Hydrogen bonding with a hydrogen bond: The methane–water complex and the penta-coordinate carbon

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**Abstract**

Ab initio and atoms in molecules (AIM) theoretical studies have been used to show that in a 1:1 complex formed between CH₄ and H₂O, CH₄ acting as a hydrogen bond acceptor leads to the global minimum structure. There is a bond path connecting C to the H of H₂O revealing a penta-coordinate carbon that could be the precursor to the CH₅⁺. It appears to be a general feature in CH₄–HX complexes (X = F, Cl, and SH). It is in agreement with the experimental structure for analogous complexes and also the C₂H₆⁻ · HF/HCN complexes, suggesting that it is also a general feature for hydrocarbon–HX interaction.

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1. Introduction

The title of this manuscript draws from the title of a recently published article ‘Chemical bonding without chemical bonds’ [1]. In this work, the Authors discussed the intra-molecular interactions in iron trimethylenemethane complex and pointed out that contrary to chemical wisdom, a bond path was not found connecting the metal atom to the three methylene carbons. The ‘chemical wisdom’ was that the three methylene carbons were ‘bonded’ to the Fe atom as a triply coordinating ligand. Atoms in molecules [2] theoretical calculations, however, revealed that there were no bond paths connecting the three methylene carbons to the Fe which according to this theory implied that there are no ‘chemical bonds’ between them leading to the title as given above. The central carbon, however, was connected to the Fe through a bond path. In the current manuscript, we discuss the hydrogen bonding in CH₄···H₂O and analogous complexes. Results from microwave spectroscopic experiments showed that the structure of this complex has the H from water pointing towards a tetrahedron plane in CH₄ [3]. This was in agreement with a thorough theoretical study [4], published in the previous year, finding this geometry to be the global minimum. This work also revealed that a structure having C–H···O hydrogen bonding is a local minimum in the intermolecular potential energy hyper-surface.

Hydrogen bonding in CH₄···H₂O complex has attracted a lot of theoretical attention [4–11]. Except for Ref. [4], many of the other papers published before and after, discussed only the C–H···O interactions in this complex. The AIM theoretical calculations on CH₄···H₂O complex were reported earlier, revealing a bond path connecting H from CH₄ to the O and a characteristic (3,–1) bond critical point between these two atoms as expected [11]. However, this work did not consider the global minimum geometry and concentrated on the C–H···O hydrogen bond, no wonder influenced by the increasing attention devoted to this weak, nevertheless important interaction [12]. What is the nature of the interaction or bonding in the experimentally observed structure, which is found to be the global minimum theoretically? Similar structures have been observed experimentally for several other CH₄···HX (X = F, Br, Cl, and CN) complexes, in which H of HX is pointing towards the centre of a tetrahedral face of methane, represented here as X–H···Δ (triangle symbol represents one of the tetrahedron faces of CH₄) [13–17]. Evidently, the interaction is similar in all these complexes and one can see that all the HX referred above are typical hydrogen bond donors. These spectroscopic studies, however, could not establish whether there is a ‘bond’ between C of CH₄ and H of HX.

A structure in which O–H points towards a tetrahedron plane of CH₄ could be interpreted as the result of close packing as the approach towards a corner or an edge of the tetrahedron would lead to relatively larger intermolecular distances. Moreover, such close approach can lead to better stabilization, when dispersive (van der Waals?) forces dominate the interaction. Indeed, Szczepańiak et al. concluded that inclusion of dispersion is important in determining the global minimum of CH₄–H₂O complex [4]. However, they pointed out categorically that ‘although the dispersion energy determines the overall trend in the stabilities, it is important to stress that none of the single components of the interaction energy is capable of a qualitatively correct description of the anisotropy (in the intermolecular potential)’ [Emphasis and words in parenthesis ours]. Anisotropy (directionality) is generally thought to be the defining feature of hydrogen bonding compared to the more general ‘van der Waals interactions’ between molecules.

The CH₄–HX complexes are important as they can give some insight about the CH₅⁺, which has proven to be a very difficult ion to...
The electron rich regions include the traditional lone pairs in H2O within the same or with another atom/molecule. Examples for tive interaction between an electron-deficient hydrogen atom al- electron density. Ref. [22] defined the hydrogen bond as 'an attrac- hydrogendeinition as 'an intermediate range intermolecular interac- acceptor atom from Ref. [23].

Hydrogen bonds have been around for a long time and their study, both experimentally and theoretically. The detailed analysis of the structure of (CH4)+ is somewhat intriguing and all the evidence indicate that the global minimum can be viewed as a CH4+ tripod with a H2 moiety attached to the carbon in an eclipsed C configuration [18–20]. Both H2O and NH3 have lone pairs which can not only accept hydrogen bonds but also a proton to form H3O+ and NH4+, respectively. Evidently, CH4 does not have a lone pair to accept a hydrogen bond or a proton. Our understanding about hydrogen bonding has evolved over the last century and it has been well established now that any electron rich region can act as a hydrogen bond acceptor [21,22]. Ref. [21] defined the hydrogen bond as 'an intermediate range intermolecular interaction between an electron-deficient hydrogen and a region of high electron density'. Ref. [22] defined the hydrogen bond as 'an attractive interaction between an electron-deficient hydrogen atom already bonded to one atom and an electron rich region either within the same or with another atom/molecule'. Examples for the electron rich regions include the traditional lone pairs in H2O and NH3 [23], π electrons in C2H4 [24], σ electrons in H2 [25], and even an unpaired electron in CH2 radical [26,27]. Where is the electron rich region in CH4? Analysis of the molecular electrostatic potential can help in identifying the site of an electrophilic attack, in this case the approach of H from the donor [28,29]. A look at the electrostatic potential of CH4 clearly identifies the centre of each of the four tetrahedron faces as regions of high electron density (see Fig. 1). Clearly, the hydrogen bond donors such as H2O would have their hydrogen atom approaching this region to form the 'hydrogen bond'.

Atoms in molecules theory has proved to be quite useful in understanding bonding [2]. Koch and Popelier have come up with a set of criteria to characterize interactions involving hydrogen as hydrogen bonding or van der Waals interaction and they have been extensively used [30,31]. Such an analysis on structures corres- panding to both minima i.e. C–H–O and O–H–X, would be quite useful and it is reported in this Letter for CH4·H2O (X = F, Cl, OH, and SH) complexes. Interestingly, a bond critical point is observed in all these complexes connecting the C of CH4 to the H of HX. The bond path goes from H of HX through the tetrahedral plane formed by the three H atoms of methane and connects to the cen- tral C atom. This is similar to what was found in Ref. [1] between the central C atom and the Fe atom through a plane formed by three C atoms!

### 2. Computational details

Ab initio molecular orbital and AIM theoretical studies have been carried out to gain more insight about both C–H–X and O–H–X interactions. Geometry optimization has been carried out at a reasonably higher level calculation i.e. MP2(FULL)/aug-cc-pVTZ level using the commercial Gaussian03 software [32]. Frequency calculations at the same level were done to calculate the frequency shifts on complex formation as well as to ensure that the optimized geometries are true minima. Single point energies at CCSD(T)/aug-cc-pVTZ level were calculated with the optimized geometries in order to get more accurate values of interaction energies. Four systems were chosen for our study involving CH4 interaction with HF, HCl, H2O, and H2S, and both C–H–X and X–H–X geometries were considered. The interaction energies were corrected for basis set superposition error using the counterpoise method [33]. Wave function for the optimized geometry is generated using the key words OUPUT = WFN, DENSITY = CURRENT and SCF = TIGHT in Gaussian03. The AIM (atoms in molecules) calculations were done using the Am1 2000 software [34]. Non-bonded ra- dii of acceptor atom and interacting 'H' atom were calculated using MOPAC98 [35,36] program.

### 3. Results and discussion

Table 1 lists the interaction energy, the H–A bond distance, the X–H–A bond angle (A is the H-bond acceptor atom), the increase in bond length of X–H in the complex compared to the monomer and the vibrational frequency shift in X–H mode following complex formation for both X–H–X and C–H–X minima. All these results are from MP2/aug-cc-pVTZ level calculations. The single point interaction energies calculated at CCSD(T)/aug-cc-pVTZ are also reported in the Table. These are the traditional parameters that were considered for inferring a hydrogen bond [23,24]. In all four complexes investigated, the X–H–X geometry has a larger complexa- tion energy compared to C–H–X geometry. The results from the single point CCSD(T) calculations predict the binding energies to be uniformly lower than those from MP2 calculations but do not change the general trend or even the quantitative difference between the two structures for the same complex. All X–H–X geometries have stabilization energy more than 4 kJ mol⁻¹ and the C–H–X geometries have it less than 4 kJ mol⁻¹. The difference between the two geometries is higher for CH4–HF/HCl complexes (~6.0 kJ mol⁻¹) compared to CH4–H2O/H2S complexes (~2.0 kJ mol⁻¹).

<table>
<thead>
<tr>
<th>Complex</th>
<th>ΔE MP2</th>
<th>ΔE CCSD(T)</th>
<th>Rm,A</th>
<th>ΔXHA</th>
<th>ΔRm,X</th>
<th>Δν</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2O/HF</td>
<td>−8.8</td>
<td>−7.9</td>
<td>2.269 (2.20/2.90)</td>
<td>179.5</td>
<td>0.002</td>
<td>60.2</td>
</tr>
<tr>
<td>H2O/HCl</td>
<td>−5.6</td>
<td>−5.0</td>
<td>2.388 (2.47/2.90)</td>
<td>178.7</td>
<td>0.002</td>
<td>17.2</td>
</tr>
<tr>
<td>H2O/H2S</td>
<td>−6.3</td>
<td>−5.0</td>
<td>2.491 (2.47/2.90)</td>
<td>176.0</td>
<td>0.000</td>
<td>13.8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Complex</th>
<th>ΔE MP2</th>
<th>ΔE CCSD(T)</th>
<th>Rm,A</th>
<th>ΔXHA</th>
<th>ΔRm,X</th>
<th>Δν</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2O/HF</td>
<td>−2.9</td>
<td>−2.2</td>
<td>2.520 (2.43/2.55)</td>
<td>179.3</td>
<td>0.001</td>
<td>11.5</td>
</tr>
<tr>
<td>H2O/HCl</td>
<td>−3.3</td>
<td>−3.3</td>
<td>2.530 (2.87/3.00)</td>
<td>179.4</td>
<td>0.000</td>
<td>5.8</td>
</tr>
<tr>
<td>H2O/H2S</td>
<td>−5.4</td>
<td>−5.4</td>
<td>2.542 (2.47/2.60)</td>
<td>179.3</td>
<td>0.001</td>
<td>8.3</td>
</tr>
<tr>
<td>H2O/H2S</td>
<td>−5.4</td>
<td>−5.4</td>
<td>3.025 (2.90/3.05)</td>
<td>178.2</td>
<td>0.000</td>
<td>0.6</td>
</tr>
</tbody>
</table>

*Numbers in parentheses are the sums of hydrogen bond radii defined for the corresponding complexes (Ref. [22]) followed by the sums of van der Waals radii of H and the acceptor atom from Ref. [23].
All complexes have ‘linear H bonds’ with X–H•••A angle close to 180°. The values vary from 176.0° for H₂C–H₂O to 179.5° for HCl–HF. The H–A distances in all these complexes, R₂Hₐ, listed in Table 1 highlight something important about the hydrogen bond distances. These are compared to the sum of van der Waals radii [23] of H and A atoms and also the sum of the recently recommended hydrogen bond radii [22] for H and A atoms. The reader is referred to Ref. [22] for the details of the hydrogen bond radii and these are defined for strong, medium and weak hydrogen bonds. The most striking observation is that the R₂Hₐ distances are significantly smaller than the sum of van der Waals radii for X–H•••A structures but only marginally smaller for the C–H•••X structures. These distances are within 0.1 Å from the sum of the hydrogen bond radii recommended for these atoms. More importantly, for all the four X–H•••X structures, the R₂X is very close to the sum of hydrogen bond radii for H and C and in two cases (HCl and H₂S) it is less than the sum of hydrogen bond radii. However, all the four C–H•••X structures have R₂X slightly larger than the sum of hydrogen bond radii of H and A, but within about 0.1 Å, typical uncertainty in these radii. In other words, the X–H•••X structures have shorter than average H–A distances and the C–H•••X structures have longer than average H–A distances. All the X–H•••A geometries show red-shift in X–H frequencies and the C–H•••X geometries show small blue shift in C–H stretching frequency and these are well established [24,37] for similar hydrogen bonded complexes. Clearly, all the traditional criteria employed for identifying a hydrogen bond suggest that the X–H•••A structures qualify better as hydrogen bonds than the C–H•••X structures.

Let us now turn our attention to the results from AIM theoretical calculations which are quite revealing. The most important observation is that all eight complexes show a (3,–1) bond critical point along a bond path corresponding to X–H•••A and C–H•••X interactions. Interestingly, for the X–H•••A geometry the bond critical point (BCP) connects the C from CH₄ to H from HX through a bond path (see Fig. 1) and from now on it will be referred to as X–H•••C hydrogen bond. According to Bader, the presence of a (3,–1) critical point along the bond path is the necessary and sufficient condition for the existence of a bond [2]. Clearly B is bonded to the H of HX and CH₄ would have been possible with a penta-coordinate C. However, as the proton is approaching the C through the tetrahedron plane, the H–H interaction starts dominating the intermolecular potential surface and CH₄ ends up with a structure that has been experimentally and theoretically found. Evidently, in the case of H₂O and NH₃, the proton approaches the central atom away from the hydrogens and these can form the hydronium and ammonium ions readily. Not surprisingly, attempts to look for NH₂⁺ have not been very successful as the second proton is again looking at a tetrahedron NH₃⁺ [38]. On the other hand the existence of H₂O₂⁻ has been shown experimentally and theoretically [39].

If one is not satisfied with the criterion by Bader for classification as hydrogen bonding, Koch and Popelier [30,31] have given a set of eight criteria to settle this issue. Interestingly, most of these criteria were met by all the eight structures investigated here. According to Koch and Popelier, mutual penetration of H and acceptor atoms is the necessary and sufficient condition [30]. Table 2 lists the values of Δrₓ and Δqₓ, namely the difference between non-bonded and bonded radii of the acceptor and hydrogen atoms. These values give a measure of the mutual penetration. The bonded radius is the distance from the bonded atom to the bond critical point along the bond path. The non-bonded radius is calculated as the distance from the atom to the point at which the electron density becomes 0.001 au along the bond path in the isolated molecule. For comparison, values for H₂O···HX and Ar···HX are included in Table 2, the former a typical hydrogen bond for all and the latter a hydrogen bond for some [2,40]. It is interesting to note that the sum of Δrₓ and Δqₓ is about 0.7–0.9 Å for X–H···C structures and it is larger than that for the C–H···X structures, 0.5–0.8 Å. For comparison, the H₂O···HX complexes have this value in the range 1.1–1.4 Å and the Ar···HX complexes have 0.6–0.9 Å. If one looks at Δqₓ alone, it is clear that the H₂O···HX complexes have much higher values (0.6–0.8 Å) and the others have values of 0.3–0.4 Å. In any case, it is clear that X–H···C has more ‘hydrogen bonding’ nature than what C–H···X shows, based on this criterion.

Koch and Popelier have also given a range for values of electron density and Laplacian of the electron densities at the hydrogen BCP. These parameters are also listed in Table 2. The Laplacian values reported in this Table are defined as \(L = -1/4\pi\rho^2\) as given in Ref. [31]. Electron densities and Laplacian at the hydrogen BCPs are well within the range suggested for H-bonds. Here again, X–H···C qualifies as a hydrogen bond better than C–H···X. For example, electron density at the BCP for the complexes of H₂O···HF, H₂C···HF, Ar···HF and H₂CH···HF are 0.0436, 0.0121, 0.0158 and 0.0061 au, respectively. All of them fall within the range (0.002–0.04 au) quoted by Koch and Popelier for a hydrogen bond.

Interestingly, the electron density at BCP for C···HF geometry is twice that for CH···F geometry and both are smaller than that of Ar···HF. For H₂O and H₂S complexes, the electron densities at BCP are very similar (∼0.008 au) for both X···H···C and C···H···X geometries. The Laplacian for all the complexes shown in Table 2 are negative, indicating that they are all closed shell interactions [31].

The other parameters given by Koch and Popelier such as change in atomic volume, \(\Delta V\), change in total atomic energy, \(\Delta E\), change in atomic population, \(\Delta N\) and change in atomic first moments, \(\Delta M\), all for the H-bonded hydrogen atom all satisfy the criteria for these interactions to be classified as hydrogen bonds. (See Supporting materials) However, one exception is that the change in atomic population of H, \(\Delta N\), is small but positive for X···H···C (0.004–0.009) and X···H··· Ar complexes and it is negative for both X···H···OH₂ and C···H···X complexes. According to Koch and Popelier criteria, it should have been negative for hydrogen bonded complexes. Interestingly, they have pointed out that for FH···PH₃,

### Table 2

Atoms in molecule theoretical parameters for the eight complexes under investigation and the analogous Ar and H₂O complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>(\rho^b)</th>
<th>(L^b)</th>
<th>(r^{b}_{\rho})</th>
<th>(r^{b}_{L})</th>
<th>(r^{b}_{\rho})</th>
<th>(r^{b}_{L})</th>
<th>(r^{b}_{\rho})</th>
<th>(r^{b}_{L})</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂C–HF</td>
<td>0.01208</td>
<td>−0.1156</td>
<td>2.0</td>
<td>1.5</td>
<td>0.5</td>
<td>1.1</td>
<td>0.8</td>
<td>0.3</td>
</tr>
<tr>
<td>H₂C–HCl</td>
<td>0.00066</td>
<td>−0.01105</td>
<td>2.0</td>
<td>1.5</td>
<td>0.5</td>
<td>1.3</td>
<td>0.9</td>
<td>0.4</td>
</tr>
<tr>
<td>H₂C–H₂O</td>
<td>0.00795</td>
<td>−0.00827</td>
<td>2.0</td>
<td>1.6</td>
<td>0.4</td>
<td>1.2</td>
<td>0.9</td>
<td>0.3</td>
</tr>
<tr>
<td>H₂C–HCl</td>
<td>0.00738</td>
<td>−0.00715</td>
<td>2.0</td>
<td>1.6</td>
<td>0.4</td>
<td>1.4</td>
<td>1.0</td>
<td>0.4</td>
</tr>
<tr>
<td>H₂C–H₂S</td>
<td>0.00456</td>
<td>−0.00262</td>
<td>1.9</td>
<td>1.2</td>
<td>0.7</td>
<td>1.3</td>
<td>0.7</td>
<td>0.6</td>
</tr>
<tr>
<td>H₂O–HF</td>
<td>0.03503</td>
<td>−0.02388</td>
<td>1.9</td>
<td>1.2</td>
<td>0.7</td>
<td>1.6</td>
<td>0.7</td>
<td>0.6</td>
</tr>
<tr>
<td>H₂O–HCl</td>
<td>0.02258</td>
<td>−0.02109</td>
<td>1.9</td>
<td>1.3</td>
<td>0.6</td>
<td>1.2</td>
<td>0.7</td>
<td>0.5</td>
</tr>
<tr>
<td>H₂O–H₂S</td>
<td>0.01694</td>
<td>−0.01633</td>
<td>1.9</td>
<td>1.3</td>
<td>0.6</td>
<td>1.4</td>
<td>0.8</td>
<td>0.6</td>
</tr>
</tbody>
</table>

\(\rho^b\) Results from calculation at MP2(FULL)/aug-cc-pVTZ level.

\(L^b\) Electron density at BCP, \(\rho\), and Laplacian of the electron density at BCP, \(L\), defined as \(L = -1/4\pi\rho^2\).

\(r^{b}_{\rho}\) Non-bonded radii of the acceptor atom and hydrogen atom, \(r^{b}_{\rho} = r^{b}_{\rho} - r_\rho\) and \(r^{b}_{L}\) bonded radii of acceptor and hydrogen atoms, \(r^{b}_{L} = r^{b}_{L} - r_{L}\) which are the penetration parameters in Å.
complex, which they had classified as a hydrogen bonded complex, the ΔN was found to be small and positive. This was attributed to possible errors in integration. In any case, according to seven of the eight criteria given by Koch and Popelier [30], and the conventional wisdom (stabilization energy, H–A distance, elongation of X–H bond and red-shift in the X–H vibrational frequency), X–H···C interaction is attractive hydrogen bonding interactions. It is more so than the C–H···X interaction that is often discussed with respect to the CH4···HX complexes in every case considered in this work, from the strongly hydrogen bonding HF donor to the weakly hydrogen bonding H2S donor. The experimental geometry of C2H6···HF/HCN complexes also have the H from HX pointing towards the tetrahedron plane formed by the CH3 group [41,42] and, not surprisingly the electrostatic potential for C2H6 has a corresponding minimum [29]. The C2H6···HCN complex has indeed been characterized as a complex with CH3 group as hydrogen bond acceptor [42]. Hence, it is expected that the conclusions reached here would be applicable for interactions in all hydrocarbon–HX interactions, in which HX is a hydrogen bond donor.

4. Conclusion

To conclude, high level ab initio calculations coupled with AIM theoretical calculations have been carried out on CH4···HX (X = F, Cl, OH, and SH) complexes. Two geometries for each complex, one in which CH4 is the hydrogen bond donor and another in which it is the acceptor have been considered. In each of these cases, the X–H···C interaction is stronger than the C–H···X interaction. It has been shown that the former resembles a hydrogen bond more closely than the commonly considered C–H···X interactions. In all these cases, the H–A distances are very close to the sum of the hydrogen bond radii proposed [22] recently. All the experimental and theoretical results available so far suggest that this conclusion would be general and applicable for all hydrocarbon–HX complexes.

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Appendix. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cplett.2008.11.009.

References