An ab initio study of the C$_2$H$_2$–HF, C$_2$H(CH$_3$)–HF and C$_2$(CH$_3$)$_2$–HF hydrogen-bonded complexes

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Abstract

MP2/6-31+G** and B3LYP/6-31+G** ab initio molecular orbital calculations have been performed in order to obtain molecular geometries, binding energies and vibrational properties of the C$_2$H$_2$–HF, C$_2$H(CH$_3$)–HF and C$_2$(CH$_3$)$_2$–HF H-bonded complexes. As expected, the more pronounced effects on the structural properties of the isolated molecules due to complexation was verified for the C–C and H–F bond lengths, which are directly involved in the H-bond formation. These bond distances increased after complexation. BSSE uncorrected B3LYP binding energies are always lower than the corresponding MP2 values. However, the opposite trend has been verified after BSSE correction by the counterpoise method since it is much lower at B3LYP than at MP2 level. The binding energies for these complexes as well as for the HF acid submolecule modes (the HF stretching and vibrational frequency modes) showed an increasing hydrogen-bonding strength with increasing methyl substitution. The splitting in the HF in-plane and out-of-plane bending modes reflects the anisotropy in the hydrogen-bonding interaction with the C=C bond. The H–F stretching frequency is shifted downward after complexation and it increases with the methyl substitution. The IR intensities of the HF acid submolecule fundamentals are adequately interpreted through the atomic polar tensor of the hydrogen atom using the charge–charge flux-overlap model. The skeletal stretching modes of the Alkyne submolecule are decreased in the complex. The new vibrational modes arising from complexation show several interesting features.

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1. Introduction

A variety of experimental techniques and theoretical calculations has been employed in order to understand the hydrogen-bonding interaction with π-bonded systems. From the experimental point of view, the ground vibrational molecular structures of weakly hydrogen-bonded complexes have been characterized by means of microwave and infrared molecular beam techniques with a Fourier transform [1–7]. Nowadays, it is already well established that the molecular interaction between hydrogen halides as proton donors and alkynes or alkenes as proton acceptors produces T-type hydrogen complexes, which are T-shaped near-prolate asymmetric rotors. These complexes yield to X–H–π type interactions, i.e., the interaction between the hydrogen halide molecule XH and the π-electron density of a carbon–carbon triple or double bond. For example, Andrews et al. [7] have performed high-resolution FT-IR matrix isolation studies to identify a hydrogen-bonded π complex for C$_2$H$_2$–HX with C$_2v$ symmetry through comparison of the relatively small shifts for the C=C stretching frequencies and relatively larger shifts for in-plane fundamental bending frequencies in the acetylene monomers and it was obtained a loss of degeneracy in all observed bending modes. On the other hand, theoretical calculations [8–13] have been particularly useful to estimate binding energies, H-bond lengths

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HF and C₂(CH₃)₂ complexes, HF and C₂(H(CH₃))₂-HF complexes, the H-bond distance for HF H-bonded complexes has been previously investigated by Andrews et al. [6] using Fourier transform infrared spectra, and H-bonded complexes have been fully optimized. The binding energies were computed at MP2/6-31+G** and B3LYP/6-31+G** calculation levels. The results are shown in Fig. 1. As expected, the more pronounced effects verified after complexation were obtained for C≡C and H-F bond lengths, which are directly involved in the H-bond formation. Their increments (δr₁(F), δr₂(H), δµ₁) are given in Table 1 as well as the H-bond lengths measured from the fluorine atom of the H-F bond to the midpoint of the C≡C bond of the C₂H₂-HF and C₂(CH₃)₂-HF complexes. For the C≡C(H(CH₃))₂-HF complex, the H-bond distance is slightly closer to the carbon atom (of the triple bond) bonded to the hydrogen atom, so that the electronic repulsion between the methyl group and the hydrogen atom in HF is minimized. From Table 1, we can note that the C≡C and H-F bond distances increments after complexation increase with methyl substitution. For example, B3LYP values concerning the increment of H-F bond distances (δr₂(H)) for the C₂H₂-HF, C₂(H(CH₃))₂-HF and C₂(CH₃)₂-HF complexes are 0.010 Å, 0.014 Å and 0.017 Å, respectively. Thus, methyl substitution leads to a progressive increase in the increment of H-F bond distance with complexation. Although of smaller magnitude, the same trend holds for C≡C bond distances, for which δr₁(F) values are 0.001 Å, 0.002 Å and 0.003 Å for the C₂H₂-HF, C₂(H(CH₃))₂-HF and C₂(CH₃)₂-HF complexes, respectively, at both B3LYP and MP2 levels. On the other hand, the F···|| hydrogen bond length is reduced by 0.07 Å on substitution of one hydrogen atom by a methyl group, at both B3LYP and MP2 levels. A second replacement causes a further decrease by the same quantity at MP2 level and by about 0.06 Å at B3LYP level. Therefore, our calculations indicate that methyl substitution produces a stronger hydrogen bond, in agreement with the results obtained by Andrews and Johnson [6,7]. Moreover, it is interesting to note that the hydrogen bond lengths obtained from MP2 results are always longer than the corresponding B3LYP values. For example, the MP2 value for r₁(F) is 3.107 Å in C₂H₂-HF, whereas its corresponding B3LYP value is 3.081 Å.

Table 2 shows the binding energies, ΔE, the binding energies including zero point energy and BSSE correction, ΔE₀, dipole moments (µ) and polarity enhancements (Δµ) for the C₂H₂···HF, C₂(H(CH₃))₂···HF and C₂(CH₃)₂···HF complexes. Δµ stands for the dipole moment difference between the complex and the free molecules (Δµ = µ(complex) − Σµ(free molecules)). ΔE was determined by subtracting the sum of the total energies of the isolated molecules from the total energy of the hydrogen complex. Initially, we can note that the uncorrected binding energies, and structural (electrostatic and vibrational) changes that take place in the isolated molecules after complexation. Moreover, theoretical calculations have been successful in predicting the new low-frequency vibrational modes, which, in general, show very weak intensities and, therefore, are difficult to characterize experimentally. These modes show several interesting features. However, high-level quantum chemical calculations with electron correlation and large basis set are necessary in order to obtain a proper description of a weakly bound hydrogen-bonded system. Generally, electron correlation effects are crucial to take into account dispersion forces. This can be reached through both Møller–Plesset perturbation theory at second-term level (MP2) [14] and density functional theory (DFT) [15] with B3LYP exchange-correlation functional. Furthermore, it is now well established that diffuse and polarization functions must be included in the basis set in order to adequately describe the non-spherical atomic densities and polarizability effects. This is particularly important in studying long-range electrostatic interactions.

The goal of the present paper is to study hydrogen-bonded complexes of the X−H−···C=C type, with hydrogen fluoride (HF) as proton donor, and acetylene (C₂H₂), methacetylene (C≡C(CH₃)) and dimethylacetylene (C≡C(CH₃)₂) as π charge centre. The C₂H₂−HF, C₂(H(CH₃))₂−HF and C₂(CH₃)₂−HF H-bonded complexes have been previously investigated by Andrews et al. [6] using Fourier transform infrared spectra, including also complexes of the type C≡C−HF with X=F and Cl [7]. They have shown that methyl substitution gives a stronger hydrogen bond and that halogen substitution gives a weaker hydrogen bond in a π complex involving the halogen. Their investigations consider the vibrational mode of the HF submolecule, leading to the conclusion that the more methyl groups replace hydrogen atoms the stronger the hydrogen bond becomes.

In this paper, a comparative investigation in terms of structural, electronic and vibrational properties of the C₂H₂−HF, C₂(H(CH₃))₂−HF and C₂(CH₃)₂−HF H-bonded complexes have been performed at MP2 and B3LYP levels, with the 6-31+G** basis set.

2. Calculations

MP2/6-31+G** and B3LYP/6-31+G** ab initio calculations were performed by using the Gaussian 98W program [16]. In this procedure, the molecular geometries of the isolated compounds as well as the hydrogen-bonded complexes were fully optimized. The binding energies were computed considering the basis set superposition error (BSSE) [17] due to the super molecule approach using the full counterpoise (CP) method proposed by Boys and Bernardi [18]. It is important to point out that the procedure to estimate the BSSE correction including the fragment deformation energy in the estimation of BSSE correction to binding energy, as first highlighted by Ensley et al. [19] and stressed elsewhere [20,21]. It is, in general, minimized when the CP method is employed in conjunction with a large basis set, which is flexible enough to provide a good description of the electrons in both the atomic core and the long-range region of the atoms [22,23].
Fig. 1. MP2/6-31++G** and B3LYP/6-31++G** results for the full optimized geometries of C₂H₂–HF, C₂H(CH₃)–HF and C₂(CH₃)₂–HF H-bonded complexes. B3LYP values are given in parentheses. Units in angstroms (Å).

Table 1

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Level of calculation</th>
<th>Structural changes</th>
<th>H-bond lengths (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₂H₂–HF</td>
<td>MP2/6-31++G**</td>
<td>0.007</td>
<td>0.001</td>
</tr>
<tr>
<td></td>
<td>B3LYP/6-31++G**</td>
<td>0.010</td>
<td>0.001</td>
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<tr>
<td>C₂H(CH₃)–HF</td>
<td>MP2/6-31++G**</td>
<td>0.010</td>
<td>0.002</td>
</tr>
<tr>
<td></td>
<td>B3LYP/6-31++G**</td>
<td>0.014</td>
<td>0.002</td>
</tr>
<tr>
<td>C₂(CH₃)₂–HF</td>
<td>MP2/6-31++G**</td>
<td>0.013</td>
<td>0.003</td>
</tr>
<tr>
<td></td>
<td>B3LYP/6-31++G**</td>
<td>0.017</td>
<td>0.003</td>
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</table>

Units in angstroms (Å).

* Refs. [6,7]

Table 2

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Level of calculation</th>
<th>ΔE (kJ mol⁻¹)</th>
<th>BSSE (μ)</th>
<th>ΔEc (μ)</th>
<th>(Δμ)</th>
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<tbody>
<tr>
<td>C₂H₂–HF</td>
<td>MP2/6-31++G**</td>
<td>19.23</td>
<td>4.39</td>
<td>16.61</td>
<td>2.75</td>
</tr>
<tr>
<td></td>
<td>B3LYP/6-31++G**</td>
<td>18.60</td>
<td>0.59</td>
<td>12.00</td>
<td>2.75</td>
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<tr>
<td>C₂H(CH₃)–HF</td>
<td>MP2/6-31++G**</td>
<td>24.75</td>
<td>4.76</td>
<td>12.96</td>
<td>2.83</td>
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<td>B3LYP/6-31++G**</td>
<td>23.53</td>
<td>0.38</td>
<td>16.97</td>
<td>2.97</td>
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<tr>
<td>C₂(CH₃)₂–HF</td>
<td>MP2/6-31++G**</td>
<td>28.97</td>
<td>5.10</td>
<td>16.89</td>
<td>2.89</td>
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<td>B3LYP/6-31++G**</td>
<td>26.75</td>
<td>0.21</td>
<td>20.23</td>
<td>2.93</td>
</tr>
</tbody>
</table>

Values in kJ mol⁻¹. Dipole moments and polarity enhancements (Δμ = μ-complex – Σμfree molecules) in Debye.
$\Delta E_c$ obtained from the B3LYP results are always slightly lower than the corresponding MP2 values. However, a reverse trend is verified after BSSE correction is applied to the binding energy. Now, B3LYP values become larger than the MP2 values. Corrected B3LYP binding energies ($\Delta E_c$) are higher than the MP2 values by about 4.0 kJ mol$^{-1}$. Chandra and Nguyen [13] have also verified the same behavior for the $C_2H-XH$ ($X=F$ and Cl) complexes. As expected, our results indicate that lower H-bond lengths are associated with larger binding energies. In this same sense, our results also indicate an increasing hydrogen-bond strength with increasing methyl substitution: $\Delta E_c$ ($C_2(CH_3)_2HF$) > $\Delta E_c$ ($C_2H(CH_3)_2HF$) > $\Delta E_c$ ($C_2H_2HF$) at both MP2 and B3LYP levels. Moreover, each methyl group leads to an increase of about $−4.0$ kJ mol$^{-1}$ in $\Delta E_c$. It is interesting to point out that the values of $\Delta E_c$ for $C_2HF-HF$ obtained by Chandra and Nguyen [13] employing the MP2/6-31++G** and B3LYP/6-31++G** calculations are 3.5 and 7.48 kJ mol$^{-1}$, respectively. These results confirm that methyl substitution gives a stronger hydrogen bond and that halogen substitution gives a weaker hydrogen bond.

Large polarity enhancements due to complexation are found for the $C_2H_2HF$, $C_2H(CH_3)_2HF$ and $C_2H(CH_3)_2CHF$ complexes; the values in the range of 0.6–0.8 D at MP2 level, and 0.8–1.0 D at B3LYP level. These polarity enhancements tend to increase with the methyl substitution in the $C_2X_2$ base molecule.

The vibrational spectrum of a hydrogen-bonded complex contains bands due to acid (HF) and base ($C_2X_2$) submolecules which differ from the free acid and base molecules depending on the strength and orientation of the hydrogen-bonding interaction. For the above complexes, Andrews et al. [1,2,6,7] have already observed that the strongest acid submolecule modes are the $H$-bond stretching fundamental ($\nu_{HF}$, in-plane), which are split due to an anisotropy of the HF interaction with the $\pi$ charge centre. They have also observed that the base submolecule modes are only slightly shifted by the HF ligand and, therefore, the base molecule may be useful as a model for the base submolecule in the complex. From the theoretical point of view, Chandra and Nguyen [13] confirm the experimental observations from Andrews and collaborators for the $C_2HX=IX$ complexes with $X=F$ and Cl. They have also verified that the $H$-$N$ stretching frequency shift and the intermolecular vibrational frequencies are better estimated at B3LYP than at MP2 level, using the 6-31++G** basis set. However, IR intensities have not been considered in both experimental and theoretical studies. Thus, we have listed in Table 3 the MP2/6-31++G** and B3LYP/6-31++G** results of the harmonic frequencies, frequency shifts, infrared intensities and intensity ratios after complexation of the HF stretching mode in $C_2H_2HF$, $C_2H(CH_3)_2HF$ and $C_2H(CH_3)_2HF$ complexes. The previous experimental values obtained from Andrews and Johnson [6,7] and the theoretical values for $C_2HF-HF$ obtained from Chandra and Nguyen [13] are given in Table 3. From this table, we can verify that the $H$-$F$ stretching frequency is shifted downward after complexation. Moreover, we can still notice that larger shifts are associated with stronger hydrogen-bond strengths in considering values of $\Delta E_c$ shown in Table 2. In Fig. 2, the values of $\Delta E_c$ against the experimental stretching frequency shifts are given. The greater shift ($\Delta (\nu_{HF})$) is found for the $C_2H(CH_3)_2HF$ system, which corresponds to the more strongly bound complex, whereas the lower shift is found for the $C_2HF-HF$ complex that represents the more weakly bound complex. From Table 3 we can also note that the $\Delta \nu_{HF}$ experimental values are situated between those obtained from MP2 and B3LYP methods. However, they are slightly nearest to the B3LYP ones.

From Table 3 one can see that the $H$-$F$ stretching intensity of the proton donor molecule is much enhanced upon $H$-bond formation. For example, the $A_{HF}/A_{HF}^0$ ratio in $C_2H_2=CHF$ is 6.1 and 8.0 at MP2 and B3LYP levels, respectively. The intensity ratios obtained from B3LYP are always higher than the MP2 ones. Unfortunately, as far as we are concerned, the experimental value for the $H$-$F$ stretching intensity after complexation is unknown. Thus, this prevents

<table>
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<tr>
<th>Compounds</th>
<th>Level of calculation</th>
<th>$\nu_{HF}$</th>
<th>$\nu_{HF}-\nu_{HF}^0$</th>
<th>$A_{HF}$</th>
<th>$A_{HF}/A_{HF}^0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>MP2/6-31+G**</td>
<td>319</td>
<td>126</td>
<td>114 (77)$^a$</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td>B3LYP/6-31+G**</td>
<td>4068 (3981)$^b$</td>
<td>–</td>
<td>144 (77)$^b$</td>
<td>1.4</td>
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<tr>
<td>$C_2H_2HF$</td>
<td>MP2/6-31+G**</td>
<td>–</td>
<td>161</td>
<td>–</td>
<td>4.7</td>
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<tr>
<td></td>
<td>B3LYP/6-31+G**</td>
<td>–</td>
<td>241 (208.3)$^c$</td>
<td>–</td>
<td>6.3</td>
</tr>
<tr>
<td>$C_2H(CH_3)_2HF$</td>
<td>MP2/6-31+G**</td>
<td>–</td>
<td>233</td>
<td>–</td>
<td>5.2</td>
</tr>
<tr>
<td></td>
<td>B3LYP/6-31+G**</td>
<td>–</td>
<td>326 (281.4)$^d$</td>
<td>–</td>
<td>7.2</td>
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<tr>
<td>$C_2H(CH_3)_2HF$</td>
<td>MP2/6-31+G**</td>
<td>–</td>
<td>308</td>
<td>–</td>
<td>6.1</td>
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<tr>
<td></td>
<td>B3LYP/6-31+G**</td>
<td>–</td>
<td>402 (354.9)$^d$</td>
<td>–</td>
<td>8.0</td>
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<tr>
<td>$C_2HF-HF$</td>
<td>MP2/6-31+G**</td>
<td>–</td>
<td>133</td>
<td>–</td>
<td>2.2</td>
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<td>B3LYP/6-31+G**</td>
<td>–</td>
<td>214 (184)</td>
<td>–</td>
<td></td>
</tr>
</tbody>
</table>

Experimental values are given in parentheses. Units in cm$^{-1}$ and km mol$^{-1}$.

$^a$ Ref. [6].
$^b$ Ref. [7].
$^c$ Ref. [13].
$^d$ Ref. [12].
a direct comparison between calculated and experimental intensity ratios. Nowadays, on the other hand, it is well known
that this increase in the H–X (X = F, Cl, CN, NC and CCH) stretching intensity is due to the charge–flux term [9,10,12],
which is strongly affected by complexation, in contrast to what happens with the hydrogen charge. The latter is always
positive whereas the charge–flux is slightly negative in the free molecule and becomes quite positive after complexation. In
the complex, the hydrogen charge and the charge–flux term have the same algebraic sign; then, since the HX stretching
intensity is proportional to the sum of the squares of these terms, it is enormously increased upon H-bond for-
mation.

The modified charge–flux-overlap (CCFO) model [24,25] for infrared intensities has shown the impor-
tance of the charge–flux term in the H–X stretching intensity enhancement. Here, we can confirm this behavior through
comparison between $P_{\text{HF}}$ and $P_{\text{comp}}$ elements of the atomic polar tensor for the hydrogen atom before and after complexation.
According with the modified CCFO model, the $P_{\text{HF}}$ element is a measure of the hydrogen atomic charge at equilibrium
position whereas the $P_{\text{comp}}$ element measures the sum of the hydrogen atomic charge ($P_{\text{HF}}$) and the charge–flux term
associated to the H–F stretching. Table 4 gives the results of the atomic polar tensor for the hydrogen atom ($P_{\text{HF}}$) before and
after complexation with $C_2H_2$, $C_2H(\text{CH}_3)$ and $C_2(\text{CH}_3)_2$. For example, the $P_{\text{HF}}$ element in free HF is 0.451 e and after com-
plexation with $C_2H_2$, its value is decreased to 0.359 e. On the other hand, the $P_{\text{comp}}$ element is 0.535 e in free HF and becomes
0.765 e after complexation, i.e., it is more than twice the $P_{\text{HF}}$ element in the complex. The modified CCFO model shows that the $P_{\text{comp}}$ element can be represented by:

$$P_{\text{comp}} = P_{\text{HF}} + \text{K} \Delta q$$

whereas the $P_{\text{HF}}$ element is given by:

$$P_{\text{HF}} = \langle H | q | H \rangle$$

Moreover, the H–X stretching intensity can be represented by:

$$A_{\text{HF}} = K \langle H | q | H \rangle^2$$

where $K = 975 \text{ km mol}^{-1} \text{ e}^{-2}$ for values of IR intensities in $\text{km mol}^{-1}$. These three equations allow us to get a bet-
ter understanding of why the H–F stretching intensity is much enhanced after complexation, specially the effect of
the charge–flux term ($\Delta q$) on its value. For the H-bonded complexes systems investigated in this work, the
charge–flux term changes from 0.334 e in free HF to 0.849 e in $C_2H_2$–HF, to 0.913 e in $C_2H(\text{CH}_3)$–HF and finally, to
0.954 e in $C_2(\text{CH}_3)_2$–HF complex at B3LYP level. Similar behavior was obtained at MP2 level. It is also interesting to
verify that the charge–flux is negative in the free molecule ($P_{\text{HF}} < P_{\text{comp}}$, $-0.113 e$ for B3LYP and $-0.099 e$ for MP2 in HF)
and becomes quite positive after complexation ($P_{\text{HF}} < P_{\text{comp}}$, +0.509 e for B3LYP and +0.406 e for MP2 in $C_2H(\text{CH}_3)$–HF).
Other important observed feature is that the $P_{\text{comp}}$ element increases with the H-bond strength.

Using the Eq. (3) we can make a self-check of the calcu-
lated H–F stretching intensities. In free HF, the intensi-
ties obtained from this equation are 121 and 109 $\text{km mol}^{-1}$, using the MP2 and B3LYP results for $P_{\text{comp}}$, whereas the corre-
csponding values obtained from a normal mode analysis are 126 and 114 $\text{km mol}^{-1}$, respectively. Concerning
$C_2H(\text{CH}_3)$–HF complex, the values obtained from Eq. (3) together with the polar tensors obtained from MP2 and
B3LYP calculations are 659 and 813 $\text{km mol}^{-1}$, respectively, whereas the corresponding values obtained from a normal
mode analysis are 658 and 823 $\text{km mol}^{-1}$, respectively. The values coming from Eq. (3) are clearly in very good agree-
ment with the obtained directly from a frequency calculation. This means that the normal mode for this vibration is dom-
inated by the movement of the hydrogen atom along the axis of the H–F bond, which is here represented by the

![Fig. 2. Values of ΔE against the |H–F| experimental stretching frequency shifts in the $C_2H_2$–HF, $C_2H(\text{CH}_3)$–HF, $C_2(\text{CH}_3)_2$–HF and $C_2(\text{CH}_3)_2$–HF series.](image)
HF stretching in C₂H(CH₃)₂HF, i.e., 204 cm⁻¹. The ratio of the HF stretching frequencies (νHF) obtained from the B3LYP calculation is equal to 1.3.

In contrast to what happens with the HF stretching mode after complexation, the stretching frequencies of the C₂X₂ moiety are only slightly modified by the HF acid. In Table 5 we can verify that the experimental and B3LYP values for ΔνC≡C are only −9 cm⁻¹ and −12 cm⁻¹, respectively. These same displacements are also verified to ΔνC≡C. Our results show that the alkyne submolecule stretching modes are decreased after complexation. It is still interesting to note that ΔνC≡C increases upon methyl substitution: −7 cm⁻¹ for C₂H₃=HF, −12 cm⁻¹ for C₂H(CH₃)=HF and −16 cm⁻¹ for C₂(CH₃)=HF, at B3LYP level. Their IR intensities are very weak in both free molecule and the complex. On the other hand, the C≡H stretching intensity of the HCCX base molecule both before and after complexation are relatively large. For example, the C≡H stretching intensity is 64 km mol⁻¹ in C₂H(CH₃)₂ and changes to 85 km mol⁻¹ after complexation. Therefore, its ΔνH/Pₐ value is equal to 1.3.

The formation of the C₂H₂=HF, C₂H(CH₃)=HF and C₂(CH₃)=HF complexes gives rise to new vibrational modes, which the low-frequency ones are given in Table 6. Fig. 4 shows the schematic representation of these new normal modes in C₂H₂=HF obtained at B3LYP calculation. These new modes exhibit several interesting features.

(i) Initially, we can verify that the H-stretch frequency follows the order: C₂(CH₃)=HF > C₂H(CH₃)=HF > C₂ H₂=HF > C₂H=HF, i.e., 204 cm⁻¹, 157 cm⁻¹, 139 cm⁻¹ and 135 cm⁻¹[11], respectively. Therefore, its value increases with increasing methyl substitution. Its IR intensity is, in turn, very weak and thus, it is not easy to be characterized from its experimental vibrational spectrum. (ii) The two H-F bending modes, which are associated with the in-plane (ν₁) and out-of-plane (ν₂) bending modes, where the proton of the HF molecule moves along a line which is perpendicular to the H-F chemical bond axis, have appreciable intensities. These modes, which are pure rotations in the HF isolated molecule, become infrared-active after complexation. The out-of-plane bending intensity is practically determined by the hydrogen equilibrium charge, i.e., the P₀ element of the atomic polar tensor of the hydrogen atom in HF (Table 4). From Table 6 we can see that its B3LYP calculated values (from a frequency calculation) for the C₂H₂=HF, C₂H(CH₃)=HF and C₂H=HF are 100.9, 76.3 and 95.9 km mol⁻¹, respectively, whereas the values obtained by using the equation:

\[ \Delta\nu_i \text{ out-of-plane} = K(\rho_{iH}^2) \]  

are 113, 97 and 85 km mol⁻¹, respectively, which are in reasonable agreement with the calculated ones. The in-plane bending mode (νᵢ, in-plane) has also appreciable intensity but its value is practically half of that relative to the out-of-plane mode. For example, this latter is 100.9 km mol⁻¹ in C₂H₂=HF whereas its corresponding value for the in-plane mode is 56.6 km mol⁻¹. Andrews and Johnson [6,7] have pointed out that this splitting reflects an anisotropic potential governing the liberation of HF against the n-charge centre of the C₂X₂ base sub molecule. They have also observed that the in-plane bending mode has the higher potential energy because of a small contribution from repulsion between the HF acid and acetylenic protons. This split tends to
Table 6: B3LYP/6-31+G** and experimental\(^{a}\) values of intermolecular harmonic frequencies (\(\nu_i\), cm\(^{-1}\)) and IR intensities (\(A_i\), km mol\(^{-1}\)).

<table>
<thead>
<tr>
<th>New vibrational modes</th>
<th>(\text{C}_2\text{H}_2\text{HF}) Exp</th>
<th>(\text{C}_2\text{H}_2\text{CH}_2\text{HF}) Exp</th>
<th>(\text{C}_2\text{(CH}_3)_2\text{HF}) Exp</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-bond stretch ((a_1))</td>
<td>87</td>
<td>139</td>
<td>–</td>
</tr>
<tr>
<td>(A_{\nu_1})</td>
<td>1.1</td>
<td>3.3</td>
<td>6.1</td>
</tr>
<tr>
<td>H-F bend ((b_1))</td>
<td>426, in-plane</td>
<td>499, in-plane</td>
<td>558</td>
</tr>
<tr>
<td>(A_{\nu_{b_1}}), in-plane</td>
<td>36.6</td>
<td>43.4</td>
<td>51.5</td>
</tr>
<tr>
<td>H-F bend ((b_2))</td>
<td>382, out-of-plane</td>
<td>432</td>
<td>489</td>
</tr>
<tr>
<td>(A_{\nu_{b_2}}), out-of-plane</td>
<td>100.9</td>
<td>76.3</td>
<td>95.9</td>
</tr>
<tr>
<td>H-bend ((b_2))</td>
<td>(\nu_{\beta})</td>
<td>96</td>
<td>61</td>
</tr>
<tr>
<td>(A_{\nu_{b_2}})</td>
<td>6.3</td>
<td>4.8</td>
<td>3.7</td>
</tr>
</tbody>
</table>

\(^a\) Ref. [13].

\(^b\) This mode consists of a combination between a HF stretching and an intermolecular mode (see Fig. 4(b) for details), which approximates the HF and alkyne molecules.

![Fig. 4](image-url) New intermolecular vibrational modes obtained from the B3LYP/6-31+G** calculations for the \(\text{C}_2\text{H}_2\text{HF}\) complex.
increase in the series: C\textsubscript{2}HF→HF, C\textsubscript{2}H\textsubscript{2}HF, C\textsubscript{2}H(CH\textsubscript{3})HF and C\textsubscript{2}(CH\textsubscript{3})\textsubscript{2}HF. The experimental values \cite{6,7} for $\Delta
u_{\text{H-F}}$ (in-plane $\nu_{\text{H-F}}$, out-of-plane $\nu_{\text{H-F}}$) are 30 cm$^{-1}$, 44 cm$^{-1}$, 58 cm$^{-1}$ and 63 cm$^{-1}$, respectively. (iii) The lowest-frequency mode of each complex consists of an intermolecular bending vibration, where the atoms in each molecule in the complex move in a direction perpendicular to the respective molecular axis, as shown schematically in Fig. 4(a). Its IR intensity is very weak and tends to decrease with the methyl substitution, as well as its vibrational frequency. For example, its B3LYP values for the C\textsubscript{2}H\textsubscript{2}HF, C\textsubscript{2}H(CH\textsubscript{3})HF and C\textsubscript{2}(CH\textsubscript{3})\textsubscript{2}HF complexes are 96 cm$^{-1}$, 61 cm$^{-1}$ and 57 cm$^{-1}$, respectively.

4. Conclusions

Our MP2/6-31++G** and B3LYP/6-31++G** calculations have confirmed the previous vibrational spectroscopic evidences obtained by Andrews and Johnson\cite{6,7}, that is, the H-bond strength increases in the C\textsubscript{2}H\textsubscript{2}HF, C\textsubscript{2}H(CH\textsubscript{3})HF and C\textsubscript{2}(CH\textsubscript{3})\textsubscript{2}HF series. Their binding energies with or without zero-point energy and BSSE correction clearly indicate this behavior, i.e., an increasing H-bond strength with increasing methyl substitution. This also produces a greater shift on the H-F stretching frequency after complexation and an increasing splitting in the H-F vibrational modes and the CCH deformation mode. The IR intensities of the HF acid submolecule modes (the H-F stretching and vibrational fundamental frequencies) are adequately interpreted through the atomic polar tensor of the hydrogen atom in HF. Our calculations also show small red shifts of the base submolecule skeletal stretching modes.

Acknowledgements

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