Understanding the influence of low-frequency vibrations on the hydrogen bonds of acetic acid and acetamide dimers†

Christopher Copeland, Omkaran Menon, D. Majumdar, Szczepan Roszak and Jerzy Leszczynski

Low-frequency vibrations coupled to high-frequency modes are known to influence the hydrogen bond strengths in a weakly interacting dimer. In this context, various acetic acid and acetamide dimers were analyzed using Møller–Plesset second-order perturbation (MP2) and density functional theory (DFT)-based approaches with explicit anharmonicity corrections. The computed low-frequency fundamentals as well as the high-frequency modes, which were found to be related to hydrogen bonding (OH/NH stretching modes), were analyzed and their computed intensities were correlated with their hydrogen-bond strengths/binding energies. There are similarities in the nature of eight low-frequency fundamentals of these two dimers, and the in-plane bending and stretch-bend fundamentals of the different dimers of these two species (in this low-frequency region) have specific roles in their relative stability order. The computed linear correlations were further verified against the results from coupled cluster calculations including triple excitation (CCSD(T)), Gaussian-G4 (G4), Gaussian-G2-MP2 (G2MP2) and complete basis set (CBS-QB3) methods of high accuracy energy calculations. As a consequence of such linear correlations, an additive property of local fragment energies (responsible for hydrogen bonding) was found to be a valid approximation to predict the binding energies of such dimers and the idea was found to be extendable to the other homologues of these acids/amides.

1. Introduction

Acetic acid and acetamide belong to the abundant family of molecular systems and are known for their importance in basic chemistry and biology. Acetic acid is an excellent model system to study the physicochemical properties of carboxylic acids, and in the gas-phase, it is a significant molecule for atmospheric and astrophysical chemistry. Acetamide, on the other hand, is an important model for peptide bond investigation in biological molecules. These molecules mostly exist in dimeric and higher polymeric forms through hydrogen bonds, and the nature of such interactions have been the objects of several theoretical and spectroscopic studies in recent times. Acetic acid, like its smaller homologue formic acid, exhibits rotational isomerism through its C–OH bond. It predominantly exists in the trans-form and is well characterized through experimental and theoretical studies. The trans-form is ~22 kJ mol⁻¹ (5.3 kcal mol⁻¹) lower in energy than the cis-form. The computed energy barrier between these two conformers is ~55 kJ mol⁻¹ (13.2 kcal mol⁻¹). The higher energy cis-form was detected in low-temperature matrices by selective IR-pumping of the overtones of the trans-conformer.

The conformational behavior of acetic acid has opened up the possibility of the formation of different dimeric forms. The number of dimeric forms is not as large as that of formic acid, but as many as six dimeric structures were predicted through combinations of trans–trans–trans forms. The high energy cis-form is unlikely to get involved in dimer formation and was not considered, and so far only three dimers with trans–trans–trans combinations have been experimentally identified. The most well-known six-membered cyclic dimer structure has two strong O–H ⋯ O hydrogen bonds. It has been characterized spectroscopically in the gas phase, in supersonic jet experiments and in low-temperature matrices. In the crystalline as well as liquid state, acetic acid exists as infinite chains that involve C–H ⋯ O–C and O–H ⋯ O–C hydrogen bonds. Acetamide does not show cis–trans isomerism like acetic acid, although their most
abundant dimers are structurally similar. The most stable isomer of acetamide was predicted to be a cyclic structure with a single hydrogen bond, but later theoretical and experimental data analysis predicted the cyclic structure to have two hydrogen bonds like acetic acid dimers. Moreover, solid state data analysis of acetamide showed that it exists in two crystalline forms under ambient conditions. The most stable rhombohedral form contains one molecule in the asymmetric unit while the metastable orthorhombic form has two molecules in the asymmetric unit. The ideas of formation of both symmetric and asymmetric hydrogen bonds are supported in the crystal structures. Thus basic structural factors governing the higher stability of the most abundant form of these dimers over the others are an important object of theoretical investigation.

The assignment of several acetic acid dimer structures (apart from the six-membered cyclic structure) has opened up research studies concerning their relative stabilities, vibrational characteristics, and formation mechanisms. These dimers have double hydrogen-bonding, although a few dimers with a single hydrogen-bond are also theoretically possible. Three more dimers were predicted for acetamide, apart from the most abundant dimer (having a six-membered ring planar structure). They are connected through hydrogen-bond/s with different orientations of the monomers. The deformation of the monomer structures affects the strength of the hydrogen bonds in various dimers and is mostly responsible for their relative stabilities. Although, the acetamide dimer is a model for many biological systems, a few experimental and theoretical studies are so far available concerning the assignments of such dimers based on the nature of hydrogen bonding.

In our previous analysis on the formic acid and formamide dimers, we observed the importance of low-frequency fundamentals coupled to the high-frequency (OH/NH stretching modes) modes for hydrogen bonding. The intensities of the respective modes were linearly correlated with the hydrogen-bond strengths/binding energies of these dimers. Acetic acid and acetamide dimers are structurally very similar to the formic acid and formamide dimers in their most stable forms. The recent spectroscopic analysis on the most abundant trans–trans acetic acid dimer has pointed out the influence of the low-frequency modes (coupled to the high frequency OH-stretch) on the di-hydrogen-bond strength. The assignments of such modes were carried out using femtosecond two-color mid-infrared pump–probe spectroscopy, linear infrared spectral studies and near-infrared (NIR) vibrational analysis. The experiments primarily point to the importance of anharmonicity effects on the observed vibrational modes and the mode/s responsible for the hydrogen-bonds were obviously more critically analyzed.

These experimental observations comprise the objectives of the present research work. Two prime features, which were investigated in the present manuscript, are related to: (a) correlation between the binding energies of such dimers and the stiffness factor (interpreted as the low/high-frequency mode/s involving hydrogen-bond vibration), and (b) connection of such modes for the similarities of hydrogen bonding patterns of the most stable acetic acid and acetamide dimers. Furthermore, we also intend to find out whether the binding energies of such weakly bound systems could have simple additive properties based on the derived local energies of the constituting fragments. Such additive properties are quite natural, and in our previous investigation on formic acid and formamide dimers we found such additive properties since the changes in the binding energies of the related isomers were quite regular with respect to their structural arrangements. This predictive part actually requires reliable computation of binding energies and vibrational frequencies of the various dimers.

We have computed the structures, binding energies (ΔEB) and vibrational characteristics of acetic acid and acetamide dimers through explicit anharmonicity corrections. Related thermodynamic quantities of binding (viz., Gibbs free energy (ΔG298), and enthalpy (ΔH298)) were also computed through such corrections. Six trans–trans monomer combinations have been considered for acetic acid dimers and the computed results are compared with four possible acetamide dimers. We did not consider the cis–cis combinations of acetic acid dimers as they are not experimentally known. The low-frequency fundamentals and their respective overtones are computed for the dimers of both acetic acid and acetamide. The related experimental data on the acetic acid dimer is compared with its computed lowest energy dimer. It will be shown that the intensities of the low-frequency in-plane bending modes together with the high frequency OH/NH stretching modes of the acetic acid/acetamide dimers correlate linearly with their binding energies (or hydrogen-bond energies) and thus influence the hydrogen-bond strengths (and hence relative stabilities) of these dimers.

2. Computational methods

The computation of the structural parameters and vibrational frequencies of the acetic acid and acetamide dimers was carried out using DFT, and MP2 techniques with aug-cc-pVDZ basis sets of the atoms. The standard B3LYP functional was used in DFT calculations. The dimer geometries were fully optimized and the minimum energy structures in the respective cases were confirmed through vibrational calculations. Similar calculations were carried out on the monomers of acetic acid (trans-conformers) and acetamide. The results were used to compute the ΔEB, ΔH298, ΔG298 of the respective dimers with counterpoise (CP) and zero-point energy (ZPE) corrections. The calculations of the thermodynamic properties have been carried out by applying the ideal gas, rigid rotator, and harmonic oscillator approximations.

The computed vibrational frequencies of the dimers (as well as monomers) and their binding energies (ΔEB, ΔH298, ΔG298) were explicitly corrected at the DFT/B3LYP/aug-cc-pVDZ and MP2/aug-cc-pVDZ levels for the effect of anharmonicity using Barone’s formalism. The computed anharmonicity-corrected frequencies for one of the high-energy acetamide dimers
The computed results should be considered for comparison purposes only (as they have incurred error for the anharmonicity corrected binding energy terms), although they are still within reasonable accuracy.

The computed energy values were further refined using single point energy calculations on the optimized structures at the DFT/B3LYP and MP2 levels using the aug-cc-pVTZ basis set of atoms. The respective $\Delta H_{298}^{B}$ and $\Delta G_{298}^{B}$ values were approximated from the corresponding values at the DFT/B3LYP/aug-cc-pVDZ and MP2/aug-cc-pVDZ levels using the following relation (1).²⁷

$$
\Delta X_{298}^{B} = \Delta X_{298}^{B}(\text{aug-cc-pVDZ}) + [\Delta E_{B}(\text{aug-cc-pVTZ})]
$$

The second term on the right-hand side of eqn (1) accounts for the higher electron-correlation effect on the energy values (due to the use of aug-cc-pVTZ basis sets). The $\Delta E_{B}$, $\Delta H_{298}^{B}$, and $\Delta G_{298}^{B}$ in eqn (1) contain anharmonicity corrected ZPEs from the fully optimized data of the acetic acid and acetamide dimers using DFT/B3LYP/aug-cc-pVDZ and MP2/aug-cc-pVDZ computations. The results have been compared against the fully optimized data of the lowest energy acetic acid and acetamide dimers using aug-cc-pVTZ basis set computations, and such approximations were found to be quite satisfactory (see Section 3A). Single-point coupled cluster calculations with triple excitations (CCSD(T))³⁸ (at the aug-cc-pVTZ level) were carried out on the MP2-optimized dimer geometries to improve the accuracy of the computed $\Delta E_{p}$ using anharmonicity corrected ZPEs from zero-point energies from MP2/aug-cc-pVDZ computations. The reliability of the computed energies was further verified against the results from G4,³⁷ G2MP2,³⁸,³⁹ and CBS-QB3⁴⁰ techniques. All the computations were carried out using Gaussian 09 and Gaussian 16 codes and the graphics presented in the manuscript were obtained through Gauss View 5 software.⁴³

3. Results and discussion

3.1 Acetic acid dimers: structural and vibrational properties

The optimized structures (at the MP2 level) of acetic acid dimers are shown in Fig. 1. Dimers formed through six trans-trans (AA-1 to AA-6) combinations of monomers are presented. These structures have also been previously computed.⁷ In the present research, further improvements on the calculated results are obtained through the inclusion of the anharmonicity-effect on the binding energies and vibrational frequencies of these dimers. The geometries of the dimers at the MP2 and DFT/B3LYP levels are compared (in terms of hydrogen bonding distances) in Table 1s of the ESI.† All the structures in Fig. 1 are arranged according to their relative energies with respect to the most abundant AA-1 dimer (Table 1), and the hydrogen bonded parts of all these dimers are nearly planar.

The computed $\Delta E_{p}$s of acetic acid dimers at the MP2, DFT/B3LYP, and CCSD(T) levels (aug-cc-pVTZ basis sets) are presented in Table 1. These dimers are considered to be formed from the lowest energy trans-acetic acid. Thus in these trans-trans dimers, the $\Delta E_{p}$s are an approximate measure of the respective hydrogen bond energies. Only the anharmonicity-corrected $\Delta E_{p}$s are presented, as in most of the cases, the maximum increase of binding energies due to the anharmonicity effect is quite small (~0.23 kcal mol⁻¹ at the MP2 level and 0.36 kcal mol⁻¹ at the B3LYP level). The computed values are also similar at different levels of theory. The best $\Delta E_{p}$s are at the CCSD(T) level (with respect to the available experiments, see below) and they are slightly higher with respect to those at the MP2 level. In view of the previously computed $\Delta E_{p}$s of the lowest energy AA-1 dimer,²³,²⁵ these binding energies are quite consistent. Table 1 also contains $\Delta H_{298}$ and $\Delta G_{298}$ of acetic acid dimers using CP and ZPE corrections (with respect to their formation from the trans-acetic acid) at the MP2 and DFT/B3LYP levels. The computed $\Delta H_{298}$ values are similar to those of $\Delta E_{p}$s, as the thermal corrections in such cases are small. The high entropic contribution to $TAS$ (T: temperature (298 K here); S: entropy) in such dimer formations causes only the most abundant (AA-1) dimer to be

3.2 Acetic acid dimers: vibrational properties

The optimized structures at the MP2 level were used to obtain harmonic frequencies using the aug-cc-pVTZ basis set. The harmonic frequencies obtained are compared against available experimental results and calculations using DFT/B3LYP and MP2/aug-cc-pVDZ levels. The computed fundamental frequencies of dimers are presented in Table 2s of the ESI.† In view of frequency data available in the literature, the corresponding harmonic vibrational intensities of these dimers were also computed.

3.3 Acetic acid dimers: electronic properties

The optimized structures of the acetic acid dimers were used to compute the charge density distribution at the MP2/aug-cc-pVTZ level. The topological analysis of the charge density was obtained using GaussView 5 software. The charge densities were analyzed to determine the nature of the bonding in these dimers. The charge density analysis also helps in understanding the anharmonic effects in the computed binding energies.

4. Conclusion

In conclusion, the present research further improves on the calculated binding energies and vibrational frequencies of acetic acid dimers using the MP2/aug-cc-pVTZ and DFT/B3LYP/aug-cc-pVTZ methods. The optimized geometries of these dimers are presented, and the computed electronic properties are compared against available experimental results. The computed binding energies, vibrational frequencies, and electronic properties are in good agreement with available experimental data, thus validating the present computational approach.

**Fig. 1** Optimized structures of acetic acid dimers (at the MP2/aug-cc-pVDZ level) with the computed hydrogen-bond distances (Å). These dimers are formed through trans-trans (AA-1 to AA-6) combinations of the monomers. The structures are similar at the DFT/B3LYP, G4, and CBS-QB3 levels and the corresponding hydrogen-bond distances are available in Table 1s of the ESI.† It is to be noted that the structure AA-6 is not supported at the G2MP2, G4, and CBS-QB3 levels of computation.
stable at room temperature (negative $\Delta G^{\text{B}}_{298}$ after anharmonicity correction). All the other dimers are unstable at this temperature according to the computed $\Delta G^{\text{B}}_{298}$ values. This observation is supported by the fact that two less abundant dimers of acetic acid (AA-2 and AA-3) were obtained at very low temperature (below 25 K; *trans-trans* dimers). This $\Delta G^{\text{B}}_{298}$-based observation is similar to those observed earlier\textsuperscript{41} on several weakly hydrogen bonded systems. Several experimental estimates of the dimerization process of acetic acid are available. These were based on the vapor density, thermal conductivity measurements as a function of pressure and gas phase IR spectroscopy. The results are related to the cyclic AA-1 isomer only. The measured $\Delta H^{\text{B}}_{298}$ ranges from 14.1 ± 0.1 kcal mol\(^{-1}\) to 15.3 kcal mol\(^{-1}\),\textsuperscript{44} although the gas-phase dissociation is dependent on the pressure and temperature of the system and could be much higher at the lower ranges of such experimental conditions. The $\Delta G^{\text{B}}_{298}$ for dimerization of acetic acid was estimated recently from the gas-phase infrared spectroscopy, and the magnitude varies from $\sim$17.2 kJ mol\(^{-1}\) (4.1 kcal mol\(^{-1}\)) to $\sim$18.6 kJ mol\(^{-1}\) (4.5 kcal mol\(^{-1}\)).\textsuperscript{22} The estimated dissociation energy ($D_0$) was found to vary from 67.2 kJ mol\(^{-1}\) (16.2 kcal mol\(^{-1}\)) to 69.6 kJ mol\(^{-1}\) (16.6 kcal mol) (Goubet *et al.*, ref. 23). These estimations are not fully experimental (pseudo-experimental), as they combine theoretical data with experimental thermal contribution and are slightly higher than the normal reports. Our estimated binding energies ($\Delta E^{\text{B}}$, $\Delta H^{\text{B}}_{298}$, and $\Delta G^{\text{B}}_{298}$) at the MP2 and DFT/B3LYP levels (with anharmonicity corrections) (Table 1) are close to the experiments reported earlier and the CCSD(T) results also present good estimation of $\Delta E^{\text{B}}$ with respect to these experiments. The binding energies of acetic acid dimers were also computed using G2MP2, G4 and CBS-QB3 techniques (Table 1). The methods use scale factors to compute the zero-point energies and thus indirectly include the anharmonicity effect. The G2MP2 generates binding energies with somewhat lower accuracies with respect to the experiments, while the results of G4 and CBS-QB3 are quite satisfactory. All these energies, computed using high-accuracy techniques, are almost 0.7 to 1 kcal mol\(^{-1}\) off from the results reported by Goubet *et al.*,\textsuperscript{22} but if we take into account the experimental thermal contribution ($\sim$0.7 kcal mol\(^{-1}\)) the computed values are close to those reported.\textsuperscript{24} The isomers AA-2 and AA-3 were detected through Raman spectra,\textsuperscript{25} but no thermodynamic data are available. It is to be noted further that the structure of the isomer AA-6 is supported at the DFT/B3LYP and MP2 levels only.

The calculated high-frequency modes of acetic acid dimers are presented in Table 2 at the MP2 and DFT/B3LYP levels with anharmonicity corrections. The anharmonic vibrations are obtained directly from the optimized geometries using Barone's technique.\textsuperscript{34,35} The vibrational frequencies of monomer subunits in the acetic acid dimer are influenced due to dimerization, and are either red or blue shifted. The anharmonicity corrected vibrational modes of *trans*-acetic acid are presented in Table 2s (ESI\textsuperscript{7}†) along with the available experimental data, and it could be easily seen that the $\nu$(OH), $\nu$(CH\(_3\)), $\nu$(CO), $\delta$(COH)$\sim$$\delta$(CH\(_3\)), $\tau$(CO$\sim$COH def. (deformation), and $\tau$(COH) modes are either red or blue shifted. Earlier papers discussed these features,\textsuperscript{8,23} and predicted that the strongest redshift of $\nu$(OH) ($\sim$−642 cm\(^{-1}\)) could be related to the formation of the most stable (AA-1) dimer. In the present calculations, the $\nu$(OH) presents a similar feature (red-shift: −563 cm\(^{-1}\)).\textsuperscript{24} Recently the high-frequency bands of acetic acid dimers have been investigated using near-infrared (NIR) spectra.\textsuperscript{24} The overtone and combination bands were assigned and were confirmed to originate from an AA-1 cyclic structure. Our present anharmonicity corrected vibrational results are presented in Table 3s (ESI\textsuperscript{7}†) for the AA-1 structure, and are in good agreement with the experiment.\textsuperscript{24}

Most of the computational techniques used to compute binding energies ($\Delta E^{\text{B}}$, $\Delta H^{\text{B}}_{298}$, and $\Delta G^{\text{B}}_{298}$) and vibrational frequencies, as discussed above, include dispersion corrections

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**Table 1** Relative ($\Delta E$) and binding ($\Delta E^{\text{B}}$) energies (including enthalpy ($\Delta H^{\text{B}}_{298}$) and Gibbs free energies ($\Delta G^{\text{B}}_{298}$) of binding) of the various isomers of acetic acid dimers (all in kcal mol\(^{-1}\)).

<table>
<thead>
<tr>
<th>Dimers</th>
<th>Calculation level</th>
<th>$\Delta E$</th>
<th>$\Delta E^{\text{B}}$</th>
<th>$\Delta H^{\text{B}}_{298}$</th>
<th>$\Delta G^{\text{B}}_{298}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA-1</td>
<td>B3LYP</td>
<td>0.0</td>
<td>−14.7</td>
<td>−14.8</td>
<td>−3.8</td>
</tr>
<tr>
<td></td>
<td>MP2</td>
<td>0.0</td>
<td>−14.4\textsuperscript{b}</td>
<td>−14.4</td>
<td>−3.2</td>
</tr>
<tr>
<td></td>
<td>CCSD(T)</td>
<td>0.0</td>
<td>−14.8\textsuperscript{b}</td>
<td>−14.4</td>
<td>−3.3</td>
</tr>
<tr>
<td>AA-2</td>
<td>B3LYP</td>
<td>8.2</td>
<td>−6.7</td>
<td>−6.3</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td>MP2</td>
<td>7.9</td>
<td>−7.8</td>
<td>−7.4</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>CCSD(T)</td>
<td>−</td>
<td>−7.9</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>AA-3</td>
<td>B3LYP</td>
<td>9.8</td>
<td>−5.8</td>
<td>−5.4</td>
<td>3.6</td>
</tr>
<tr>
<td></td>
<td>MP2</td>
<td>9.4</td>
<td>−6.5</td>
<td>−6.2</td>
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</tr>
<tr>
<td></td>
<td>CCSD(T)</td>
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<td>−</td>
<td>−</td>
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<td>−3.8</td>
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<tr>
<td></td>
<td>MP2</td>
<td>11.0</td>
<td>−5.3</td>
<td>−4.8</td>
<td>3.9</td>
</tr>
<tr>
<td></td>
<td>G2MP2</td>
<td>9.9</td>
<td>−3.8</td>
<td>−4.4</td>
<td>3.9</td>
</tr>
<tr>
<td></td>
<td>CBS-QB3</td>
<td>10.1</td>
<td>−4.5</td>
<td>−5.1</td>
<td>4.4</td>
</tr>
<tr>
<td>AA-5</td>
<td>B3LYP</td>
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<td>−2.1</td>
<td>−1.5</td>
<td>6.2</td>
</tr>
<tr>
<td></td>
<td>MP2</td>
<td>13.8</td>
<td>−3.0</td>
<td>−2.4</td>
<td>5.4</td>
</tr>
<tr>
<td></td>
<td>G2MP2</td>
<td>12.3</td>
<td>−1.8</td>
<td>−2.4</td>
<td>4.5</td>
</tr>
<tr>
<td></td>
<td>CBS-QB3</td>
<td>12.6</td>
<td>−1.9</td>
<td>−2.5</td>
<td>4.8</td>
</tr>
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<td>AA-6</td>
<td>B3LYP</td>
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<td>−4.8</td>
<td>−4.3</td>
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<tr>
<td></td>
<td>MP2</td>
<td>10.7</td>
<td>−5.5</td>
<td>−5.0</td>
<td>3.2</td>
</tr>
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</table>

\textsuperscript{a} All the binding energies ($\Delta E^{\text{B}}$, $\Delta H^{\text{B}}_{298}$, and $\Delta G^{\text{B}}_{298}$) are after counterpoise corrections (CP) and inclusion of zero-point energies (ZPE) with anharmonicity corrections. The CP corrections for CBS-QB3 are taken from G4 calculations, as these calculations are unstable during CP correction calculations. Thus there are some error bars in these results.\textsuperscript{b} Results from fully optimized geometry using aug-cc-pVTZ basis sets. Anharmonicity corrections to ZPE (as in note a) above are taken from aug-cc-pVDZ results.\textsuperscript{c} CCSD(T) (aug-cc-pVTZ) results are using optimized MP2/aug-cc-pVDZ geometries with counterpoise corrections together with anharmonicity corrected ZPE (from MP2/aug-cc-pVDZ analysis).

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with the exception of DFT/B3LYP. We have tried several dispersion-corrected techniques viz. empirical GD3 and with B3LYP and M06 functional) and more involved B2PLYPD to estimate the binding energies and anharmonicity-corrected frequencies of the most stable AA-1 isomer after full geometry optimization (using aug-cc-pVDZ basis sets). The results are documented in Table 4s of the ESI.† The binding energies using such techniques (aug-cc-pVTZ basis sets) have increased with respect to the DFT/B3LYP results by 1.0 kcal mol$^{-1}$ (B2PLYPD3) to a maximum 2.0 kcal mol$^{-1}$ (B3LYP-GD3). Such binding energies are closer to those of Goubet et al., but B3LYP-GD3, M06, and M06-GD3 results are a bit overestimated (Table 4s, ESI†). The computed frequencies, of course, do not show any appreciable improvement with respect to those of DFT/B3LYP results. In fact, the frequencies computed at the DFT/B3LYP level show better agreement with the experiment (Table 2). Moreover, the low-frequency vibrations in DFT/M06 and DFT/M06-GD3 calculations are a point of concern due to generation of several imaginary low-frequency modes during anharmonicity corrections. These cause uncertainty in the anharmonicity corrected zero-point energies as well as binding energies (with such corrections).

### 3.2 Acetamide dimers: structural and vibrational properties

The optimized structures of acetamide dimers are shown in Fig. 2. The absence of rotamers (like acetic acid) limits the probable dimers to four. The cyclic form (AMD-1) was characterized through infrared spectra. Although the presence of AMD-2 was predicted initially, the spectroscopic evidence could not resolve its presence. The AMD-3 isomer was not supported in gas-phase spectroscopy, but its presence was predicted from the hydrogen bond motifs of acetamide polymorph (ACEMID06). The last isomer AMD-4 is predicted from the theoretical calculations only. We have optimized all the dimers at the MP2, DFT/B3LYP, G2, G2MP2, G4, and CBS-QB3 levels of computation. The AMD-4 structure is different in these calculations with respect to MP2, and the corresponding hydrogen-bond distances are available in Table 1s of the ESI.†

#### Table 2  Calculated anharmonicity-corrected vibrational frequencies (cm$^{-1}$) of different acetic acid dimers at the MP2 and B3LYP levels of theory (using aug-cc-pVDZ basis sets). The available experimental (Expt.) values are also included in the table for comparison

<table>
<thead>
<tr>
<th>Formic acid dimers</th>
<th>Theory level and Expt. data</th>
<th>$\nu$(OH)</th>
<th>$\nu$(CH$_3$)</th>
<th>$\nu$(C=O)</th>
<th>$\delta$COH + $\delta$CH$_3$</th>
<th>$\nu$CO-δCOH</th>
<th>$r$(COH)</th>
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<tbody>
<tr>
<td>AA-1</td>
<td>MP2</td>
<td>2950, 2806</td>
<td>3065</td>
<td>1708</td>
<td>1347</td>
<td>1293</td>
<td>927</td>
</tr>
<tr>
<td></td>
<td>DFT/B3LYP</td>
<td>2788, 2920</td>
<td>3009</td>
<td>1704</td>
<td>1348</td>
<td>1301</td>
<td>988</td>
</tr>
<tr>
<td></td>
<td>Expt.</td>
<td>2926, 2945</td>
<td>3014</td>
<td>1720</td>
<td>1364</td>
<td>1309 (1290$^a$)</td>
<td>979 (942)</td>
</tr>
<tr>
<td>AA-2</td>
<td>MP2</td>
<td>3537, 3248</td>
<td>3074, 3069</td>
<td>1724, 1708</td>
<td>1321, 1331</td>
<td>1224, 1176</td>
<td>824, 645</td>
</tr>
<tr>
<td></td>
<td>DFT/B3LYP</td>
<td>3537, 3186</td>
<td>3010, 3008</td>
<td>1759, 1724</td>
<td>1326, 1368</td>
<td>1226, 1179</td>
<td>832, 652</td>
</tr>
<tr>
<td></td>
<td>Expt.</td>
<td>3300, 3252</td>
<td>—</td>
<td>1809, 1783</td>
<td>1340, 1370</td>
<td>1247, 1198</td>
<td>847</td>
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<td>AA-3</td>
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<td>3384, 3206</td>
<td>3073, 3070</td>
<td>1766, 1725</td>
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<td>3401, 3192</td>
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<td>1221, 1157</td>
<td>790, 678</td>
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<td>3416</td>
<td>—</td>
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<td>1276, 1214</td>
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<td>1776, 1746</td>
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<td>1212, 1152</td>
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<tr>
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<td>1162, 1165</td>
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<tr>
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<td>1312, 1367</td>
<td>1161, 1164</td>
<td>640$^b$</td>
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<td>3536, 3267</td>
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<td>3016, 3006</td>
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<td>1354, 1364</td>
<td>1195, 1172</td>
<td>808, 642</td>
</tr>
</tbody>
</table>

$^a$ Ref. 8 and 14. $^b$ Doublet.
the hydrogen bonding distances for the DFT/B3LYP/aug-cc-pVDZ, G4, and CBS-QB3-optimized geometries are shown in Table 1s (ESI†). The hydrogen bonds are formed through NH·O, NH·N, or CH·O interactions, of which the CH·O interactions are the weakest. This is reflected in the computed binding energies of the dimers. The relative energy (ΔE) and the anharmonicity-corrected binding energies (ΔE^ah, ΔH^ah, and ΔG^ah) are presented in Table 3. AMD-1 is the most abundant and strongly bound among these dimers. These anharmonicity corrected ZPEs (as discussed in Section 2) were directly included in the MP2 and DFT/B3LYP results for the binding energies using aug-cc-pVTZ basis sets. Anharmonicity corrections to ZPE are taken from aug-cc-pVDZ results. Poise corrections and inclusion of zero-point energies (ZPE) with anharmonicity corrections.

Table 3 shows that they are either red or blue shifted with respect to the monomer frequencies (Table 2s, ESI†). The strongest red-shift of νs(NH2) (~335 cm⁻¹) and νas(NH3) (~56 cm⁻¹) (at the MP2 level) could be related to the formation of the most stable (AMD-1) dimer. These results compare well with the experimental νs(NH2) (~299 cm⁻¹) and νas(NH3) (~37 cm⁻¹) values.† The other spectroscopic data presented in Table 4 compare quite well with the experiment.†

The binding energies and anharmonicity-corrected vibrational frequencies of the most stable AMD-1 isomer, like the AA-1 case, have been further tested at the DFT level using B3LYP-GD3, B2PLYPD3, M06, and M06-GD3 functionals with full geometry optimization (using aug-cc-pVDZ basis sets). The results are documented in Table 5 of the ESI†. The computed binding energies with dispersion corrections show ~1.0 kcal mol⁻¹ (B2PLYPD3) to 2 kcal mol⁻¹ (M06-GD3) increase with respect to the DFT/B3LYP results. These are, of course, some uncertainties in such estimations as M06 and M06-GD3 techniques generate several imaginary low-frequency modes during anharmonicity corrections (Table 5s, ESI†). The high-frequency mode data, on the other hand, do not show any improvements over the DFT/B3LYP results.

3.3 Low-frequency modes of acetic acid and acetamide dimers

The low-frequency modes of the most stable acetic acid dimer (AA-1) were investigated in detail using femtosecond pump-probe spectroscopy and quantum chemical techniques. The Raman-active fundamentals were assigned, which involved the in-plane and out-of-plane bending and stretching vibrations of the hydrogen bonds. It was shown that the anharmonic coupling to three low-frequency modes is responsible for the underdamped coherent oscillations observed in the time-resolved nonlinear O–H stretching absorption. Two strongly coupled modes in-plane (δ(\(\alpha\)) and stretching ν(\(\alpha\)) were identified in this respect. In this section, the results of the investigation of the role of low-frequency modes (coupled to OH stretching mode) on the hydrogen-bond stability of both acetic acid and acetamide are presented. Table 5 contains the computed first eight fundamentals of AA-1. These modes are represented in Fig. 3 separately as IR- (u-symmetry) and Raman-active (g-symmetry) modes (MP2 level, C2hi-symmetry). The lowest fundamental (ν1, A0) was not assigned through experiments. The other seven bands were assigned experimentally and are reproduced in our calculations with reasonable

<table>
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<tr>
<th>Dimers</th>
<th>Calculation level</th>
<th>ΔE</th>
<th>ΔE^ah</th>
<th>ΔH^ah</th>
<th>ΔG^ah</th>
</tr>
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<td>AMD-1 (C2hi)</td>
<td>MP2</td>
<td>0.0</td>
<td>−12.5</td>
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<td>B3LYP</td>
<td>0.0</td>
<td>−12.3</td>
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<td></td>
<td>CCSD(T)</td>
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<td>—</td>
<td>—</td>
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<tr>
<td></td>
<td>G2MP2</td>
<td>0.0</td>
<td>−13.1</td>
<td>−13.3</td>
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<tr>
<td></td>
<td>CBS-QB3</td>
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<tr>
<td>AMD-2 (C1b)</td>
<td>MP2</td>
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<td>B3LYP</td>
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<td>−6.4</td>
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<td></td>
<td>G2MP2</td>
<td>4.5</td>
<td>−7.6</td>
<td>−7.3</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td>CBS-QB3</td>
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<tr>
<td></td>
<td>C2hi</td>
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<td>AMD-3 (C1b)</td>
<td>MP2</td>
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<td></td>
<td>B3LYP</td>
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<td>−4.8</td>
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</tr>
<tr>
<td></td>
<td>G2MP2</td>
<td>5.7</td>
<td>−6.4</td>
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<tr>
<td></td>
<td>CBS-QB3</td>
<td>6.7</td>
<td>−6.5</td>
<td>−6.3</td>
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<tr>
<td></td>
<td>C2hi</td>
<td>6.9</td>
<td>−6.7</td>
<td>−6.6</td>
<td>3.5</td>
</tr>
<tr>
<td>AMD-4 (C1b)</td>
<td>MP2</td>
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<td>−4.7</td>
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<td>B3LYP</td>
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<td>−2.7</td>
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<td>G2MP2</td>
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<td>CBS-QB3</td>
<td>8.7</td>
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<td>C2hi</td>
<td>8.9</td>
<td>−4.7</td>
<td>−4.5</td>
<td>5.7</td>
</tr>
</tbody>
</table>

All the binding energies (ΔE^ah, ΔH^ah, and ΔG^ah) are after counterpoise corrections and inclusion of zero-point energies (ZPE) with anharmonicity corrections. Results from fully optimized geometry using aug-cc-pvtz basis sets. Anharmonicity corrections to ZPE are taken from aug-cc-pVDZ results. Poise corrections together with anharmonicity corrected ZPE (from MP2/aug-cc-pVDZ analysis).
These anharmonicity corrected frequencies are directly computed at the MP2 and DFT/B3LYP levels (aug-cc-pVDZ basis sets) and the extracted \( \nu_\alpha \) values at this level are used to compute the corresponding frequencies for the fully optimized AA-1 and AMD-1 dimers at the MP2/aug-cc-pVTZ and DFT/B3LYP/aug-cc-pVTZ levels. The results presented in Table 5 show that the computed frequencies at both levels are quite similar. These benchmark results show that the low-frequency modes computed using aug-cc-pVDZ basis sets are reliable and could be used for the other dimers for further analysis. Six of the low-frequency modes in Table 5 constitute intermolecular vibrations newly formed upon dimerization of the acetic acid monomers. The table contains also information on the depolarization ratio \( (\rho_i) \) and cubic coupling constant \( (F_{ji})/(F_{jj})^{2.35} \). These F terms are generally defined as:\(^{50}\)

\[
F_{ij} = \frac{\partial^2 V}{\partial \eta_i \partial \eta_j} = \frac{\partial F_{ij}}{\partial \eta_i} = -\frac{\partial^2 f_j}{\partial \eta_i^2},
\]

where \( V \) is the potential energy and \( q \) the normal coordinates around the equilibrium geometry. \( F_{ij} \) is the force constant and \( f_j \) is force (negative of the gradient) acting along the \( j \)th coordinate. These cubic coupling constants constitute the main contribution of the off-diagonal anharmonic couplings in the vibrational Hamiltonian, and thus give a measure of the mode-specific strength.

### Table 4

<table>
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<tr>
<th>AMD</th>
<th>Theory level and Expt. data</th>
<th>( \nu_{\alpha}(\text{NH}_3) )</th>
<th>( \nu_{\beta}(\text{NH}_3) )</th>
<th>( \nu_{\alpha}(\text{CH}_3) )</th>
<th>( \nu_{\beta}(\text{CH}_3) )</th>
<th>( \nu(\text{C}=\text{O}) )</th>
<th>( \delta(\text{NH}_2) )</th>
<th>( \text{rNH}_2\text{-imp} )</th>
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<tr>
<td>AMD-1</td>
<td>MP2</td>
<td>3530</td>
<td>3014</td>
<td>3030</td>
<td>2958</td>
<td>1697</td>
<td>1578</td>
<td>822</td>
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<td>DFT/B3LYP</td>
<td>3491</td>
<td>3062</td>
<td>2968</td>
<td>2920</td>
<td>1685</td>
<td>1596</td>
<td>854</td>
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<td>Expt.</td>
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<td>3149, 3140 (^{6})</td>
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<td>2970</td>
<td>1694</td>
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<td>MP2</td>
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<td>3414, 3149</td>
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<td>1576, 1553</td>
<td>637, 636</td>
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</table>

\(^{5}\) Ref. 18 and 44. \(^{6}\) \( \nu_\alpha \) and \( \nu_\beta \), respectively, represent the asymmetric and symmetric stretching modes. \(^{5}\) Ar-matrix data, ref. 18.

### Table 5

<table>
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<tr>
<th>MODES</th>
<th>CALC.</th>
<th>MP2</th>
<th>DFT/B3LYP</th>
<th>EXPT.</th>
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<th>MP2 (B3LYP)</th>
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<td>( \nu_1 )</td>
<td>( \nu_2 )</td>
<td>( \nu_3 )</td>
<td>( \nu_4 )</td>
<td>( \nu_5 )</td>
<td>( \nu_6 )</td>
<td>( \nu_7 )</td>
<td>( \nu_8 )</td>
</tr>
<tr>
<td>AA-1</td>
<td>(C(_{2h}))</td>
<td>44 (44)</td>
<td>45 (45)</td>
<td>43 (42)</td>
<td>---</td>
<td>---</td>
<td>0.75 (0.75)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>59 (53)</td>
<td>60 (54)</td>
<td>54 (49)</td>
<td>---</td>
<td>72.5</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>69 (63)</td>
<td>65 (59)</td>
<td>73 (67)</td>
<td>76 (70)</td>
<td>56</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td></td>
<td>74 (73)</td>
<td>66 (65)</td>
<td>80 (78)</td>
<td>62 (60)</td>
<td>50</td>
<td>0.75 (0.75)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>87 (83)</td>
<td>93 (91)</td>
<td>84 (81)</td>
<td>103 (101)</td>
<td>99</td>
<td>0.75 (0.75)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>120 (123)</td>
<td>114 (112)</td>
<td>128 (123)</td>
<td>106 (101)</td>
<td>99</td>
<td>0.75 (0.75)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>127 (127)</td>
<td>130 (130)</td>
<td>125 (125)</td>
<td>112 (112)</td>
<td>99</td>
<td>0.75 (0.75)</td>
</tr>
<tr>
<td></td>
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<td>179 (183)</td>
<td>173 (177)</td>
<td>183 (182)</td>
<td>176 (174)</td>
<td>170</td>
<td>0.75 (0.75)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>181 (184)</td>
<td>169 (172)</td>
<td>186 (184)</td>
<td>173 (171)</td>
<td>163</td>
<td>0.75 (0.75)</td>
</tr>
</tbody>
</table>

AMD-1 | (C\(_{2h}\)) | 23 | --- | 27 | --- | 0.75 (0.75) | --- | 105 (105) |
|       | 33 | 24 | 24 | (0.75) | 105 (105) | 43 (8) | (0.75) | 105 (105) |
|       | 38 (55) | 24 (41) | 45 (46) | 101 (102) | --- | --- | (0.75) | 105 (105) |
|       | 78 (82) | 78 (82) | 85 (83) | 125 (122) | --- | --- | (0.75) | 105 (105) |
|       | 96 (92) | 84 (81) | 100 (93) | 119 (112) | --- | --- | (0.75) | 105 (105) |
|       | 130 (128) | 125 (123) | 140 (137) | 131 (128) | 125 (122) | 0.75 (0.75) | 105 (105) | 105 (105) |
|       | 155 (157) | 145 (147) | 152 (149) | 147 (143) | --- | --- | (0.75) | 105 (105) |
|       | 157 (159) | 144 (146) | 155 (152) | 132 (129) | --- | --- | (0.75) | 105 (105) |

\(^{a}\) The computed low-frequency modes using aug-cc-pVTZ basis sets are presented within parentheses. See the text for details. \(^{b}\) Ref. 8. \(^{c}\) The coupling constants are computed using \( i = \text{Raman-active} \) \( \nu(\text{OH}) \) (2806 cm\(^{-1}\))/\( \nu(\text{NH}) \) (3036 cm\(^{-1}\)).
of anharmonic coupling between the high- and low-frequency modes. The results in Table 5 show that the Raman bands couple strongly with the \( \nu_{\text{OH}} \) (2950 cm\(^{-1}\), B\(_3\)). The IR-active modes (except \( \nu_2 \)) show coupling through \( F_{ij}^2 \) terms. The \( \nu_2 \) term actually shows moderate coupling when \( \nu_{\text{OH}} \) is the Raman-active mode (2806 cm\(^{-1}\), A\(_2\)).

The lowest energy aceticamide dimer (AMD-1, C\(_{2h}\) symmetry) is structurally very similar to AA-1 with very close binding energies. The low-frequency vibrations of AMD-1 are compared with those of AA-1 in Table 5 and six low-frequency fundamentals (at the MP2 level) are presented in Fig. 4 (indicating the IR- and Raman-active modes). We have omitted the two lowest frequency modes as they involve methyl wagging and are not of much interest to us. The displacement vectors of these fundamentals (Fig. 4) are similar to those of AA-1 (Fig. 3). The magnitudes of these frequencies are of course lower due to the difference of the nature of the atoms involved in hydrogen-bonding interactions. We have further computed the various low-frequency modes of other acetic acid (AA-2 to AA-6) and acetamide (AMD-2 to AMD-4) dimers to understand their roles to control the strength of the hydrogen-bonds in the respective dimers. There are, at present, no experimental data on the low-frequency modes of these isomers.

### 3.4 Binding energies versus the contributing high- and low-frequency modes

The local properties of hydrogen-bonded dimers could be obtained from their vibrational spectra. Usually the \(-\text{OH or } -\text{NH}_2\) stretching bands in dimers show substantial red-shift with respect to their corresponding monomers and the intensity \( (I, \text{km mole}^{-1}) \) of such modes are also highly enhanced. For example, the computed intensities of \( \nu(\text{OH}) \) \( (\nu = 2950 \text{ cm}^{-1}, I = 3437) \) and \( \nu(CO) \) \( (\nu = 1708 \text{ cm}^{-1}, I = 695) \) of the AA-1 isomer show a huge enhancement with respect to the corresponding frequencies of trans-acetic acid \( (\nu(\text{OH}) = 3543 \text{ cm}^{-1} (I = 70); \nu(CO) = 1764 \text{ cm}^{-1} (I = 280)) \). The case is similar for the acetamide dimer (AMD-1) also \( (\nu(\text{NH}_2) = 3104 \text{ cm}^{-1} (I = 1789), \Delta \nu(\text{NH}_2) = 70) \). These results are also comparable with the previously computed values.\(^{18,23}\) These modes are thus considered as marker bands (fingerprint) for such types of dimers.\(^{20,27}\) Furthermore, experimental results, in these contexts, showed that the anharmonic coupling of the high-frequency stretching modes of such groups to the low-frequency inter-dimer stretch and twist modes has a direct influence on the hydrogen bonding.\(^{20,22}\)

Such a view was actually supported through experiments on the low-frequency mode analysis of the most stable acetic acid dimer (AA-1).\(^{22}\) Several interesting features are revealed from the computed vibrational characteristics of the various acetic acid and acetamide dimers. A regular decrease of the intensities of the \( \nu(\text{OH}) \) and \( \nu(\text{NH}_2) \) modes (Table 6s, ESI\(^{\ddagger}\)) of acetic acid and acetamide dimers is observed with respect to their binding energies \( (\Delta E^\text{b}) \). Such intensities are linearly correlated with the respective \( \Delta E^\text{HR} \) and \( \nu(\text{NH}_2) \) modes are known to be responsible for hydrogen-bond formation in the respective cases and the corresponding intensities are approximately proportional to the force involved in such bond formation. In the case of AMD-4 (Fig. 2 and Table 3) the NH\(_2\) group is not involved in hydrogen-bonding, but the linear correlation is still observed (Fig. 5B), as the \( \Delta E^\text{HR} \) also represents \( \Delta E^\text{b} \) of such dimers.
There are eight fundamentals of AA-1 (Fig. 3), which could be considered for similar correlation through low-frequency mode analysis. The in-plane-bending or stretch-bend (in-plane) modes of AA-1, viz. the Raman-active $\nu_6$ and $\nu_8$ (Ag, Fig. 3g and h) and the IR-active $\nu_7$ (Bu, Fig. 3d) modes, only show importance in hydrogen bonding. Although the Raman-active modes show strong coupling with $\nu_{OH}$, they have very low intensities. The $\nu_7$ mode shows moderately strong coupling and has quite large intensity. Similar modes for the other dimers (AA-2 to AA-6) also show a regular change of intensity (Fig. 1s, ESI†) with respect to their binding strengths. The $\nu_7$ mode of AMD-1 (Bu, Fig. 4c) was used for correlation with $\Delta E^B$ from similar consideration and the related modes of the other isomers are shown in Fig. 1s (ESI†). Fig. 5C and D show that the intensities of such modes correlate linearly with the respective $\Delta E^B$ values of the acetic acid and acetamide dimers.

The linear correlations of $\Delta E^B$ with the IR intensities as shown above are quite normal in such weak interactions. It is generally known that the IR intensity of the $k$th mode of a molecular system is proportional to the square of the dipole derivative $\partial \mu / \partial Q_k$ ($\mu$ dipole moment, $Q_k$ normal coordinate of the $k$th mode). It has been shown earlier that in hydrogen bonded dimer or simple cation–π interactions, the term $\partial \mu / \partial Q_k$ could be related to the charge flux from the donor to the acceptor systems, and this charge flux is linearly related to the $\Delta E^B$. Thus from the definition of IR intensity, it could be inferred that for a specific vibrational mode (responsible for the said weak interactions in the dimer) the corresponding intensity for a series of related isomers should be linearly correlated with their $\Delta E^B$.

The $\Delta E^B$ of the trans-trans acetic acid (AA-1 to AA-6) and acetamide (AMD-1 to AMD-3) dimers are the same as their...
$\Delta E^{HB}$ values (with the exception of AMD-4). The correlations in Fig. 5 thus clearly show the involvement of the specific low-frequency modes (together with the high frequency $\nu(OH)/\nu(NH_2)$ modes) in the binding strengths of such dimers. Furthermore, the low-frequency modes (involved in correlations of the lowest energy dimers) of both acetic acid and acetamide are similar, and are responsible for the similar relative stabilities of these two dimers.

3.5 The empirical additive relation of $\Delta E^B$

We have observed previously in the case of formic acid and formamide dimers,\textsuperscript{27} that linear dependence of the intensities of both high- and low-frequency modes with their $\Delta E^B$ led to an additivity relation of binding energies amongst the dimers from the transferable local character of the individual hydrogen-bonding fragments. We can extend such an idea to the cases of acetic acid and acetamide dimers also. The additive properties are important in chemistry to explain many structural and chemical properties like parachor,\textsuperscript{53} Lewis acidity with respect to the fluorine positions of tris-(fluorophenyl)-substituted boranes,\textsuperscript{54} chemical element properties of binary zinc compounds,\textsuperscript{55} and electron localization properties of hydrogen bonded compounds.\textsuperscript{56} In several cases, these additive properties also have predictive capabilities (e.g. parachor).

These additivity relations could be obtained from the analysis of the local hydrogen-bonding/binding energies ($E_{X \cdot Y}$, where, X and Y are the atoms or the groups involved in hydrogen-bonding) of the fragments involved. Let us first consider the case of acetic acid dimers, where these fragments are OH···O, CH···O, OH···O(H), and CH···O(H) (the hydrogen within parentheses belongs to the OH group not involved in hydrogen-bonding) (Fig. 1). The local binding energies could be obtained from the individual $\Delta E^B$ of the dimers from Table 1. In the present context, $\Delta E^B$ at the MP2 level is only being considered. The dimers AA-1 and AA-5 have a double hydrogen-bond through OH···O and CH···O fragments, respectively, and thus from their respective $\Delta E^B$s (Table 1) the $E_{CH \cdot O}$ and $E_{OH \cdot O}$ turn out to be $-7.2$ and $-1.5$ kcal mol$^{-1}$. The energies of the OH···O(H) ($E_{OH \cdot O(H)}$) fragment could be obtained from the AA-4 dimer considering the following relation of binding energies.

$$E_{CH \cdot O} + E_{OH \cdot O(H)} = \Delta E^B(AA-4).$$  \hspace{1cm} (4)

Using the calculated $E_{CH \cdot O}$, the value for $E_{OH \cdot O(H)}$ turns out to be $-3.8$ kcal mol$^{-1}$. The dimer AA-3 represents a special hydrogen bonding, where the O–H center of one monomer fragment is bound to O (O–H···O) and O–H (H–O···H–O) centers of the second fragment (Fig. 1). The O–H···O fragment is similar to the OH···O(H) fragment of AA-4 (from consideration of hydrogen-bond distance), and the O–H···O fragment is quite different from the case of AA-1 in the same respect. We denote it as OH···O. The $\Delta E^B$ of AA-3 could thus be written in terms of the fragment energies as:

$$E_{OH \cdot O} + E_{OH \cdot O(H)} = \Delta E^B(AA-3).$$  \hspace{1cm} (5)

The $E_{OH \cdot O}$, thus, turns out to be $-4.00$ kcal mol$^{-1}$. These calculated $E_{X \cdot Y}$ values lead to the binding energies of other acetic acid dimers as:

Dimer AA-2:

$$E_{AA-2} = E_{CH \cdot O} + E_{OH \cdot O} = -8.7 \text{ kcal mol}^{-1}.$$

Dimer AA-6:

$$E_{AA-6} = E_{CH \cdot O} + E_{OH \cdot O} = -5.5 \text{ kcal mol}^{-1}.$$

The estimated $\Delta E^B$ of AA-2 (on the right hand side) using transferable additive fragment terms is within $\sim 1.0$ kcal mol$^{-1}$ of the computed value (Table 1) whereas it is almost the same for AA-6. The average errors in such cases with respect to the computed results in Table 1 are quite normal, as the hydrogen-bond lengths (which control the $\Delta E^B$ in different dimers) are different in the dimers, and are not taken into account. The results thus vindicated the existence of an empirical additive relation as proposed above.

The transferable local fragments for hydrogen-bonds of the acetamide dimers (Fig. 2) are NH···O and CH···O. The $E_{NH \cdot O}$ and $E_{CH \cdot O}$ could be obtained from the $\Delta E^B$s of AMD-1 and AMD-4 dimers (Table 3) at the MP2 level; but these results do not lead to any reasonable additive property, as AMD-4 does not show any direct bonding. There are no hydrogen-bond interactions as such; the dimer instead is formed through multi-center non-bonded interactions.

The B3LYP results for these dimers are more reasonable in this respect, as the predicted AMD-4 structure could be used to compute the CH···O fragment energy. Thus using $\Delta E^B$s of AMD-1 and AMD-4, the respective $E_{NH \cdot O}$ and $E_{CH \cdot O}$ turn out to be $-6.3$ and $-1.3$ kcal mol$^{-1}$. The binding energies of the dimers AMD-2 and AMD-3 ($E_{FMAD-B}$ and $E_{FMAD-D}$) could be computed using the following additive relations.

Dimer AMD-2:

$$E_{AMD-2} = E_{NH \cdot O} + E_{CH \cdot O} = -7.5 \text{ kcal mol}^{-1}.$$

Dimer AMD-2:

$$E_{AMD-3} = E_{NH \cdot O} = -6.2 \text{ kcal mol}^{-1}.$$

The $\Delta E^B$ values, thus computed, are within 1.0 kcal mol$^{-1}$ of the respective dimers (Table 3). It could be further inferred from the linear correlations in Fig. 5, that the intensities of the frequencies involved in such correlation should also show similar additive properties.

There is another important aspect of such $\Delta E^B$ plots of acetic acid and acetamide dimers. If the $\Delta E^B$ values of the trans–trans dimers of formic acid\textsuperscript{22} are plotted together with those of acetic acid dimers against their respective IR intensities of $\nu_{OH}$ vibrations, they are linearly correlated. Acetamide and formamide dimers\textsuperscript{22} also show similar features. This is shown in the ESI† (Fig. 2s) using the MP2 and G4 level of data. The low-frequency modes of these dimers also showed similar features ($R = 0.85$ (MP2) for formic acid and acetic acid dimers; $R = 0.89$ (MP2) for formamide and acetamide dimers). The results indicate that the additive properties of the fragments are not
two \(-\text{CH}_3\) (MP2/aug-cc-pvTZ level. This amounts to the fragment energy of 
\(D\) having similar di-hydrogen-bond structures like AA-1) from the 

\(\Delta E^B = \Delta E^B(\text{AA-1}) + 2E_{\text{CH}_3} = -15.4 \text{ kcal mol}^{-1}\).

\(n\)-Butyric acid dimer:

\(\Delta E^B = \Delta E^B(\text{AA-1}) + 3E_{\text{CH}_3} = -16.0 \text{ kcal mol}^{-1}\).

The experimental dissociation energies of propionic acid and 
\(n\)-butyric acid dimers are 15.2 ± 0.2 and 17.2 ± 0.8 kcal mol\(^{-1}\) 
respectively.\(^{44}\) The results show the validity of our conjecture 
regarding the empirical additive properties proposed here 
based on acetic acid dimers. Similar results could be computed 
from formamide and acetamide dimers, but we abstain from 
predicting such properties in the absence of any experimental/
theoretical results.

The validity of the correlations and the additive properties 
discussed above depends on the accuracy of the computed 
binding energies and the vibrational frequencies. It has been 
already shown in Section 3 that the computed binding energies 
and anharmonicity corrected vibrational frequencies reproduce 
the experimental data quite satisfactorily. Moreover, the plots 
of the computed \(\Delta E^B\) values of acetic acid and acetamide 
dimers (Tables 1 and 3) at the G4, G2MP2, and CBS-QB3 levels 
against the intensities of their respective hydrogen-bond 
fundamentals show similar linear correlations (Fig. 6 and 
Fig. 3s, ESI\(^\dagger\)), as observed in Fig. 5. These results show that 
the correlations and additivity of binding energies, as observed 
from our results, are fully rational and unique for such dimers.

4. Conclusions

The structures of six acetic acid and four acetamide dimers 
were optimized at the MP2 and DFT/B3LYP levels of theory to 
compute their binding energies and the nature of low- and 
high-frequency vibrational modes. The binding energies and 
the vibrational modes were corrected for the anharmonicity 
effects. Such corrections improve the computed vibrational 
frequencies substantially, and agree with the experimental 
results very well. Although, the improvements of binding 
energies (\(\Delta E^B, \Delta H^B_{298}, \text{ and } \Delta G^B_{298}\)) are marginal (∼0.23 to 
0.36 kcal mol\(^{-1}\) change) through anharmonicity corrections, 
such improvements turn out to be quite important where the 
thermochemistry regarding the relative stability (\(\Delta G^B_{298}\)) 
of different dimers is concerned. The experimental binding energies 
of acetic acid dimers is so far limited to AA-1 only, and our results 
show good agreement with experiments in this context. The other 
high-accuracy energy computation techniques (\(\text{viz. G4, G2MP2,}
\text{ and CBS-QB3}\)) also reproduce the experimental data quite 
satisfactorily.

The analyses of low- and high-frequency modes have been 
进一步 extended to other acetic acid (AA-2 to AA-6; Fig. 1) and 
acetamide (AMD-1 to AMD-4; Fig. 2) dimers. The nature of the 
six low-frequency fundamentals is very similar to both AA-1 and 
AMD-1 dimers (\(C_{3v}\)-symmetry). The low-frequency in-plane 
bending and stretch-bend fundamentals of different acetic 
acid and acetamide dimers (depending on the dimer structure),

restricted to the dimers of a particular group of such acids or 
amides, but could be extended to the other homologues also, 
provided they have similar hydrogen bonding features. For 
example, the difference of \(\Delta E^B\) of the most stable acetic 
acid (AA-1, \(\Delta E^B_{\text{B}} = -14.4 \text{ kcal mol}^{-1}\), Table 1) and formic acid (TT-1, 
\(\Delta E^B = -13.4 \text{ kcal mol}^{-1}\), ref. 27) dimer is −1.00 \text{ kcal mol}^{-1} \text{ at the} 
MP2/aug-cc-pvTZ level. This amounts to the fragment energy of 
two \(-\text{CH}_3\) \((E_{\text{CH}_3})\) groups, since the rest of the two dimers is 
similar. If we approximate the fragment energies of ethyl 
\((-\text{C}_2\text{H}_5\)) and propyl \((-\text{C}_3\text{H}_7\)) groups as fragment energies of 
two and three \(-\text{CH}_3\) groups, respectively,\(^{57}\) we can get the \(\Delta E^B\)’s 
of propionic and \(n\)-butyric acid dimers (as they are predicted to 
have similar di-hydrogen-bond structures like AA-1) from the 
following relations.

\(\text{Propionic acid dimer:}\)

\(\Delta E^B = \Delta E^B(\text{AA-1}) + 2E_{\text{CH}_3} = -15.4 \text{ kcal mol}^{-1}.\)

\(\text{\(n\)-Butyric acid dimer:}\)

\(\Delta E^B = \Delta E^B(\text{AA-1}) + 3E_{\text{CH}_3} = -16.0 \text{ kcal mol}^{-1}.\)
in particular, show coupling with the high-frequency $\nu_{OH}$ and $\nu_{NH}$ modes and hence influence the strength of the hydrogen-bond and relative stability order as well. This observation is substantiated from the previous experiments\textsuperscript{22,58,59} on the low-frequency mode analysis of weakly interacting dimers.

An additive nature of the binding energies of these dimers with respect to the local hydrogen-bond related fragment energies has been proposed from our computed $\Delta E_{\text{A}}$. The basis of this additive property lies in the existence of the linear correlation properties, as discussed. This additive nature of binding energies seems quite natural for such dimers, and shows some predictive nature on binding energies in a homologous series as well. Further systematic studies on similar systems are needed to generate transferable fragment parameters for proper understanding of such additive properties.

Conflicts of interest
There are no conflicts to declare.

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Notes and references
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57 This approximation is based on the idea that the positive inductive effect (+I) of the alkyl group series is in the order \( n-C_{n}H_{2n+1} > C_{2}H_{5} > CH_{3} \).