trans*-to-*gauche* ratio was not achieved, an interesting localized H-bonding feature was observed in the N···N and N···H spatial distribution functions of the pure liquid simulation (Fig. 7 of ref. 24). This feature was identified as coming from a weakly H-bonded neighbour where the molecular arrangement is consistent with the triangle intermonomer structure identified here.

3.3. Density functional theory Raman spectra predictions

Fig. 5 presents exemplary sets of predictions of Raman spectra, assuming low-energy monomers TGG′, GGG′, and TTT. Note the very good agreement with the predicted TTT spectra (bottommost trace) with the experimental spectrum of the solid (known to be purely TTT conformers). This lends confidence in the frequencies and activities from the M06-2X/6-31+G(d,p) SCRF electronic structure method. The predicted spectra in Fig. 5 (and animation of the normal modes underlying the peaks) were used to make the peak assignments in Table 2.

4. Discussion

4.1. Corrected Raman assignments

- 1054 cm^{-1} (sol, liq only): CC str, *trans* conformers. It is a strong peak in the solid spectrum, weakened (due to reduced population) in the liquid state. It is curiously absent in the aqueous spectrum, but this could be due to a shift to the blue to merge with the CN str peak, due either to hydration (see TTT·2W in Fig. 5) or conversion to a different *trans* conformer (see TTG in Fig. 5). The CC str peak for *gauche* conformers is far removed, at 841 cm^{-1}, seen in the liquid and aqueous spectra. The relevant predicted peaks are circled in Fig. 5b.
- 933–1017 cm^{-1}: CH_2 rocks of all conformers, and NH_2 wags and CH_2 twists of *gauche* conformers. The NH_2 wags and CH_2 twists of *trans* conformers are far removed, at 890–900 and 1330–1350 cm^{-1} respectively.
- 878 cm^{-1} (liquid only): NH_2 wag of GGX *gauche* conformers in NNN-triangle intermonomer structures (see Fig. 6). This peak disappears (shifts to higher frequency and lower intensity) when diluted (due to fixing of the relevant N lone pair by H-bonding to water molecules) or when solidified (due to conversion from *gauche* to *trans*).

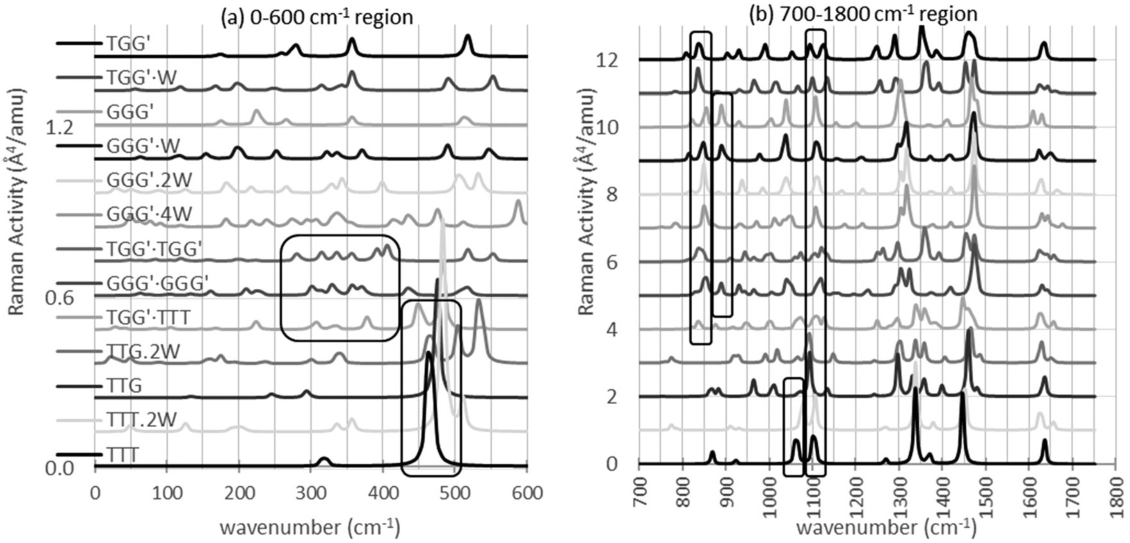


Fig. 5 Predicted Raman spectra (M06-2X/6-31+G(d)/IEFPCM) of exemplary monomers, hydrated monomers, and dimers of ethylenediamine. TGG′, GGG′, and TTT: conformers (see Fig. 2). Harmonic wavenumbers from 700–1800 cm^{-1} have been scaled by 0.97 for anharmonicity. Activities of the three dimer spectra were halved for comparison to monomer spectra. Regions of interest for assignment of the experimental spectra are boxed.

Table 2 Updated assignments of Raman spectra peaks of solid, liquid, and aqueous ethylenediamine (see Fig. 1)

ν (cm^{-1})	Assignment, this work	1999 asgt[4]	1975 asgt[2]
3330–3370	NH_2 antisym str, all conf.	Same as current	
3170–3310	NH_2 sym str, all conf.	Same as current	
2900–2940	CH_2 antisym str, all conf.	Same as current	
2855–2880	CH_2 sym str, all conf.	Same as current	
1600–1624	NH_2 scissors, all conf.	Same as current	
1439–1459	CH_2 scissors, all conf.	Same as current	
1245–1361	CH_2 wags and CH_2 and NH_2 twists, all conf.	Same as current	
1086–1109	CN str, all conf.	Same as current	
1054 (sol, liq)	CC str, TTT *trans* conf.	CC str	
933–1017	CH_2 rocks (all), NH_2 wags and CH_2 twists (*gauche*)	CH_2 rock + CN str	
878 (liq)	NH_2 wag, GGX *gauche* conf. in NNN triangles	NH_2 wag + CC str, *gauche* conf.	
841 (liq, aq)	CC str, *gauche* conf.	NH_2 wag + CN str	CH_2 rock, *gauche* conf.
470–476	sym CCN bend, *trans* conf.	CCN deform, *trans* conf.	CCN deform, *trans* conf.
341 (liq)	sym CCN bend and CN tors, *gauche* conf. in NNN triangles	CCN deform + NH_2 tors, *gauche* conf.	CCN deform, *gauche* conf.

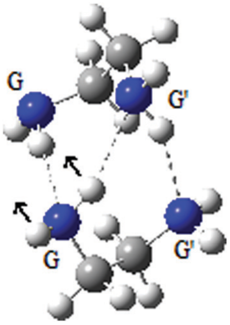


Fig. 6 A possible contributor to the liquid-only 878 cm^{-1} Raman band: the lowest-frequency NH_2 wag (of the 4 NH_2 wags possible) in the (GGG′)$_2$ H-bonded intermolecular structure of ethylenediamine. The other three NH_2 wag modes of (GGG′)$_2$ are predicted to be 40–80 cm^{-1} to the blue. In (TGG′)$_2$ the lowest-frequency NH_2 wag is 20 cm^{-1} to the blue of this one, hence our proposed assignment of 878 cm^{-1} to structures involving GGX monomers.

- 841 cm^{-1} (liq, aq only): CC str, *gauche* conformers. It is a strong peak in the liquid and aqueous spectra. Shimanouchi had correctly assigned this to *gauche* conformers, though he thought it was a CH_2 rock mode. No peak appears in this region of the solid spectrum, because the solid features only *trans* conformers, for which the CC str absorption is at 1054 cm^{-1}. The relevant predicted peaks are circled in Fig. 5b.
- 470–476 cm^{-1}: sym CCN bend, *trans* conformers. This assignment is merely a more precise description of the "deformation" already assigned by previous workers. The sym CCN bend of *gauche* conformers has very little Raman intensity (Fig. 5a).
- 341 cm^{-1} (liquid only): sym CCN bend and CN torsions of *gauche* conformers within NNN-triangle intermonomer structures. In the 200–400 cm^{-1} region, *gauche* monomers do exhibit three vibrational fundamentals of this type (the two CN torsions and the symmetric NCC bend, variously mixed), but as shown in Fig. 5a, these three do not contribute much intensity in the 300–400 cm^{-1} region. In the model dimers, however, an accumulation of intensity is here, shifted up in frequency due to H-bonding: note for example the predicted spectrum for TGG′·TGG′ dimer which shows intensity for all 6 modes here (3 modes per monomer × 2 monomers, coupled).

4.2. Present conformers in each phase

Both *gauche* and *trans* conformers are present in the liquid, and both also in 1 M aqueous solution, due to the Raman bands seen at ~475 cm^{-1} (sym CCN bend of *trans* conformers only) and ~841 cm^{-1} (CC str of *gauche* conformers only). The act of freezing, into purely *trans* conformers, removes the 841 cm^{-1} *gauche* band. The act of diluting the liquid to 1 M aqueous solution maintains both the 841 cm^{-1} *gauche* and 475 cm^{-1} *trans* bands, but eliminates the intermonomer peaks at 878 and 341 cm^{-1}. It is not clear to us that anything can be concluded regarding the *trans*-to-*gauche* ratios in either the liquid or aqueous states. (A 2014 molecular mechanics simulation of a 7 : 3 amine : water solution showed predominantly *trans* conformers,[26] but this result is very sensitive to the particular attraction and repulsion force field parameters employed.)

4.3. Corrected assignment of blue shifting of CH and NH stretch bands

Cáceres *et al.*[5] compared the blue shifting they observed to the steady blue shifting one would predict from increased internal pressure p_{sol} upon solvation (arising from the larger cohesive forces of water *vs.* ethylenediamine). Their solvation pressure model predicts p_{sol} upon ethylenediamine molecules to rise from 0 to 1.75 GPa as the liquid is made infinitely dilute in water. They performed an anvil test on pure solid ethylenediamine, predicting blue-shift rates (cm^{-1} per GPa) of 7.3 and 3.7 for CH and NH stretches, respectively, for total predicted blue shifts of 12.8 and 6.5 cm^{-1} respectively from solvation pressure. Their total (infinite-dilution) blue shifts (Fig. 1 here) are larger: 24 and 26 cm^{-1} for CH stretches, 11 and 14 cm^{-1} for NH stretches. They concluded that (i) the larger-than-predicted blue shifts are due to additional hydrophobic pressure, and (ii) the reason for the slope change at 60% water was is due to a conformer change from intermolecular *trans*–*trans* to monomeric *gauche*.

We agree with their 1st conclusion but not their 2nd one. In the 2nd region (above 60% water), the blue shifts here are all ~12 cm^{-1}, due to the increase in solvation pressure. In the 1st region (up to 60% amine), the blue shifts increase significantly more mildly for the NH stretches, because there is a growing attractive force on these bonds that counteracts the rising solvation pressure. This growing attractive force is the replacement of NH···N hydrogen bonds with NH···O, not a conformer change. This replacement is approximately complete at 0.66 mole fraction (the four NH bonds now H-bonded to four O lone pairs); beyond this point, this pressure-counterbalancing effect increases no further, and the full effect of the ever-increasing solvation pressure is seen. Their proposal of a transition to *gauche* monomers was made to avoid the red-shift effect of NH···O H-bond creation, to allow the observed blue-shifting, apparently not realizing that they needed this red-shift effect to counterbalance the blue-shift effect of solvation and hydrophobic pressures in the 1st region. (There is a possibility that there is a concomitant change in the *trans*/*gauche* ratio in the 1st region as well, but the blue-shift data is unable to reveal this.)

5. Conclusions

Aqueous 1–6 M solutions of ethylenediamine are composed of both *trans* and *gauche* monomers, due to the presence of the Raman peaks at 473 cm^{-1} (sym CCN bend of *trans*) and 841 cm^{-1} (CC str of *gauche*). Liquid ethylenediamine also features both bands, and hence such a mixture.

The pure solid has entirely *trans* conformers, and hence the act of freezing results in the loss of the liquid-phase Raman peak at 841 cm^{-1} (CC str of *gauche*, newly assigned here). Aqueous solutions diluted to less than 6 M concentration (mole fractions of $x_{\text{water}} > 0.6$) are likely devoid of NH···N hydrogen bonds, and hence the act of such dilution results in the loss of the liquid-phase Raman peaks at 341 (sym CCN bend and CN tors in NNN-triangle intermonomer structures) and 878 cm^{-1} (NH_2 wag in NNN-triangle intermonomer structures).

The previous conflicting claims of ref. 4 and 5, that peak evolution upon dilution of the liquid with water indicates an increase (ref. 4) or decrease (ref. 5) in the *trans*-to-*gauche* ratio, were due to errors in interpretation. The disappearing peaks at 341 and 878 cm^{-1}, thought by ref. 4 to be due to loss of *gauche* conformers, cannot be explained this way, due to the non-loss of the *gauche* peak at 841 cm^{-1}; they are due to loss of intermonomer interactions. The slow-then-mild blue-shifting of the N–H stretch frequencies, thought by Ref. 5 to be evidence of *trans* → *gauche* conversion, is not; it is due to the mild solvent compression effect (water cohesion) which is initially (until $x_{\text{water}} \approx 0.66$) somewhat offset by the increasing replacement of NH···N H-bonds with stronger NH···O ones.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The work was supported by the Natural Sciences and Engineering Research Council (Discovery Grant RGPIN-2017-06247) and the Canada Foundation for Innovation (Leading Edge Fund 2009, grant 21625). P. Kusalik (Calgary) is thanked for useful discussions.

References

1 Y. Omura and T. Shimanouchi, Infrared spectra and rotational isomerism of ethylenediammonium ion in aqueous solution, *J. Mol. Spectrosc.*, 1973, **45**, 208–220.

2 Y. Omura and T. Shimanouchi, Skeletal deformation vibrations and rotational isomerism of ethylenediamine and monoethanolamine, *J. Mol. Spectrosc.*, 1975, **57**, 480–489.

3 Y. Omura and T. Shimanouchi, Raman spectra and rotational isomerism of ethylenediammonium and monoethanolammonium ions in aqueous solution, *J. Mol. Spectrosc.*, 1975, **55**, 430–434.

4 L. A. E. Batista de Carvalho, L. E. Lourenço and M. P. M. Marques, Conformational study of 1,2-diaminoethane by combined ab initio MO calculations and Raman spectroscopy, *J. Mol. Struct.*, 1999, **482**, 639–646.

5 M. Cáceres, A. Lobato, N. J. Mendoza, L. J. Bonales and V. G. Baonza, Local solvation pressures and conformational changes in ethylenediamine aqueous solutions probed using Raman spectroscopy, *Phys. Chem. Chem. Phys.*, 2016, **18**, 26192–26198.

6 M. J. Frisch, *et al.*, *Gaussian09, Rev. C.01*, Gaussian, Inc., Wallingford CT, 2009.

7 J. Tomasi, B. Mennucci, R. Cammi and M. Cossi, Quantum mechanical continuum solvation models, *Chem. Rev.*, 2005, **105**, 2999–3094.

8 C. Lee, W. Yang and R. G. Parr, Development of the Colle-Salvetti correlation-energy formula into a functional of the electron, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1988, **37**, 785–789.

9 A. D. Becke, Density-functional thermochemistry. III. The role of exact exchange, *J. Chem. Phys.*, 1993, **98**, 5648–5652.

10 Y. Zhao and D. G. Truhlar, Density functional for spectroscopy: No long-range self-interaction error, good performance for Rydberg and charge-transfer states, and better performance on average than B3LYP for ground states, *J. Phys. Chem. A*, 2006, **110**, 13126–13130.

11 C. Moller and M. S. Plesset, Note on an approximation treatment for many-electron systems, *Phys. Rev.*, 1934, **46**, 618–622.

12 G. Kresse and J. Hafner, Ab initio molecular dynamics for liquid metals, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1993, **47**, 558–561.

13 G. Kresse and J. Furthmüller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1996, **54**, 11169–11186.

14 G. Kresse and J. Hafner, Norm-conserving and ultrasoft pseudopotentials for first-row and transition elements, *J. Phys.: Condens. Matter*, 1994, **6**, 8245–8257.

15 G. Kresse and D. Joubert, From ultrasoft pseudopotentials to the projector augmented-wave method, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1999, **59**, 1758–1775.

16 J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pedersen, D. J. Singh and C. Fiolhais, Atoms, molecules, solids, and surfaces: Applications of the generalized

gradient approximation for exchange and correlation, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1992, **46**, 6671–6687.

17 S. Grimme, Semiempirical GGA-type density functional constructed with a long-range dispersion correction, *J. Comput. Chem.*, 2006, **27**, 1787–1799.

18 S. Nosé, A unified formulation of the constant temperature molecular dynamics methods, *J. Chem. Phys.*, 1984, **81**, 511–519.

19 A. R. Leach, *Molecular Modelling: Principles and Applications*, Pearson, Harlow, UK, 2nd edn, 2001.

20 W. Humphrey, A. Dalke and K. Schulten, VMD: Visual Molecular Dynamics, *J. Mol. Graphics*, 1996, **14**, 33–38.

21 A. Klamt and V. Jonas, Treatment of the outlying charge in continuum solvation models, *J. Chem. Phys.*, 1996, **105**, 9972–9981.

22 M. Cossi, B. Mennucci, J. Pitarch and J. Tomasi, Correction of cavity-induced errors in polarization charges of continuum solvation models, *J. Comput. Chem.*, 1998, **19**, 833–846.

23 E. Cances and B. Mennucci, The escaped charge problem in solvation continuum models, *J. Chem. Phys.*, 2001, **115**, 6130–6135.

24 A. V. Gubskaya and P. G. Kusalik, Molecular dynamics simulation study of ethylene glycol, ethylenediamine, and 2-aminoethanol. 1. The local structure in pure liquids, *J. Phys. Chem. A*, 2004, **108**, 7151–7164.

25 A. V. Gubskaya and P. G. Kusalik, Molecular dynamics simulation study of ethylene glycol, ethylenediamine, and 2-aminoethanol. 2. Structure in aqueous solutions, *J. Phys. Chem. A*, 2004, **108**, 7165–7178.

26 G. A. Orozco, V. Lachet and A. D. Mackie, A molecular simulation study of aqueous solutions of amines and alkanolamines: mixture properties and structural analysis, *Mol. Simul.*, 2014, **40**, 123–133.