Ab Initio Calculations of the Three-body C₂ + H + H Dissociative Recombination Channel for the C₂H₂⁺ + e Reaction

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Ab Initio Calculations of the Three-body C_2 + H + H Dissociative Recombination Channel for the C_2H_2^+ + e Reaction

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Abstract

Recent experiments in ion storage rings have shown the three-body break-up dominance in the dissociative recombination (DR) for a number of ions, e.g., H_2O^+, H_3O^+, NH_2^+, CHF_2^+, etc. This work presents ab initio calculations of the three-body dissociative channel C_2 + H + H for acetylene cation recombination with electrons. All calculations have been performed for the linear geometries of C_2H_2 and C_3H_2 species. The MCSCF linear response (LR) method was used to perform the calculations and to obtain potential energy curves along the linear reaction path. The calculations give suitable agreement with the vertical energies. Two possible dissociative recombination mechanisms are proposed for the three-body break-up, which can lead to the formation of C_2 molecule and two hydrogen atoms in their ground state.

1. Introduction

The physics and behaviour of cold plasmas, especially in the context of interstellar media is one of the most attractive subjects for physicists, astrophysicists and chemists. There are two factors that mainly contribute to the chemical modelling of interstellar media. These are the rates and the products distribution (the branchings ratios, for example). It is known that the dissociative recombination (DR) plays a key role, and is the process mainly responsible for ion neutralisation and electron removal in media such as diffuse interstellar clouds, the inner coma of comets and in the ionised upper layers of the Earth’s atmosphere.

The branching ratios are the probabilities for producing different sets of the neutral products into the available DR channels. The information about branching ratios in DR of polyatomic molecular ions with electrons is very important for the chemical modelling of plasmas. For example, for triatomic ion four different dissociative channels would be as:

\[
\begin{align*}
\text{AB} + \text{C} + \text{KER}, \\
\text{ABC}^+ + \text{e} &\rightarrow \text{A} + \text{BC} + \text{KER}, \\
\text{AC} + \text{B} + \text{KER}, \\
\text{A} + \text{B} + \text{C} + \text{KER},
\end{align*}
\]

where \(\text{ABC}^+\) is a polyatomic ion; A, B, C, etc. are neutral products and KER is the kinetic energy release into that channel.

Trends in how different molecular ions recombine with electrons and then dissociate into a particular pathway can give a lot of information about the physics of the dissociative recombination processes. Several recent experiments reported from the heavy-ion storage rings CRYRING and ASTRID [1] have shown a strong dominance of three-body break-up in the dissociative recombination of a number of ions, e.g., H_2O^+ [2], H_3O^+ and D_2O^+ [3], NH_2^+ [4], CHF_2^+ [5], CH_2^+ [6], etc. A recent review by Larsson and Thomas [7] gives a very detailed overview of the three-body break-up phenomenon, in particular the DR of the H_2O^+ and H_3^+ polyatomic ions. Another work by Strasser et al. [8] provides quite detailed investigations of the DR of H_3^+ molecules. These results are in disagreement with the earlier standard model, which suggests that the most probable mechanism is single hydrogen detachment [9].

There is no clear answer in the published literature how to describe exactly the observed three-body dominance. The main problem in answering this question is that one must consider many accurate potential energy surfaces to obtain a reasonable answer. Bates [10] suggested that one possible mechanism could be a secondary fragmentation, when, after the primary dissociation, there is still enough intramolecular energy available to break second bond(s). Larsson and Thomas [7], for example, suggest two possible mechanisms that may be involved in the DR of the water ion. These are synchronous concerted and asynchronous concerted reactions, i.e., simultaneous and short time-scale sequential break-up. However, without taking into account the variety of many mixed excited valence and Rydbergs states, even for small molecules, it is not possible to make a final conclusion. Consideration of all possible potential energy surfaces (PES) along the different reaction pathways leading to the observed favourable products is required to help us to understand the physics of the DR process, DR for acetylene ion has been studied recently [11]. The three-body break-up channel is about 30%, but it is not the most dominant DR channel for acetylene [11]. Furthermore, this reaction is almost thermoneutral, having a rather small available reaction energy [11]:

\[ \text{C}_2\text{H}_2^+ + \text{e} \rightarrow \text{C}_2 + \text{H} + \text{H} + 0.2 \text{eV(KER)}, (\gamma). \]

So far, no ab initio calculations have been done for this particular channel.

At the effective collision energy of 0 eV there are four more DR channels that are open [11]:

\[
\begin{align*}
\text{C}_2\text{H} + \text{H} + 5.8 \text{eV} [50\%] \quad (\alpha), \\
\text{CH} + \text{CH} + 1.2 \text{eV} [13\%] \quad (\beta), \\
\text{CH}_2 + \text{C} + 2.4 \text{eV} [5\%] \quad (\delta), \\
\text{C}_2 + \text{H}_2 + 5.1 \text{eV} [2\%] \quad (\epsilon).
\end{align*}
\]

A number of studies [12–14] report ab initio calculations on the excited states for the acetylene molecule, particularly
for the two-body $\text{C}_2\text{H} + \text{H}$ photodissociation channel. The spectroscopy and dynamics of the Rydberg states of $\text{C}_2\text{H}_2$ have been reported in [15,16]. We choose to study the $\text{C}_2\text{H}_2$ molecule because of its linear structure in the ground state, which simplifies the ab initio calculations.

2. Theory and computational details

This work presents ab initio calculations for the three-body dissociative channel $\text{C}_2 + \text{H} + \text{H}$ of the $\text{C}_2\text{H}_2$ molecule, Eq. (2). The acetylene molecule ($\text{C}_2\text{H}_2$) is linear in its electronic ground state and thus it belongs to the $\text{D}_{\text{hh}}$ point group. Malsch et al. [12] have described in detail the vertical spectra and equilibrium configurations of the electronically excited states of acetylene. Our calculations of these properties are very similar, thus we shall present the vertical spectrum in the context of the DR process, Eq. (2).

Four singlet and four triplet states of all eight symmetries $\Sigma^+_g$, $\Pi^+_g$, $\Pi^+_u$, $\Sigma^+_u$, $\Pi^+_u$, $\Pi^+_g$, and $\Sigma^+_u$ have been calculated. For technical reasons, the calculations were carried out in the $\text{D}_{\text{hh}}$ point group. The corresponding irreducible representations are $\Lambda_g$, $\Lambda_u$, $\Pi_g$, $\Pi_u$, $\Lambda_g$, $\Lambda_u$, $\Pi_g$, $\Pi_u$, $\Sigma_g$, $\Sigma_u$, respectively. The ground state of acetylene is a linear $\Sigma^+_g$ state, and it can be represented by the following electronic configuration:

$$1\sigma^+_g 1\sigma^+_u 2\sigma^+_g 2\sigma^+_u 3\sigma^+_g 1\pi^+_g X^1\Sigma^+_g.$$  (4)

The lowest triplet of acetylene molecule is a linear $3\Sigma^+_u$ state. This is resulting from the $\pi_u \rightarrow \pi^+_g$ excitation, which produces configuration:

$$1\sigma^+_g 1\sigma^+_u 2\sigma^+_g 2\sigma^+_u 3\sigma^+_g 1\pi^+_g 1\pi^+_g 1\pi^+_u 3\Sigma^+_u.$$  (5)

The ground state of the $\text{C}_2\text{H}^+$ ion is also linear. This is a $2\Pi_u$ state of the type [17]:

$$1\sigma^+_g 2\sigma^+_g 2\sigma^+_u 3\sigma^+_g 1\pi^+_g 2\Sigma^+_u.$$  (6)

Thus for DR study (Eq. (2)), it is natural to consider linear reaction coordinates. We performed all calculations using the linear geometries of $\text{C}_2\text{H}_2$ and $\text{C}_2\text{H}^+$. First, the reaction coordinates for singlet $1\Sigma^+_g$ and triplet $3\Sigma^+_u$ states of the neutral $\text{C}_2\text{H}_2$ molecule and for the doublet $2\Pi_u$ state of the ion have been obtained by the density functional theory (DFT) method with the 6-311G basis set using the Gaussian 94 program. The behaviour of the $\text{C}–\text{H}$ bond length as a function of the bond elongation, $\Delta r(\text{C}–\text{H})$, for all three states, mentioned above, is shown in Fig. 1. Along these reaction coordinates the multi-configuration self-consistent (MCSCF) calculations have been performed for the corresponding reference [18]. The three lowest potential energy curves (PECs) for the singlet and triplet excited states of each symmetry have been calculated by the linear response (LR) method [18]. At the equilibrium geometry, the $\text{C}–\text{C}$ and $\text{C}–\text{H}$ bond lengths are 1.2029 Å and 1.0613 Å, respectively, for the ground $1\Sigma^+_g$ state; 1.3456 Å and 1.0629 Å for the lowest triplet $3\Sigma^+_u$ state, and 1.2536 Å and 1.077 Å for the ground cation $2\Pi_u$ state. These values are in a good agreement with previously obtained data [12,19].

The correlation consistent (CC) basis set of double-zeta quality (aug-cc-pVDZ) was applied for the MCSCF LR calculations, which are found to give a quite good agreement with earlier published results for vertical electronic excitation energies.

The $\text{C}_2\text{H}_2$ molecule has 14 electrons and $\text{C}_2\text{H}^+$ has one electron less. The two lowest lying occupied core orbitals $\pi^+_g$ and $\sigma^+_u$ with an energy of $–11.25$ hartree and one low-lying valence $2\pi^+_g$ orbital with an energy $–1.03$ hartree were frozen in our MCSCF calculations. The complete active space (CAS) was chosen after a few test calculations of the acetylene species. Thus the chosen CAS includes $2\sigma^+_g$, $3\pi^+_g$, $1\sigma^+_u$, $1\pi^+_u$, $2\pi^+_u$, $2\pi^+_g$, $1\pi^+_g$, $1\pi^+_u$, $5\sigma^+_u$, $4\sigma^+_u$, $6\sigma^+_u$ with 8 electrons among these 13 orbitals. This CAS consists of 65,000 determinants. Molecular orbitals (MO) of $\delta_u$ and $\delta_g$ symmetries were not included in the CAS because of the high energies of these empty MOs compared with the others.

Linear response calculations were performed with the CASSCF wavefunctions for a number of excited states of the $\text{C}_2\text{H}_2$ and $\text{C}_2\text{H}^+$ species along the considered reaction path. The $\text{C}–\text{H}$ bond length was increased equally for both H atoms, which simulate the three-body break-up, until the complete dissociation into $\text{C}_2 + \text{H} + \text{H}$ occurred. This was monitored by the $\text{C}–\text{C}$ and $\text{C}–\text{H}$ bond lengths (Fig. 1) in comparison with the experimental values [12] for the equilibrium geometry of the acetylene species and for the final products. The $\text{C}–\text{C}$ bond length at the end of the reaction coordinate in the dissociated $1\Sigma^+_g$ and $2\Sigma^+_u$ states (at the dissociation point) is equal to 1.26 Å, which corresponds to the length of a double $\text{C}≡\text{C}$ bond in a carbon molecule in its ground state ($1\Sigma^+_g$). Our calculations show that the molecule dissociates into $\text{C}_2$ and two hydrogen atoms at $\Delta r(\text{C}–\text{H}) = 2.0$ Å. The strong triple $\text{C}≡\text{C}$ bond in the neutral ground state minimum is reduced through the stretching to a weaker double $\text{C}≡\text{C}$ bond. The reaction coordinates for the singlet $1\Sigma^+_g$ and triplet $3\Sigma^+_u$ states converges to the same dissociation limit in $\text{C}_2$ ground state molecule, since two separated H-atoms can be presented by the degenerate singlet ($1\Sigma^+_g$) and triplet ($3\Sigma^+_u$) radical pair.
The vertical energy differences for singlet and triplet states are given in Table I and II, respectively. It is known that most of the excited states of acetylene are more stable in bent trans- or cis-geometries compared with the linear geometry. Both the C–C and C–H bond distances are different for the different states. We conclude that in our calculations there are some vertical transitions which are not from minimum to minimum, due to the facts mentioned above, but are from minimum to close-to-minimum point, i.e., near-vertical transitions. We have optimised most of the excited states in order to get a true idea about the difference between vertical and adiabatic excitations. Comparison with the results reported by Malsch et al. [12] and Lischka et al. [21] indicates that all qualitative features of the excited states potentials near the equilibrium are reproduced in our MCSCF and LR treatment. The states are labelled with respect to the D_{och} symmetry point group of linear molecular geometry.

The assignment of the states, in particular for acetylene, can be complicated due to possible Rydberg/valence mixing or Renner–Teller splitting. Further complexity of these calculations arises from the fact that the lowest Rydberg states are energetically not well separated from the valence states. A pronounced Rydberg character is known for the states around 8 eV [12]. In our calculations, the first triplet state \(^1 \Sigma^+_g\) was found to be lying 5.3 eV higher compared with that of the ground state, which is in agreement with Malsch et al., and Lischka and Karpfen [12,21]. The lowest excited states arise from \(\pi \rightarrow \pi^*\) excitation(s). The lowest state of a singlet multiplicity \(^1 \Sigma^+_u\) is predicted to lie at about 7.2 eV, followed by the \(^1 \Delta_u\) valence state at 7.6 eV. Our results give 7.43 eV for the \(^1 \Sigma^+_u\) state and 7.83 eV for the \(^1 \Delta_u\) state. The gap between first low-lying singlet and triplet states is about 2.1 eV, while it is 1.7 eV from the calculations in Malsch et al. [12], giving about 20% of a discrepancy. Kraemer and Koch [22] obtained for the second vertical ionisation potential of acetylene a value of 16.9 eV, which corresponds to a vertical excitation energy of approximately 5.5 eV for the first excited state of cation with respect to the ground state of acetylene. Since most of the excited states of the ion are lying much higher in comparison with those of neutral acetylene, we have included in the calculations only the first two excited states of each symmetry of \(\text{C}_2\text{H}_2^+\).

### Table I. Vertical electronic excitation energies for the singlet states of acetylene, as calculated by LR MCSCF method.

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>(3^3 \Pi_u)</td>
<td>–</td>
<td>–</td>
<td>12.65</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>(2^3 \Pi_g)</td>
<td>–</td>
<td>–</td>
<td>11.05</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>(^1 \Sigma^+_u)</td>
<td>9.4–9.58</td>
<td>9.27</td>
<td>9.9</td>
<td>3</td>
<td>7</td>
</tr>
<tr>
<td>(^2 \Sigma^+_u)</td>
<td>9.36–9.4</td>
<td>9.24</td>
<td>9.94</td>
<td>6</td>
<td>8</td>
</tr>
<tr>
<td>(^1 \Sigma^+_g)</td>
<td>9.03</td>
<td>9.21</td>
<td>9.99</td>
<td>11</td>
<td>9</td>
</tr>
<tr>
<td>(^1 \Delta_g)</td>
<td>8.9–8.95</td>
<td>–</td>
<td>9.77</td>
<td>9</td>
<td>–</td>
</tr>
<tr>
<td>(^1 \Delta_u)</td>
<td>8.87–8.9</td>
<td>9.02</td>
<td>9.63</td>
<td>8</td>
<td>7</td>
</tr>
<tr>
<td>(^1 \Pi_g)</td>
<td>8.4–8.46</td>
<td>9.01</td>
<td>8.84</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>(^1 \Pi_u)</td>
<td>7.92–8.0</td>
<td>8.16</td>
<td>8.38</td>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td>(^1 \Delta_u)</td>
<td>7.56–7.65</td>
<td>7.2</td>
<td>7.83</td>
<td>2</td>
<td>9</td>
</tr>
<tr>
<td>(^1 \Sigma^+_g)</td>
<td>7.2–7.42</td>
<td>7.1</td>
<td>7.43</td>
<td>&lt;1</td>
<td>5</td>
</tr>
<tr>
<td>(^1 \Sigma^+_u)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

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Table II. Vertical electronic excitation energies for the triplet states of acetylene, as calculated by LR MCSCF method. “Opt” means optimised state with the MCSCF method.

<table>
<thead>
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<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$^2\Sigma^+_u$</td>
<td>9.94</td>
<td>-</td>
<td>10.6$^{\text{opt}}$</td>
<td>7</td>
<td>-</td>
</tr>
<tr>
<td>$^1\Pi^+$</td>
<td>8.86</td>
<td>9.08</td>
<td>8.9</td>
<td>10</td>
<td>7</td>
</tr>
<tr>
<td>$^1\Pi_u$</td>
<td>8.53</td>
<td>8.9</td>
<td>7.9$^{\text{opt}}$</td>
<td>7</td>
<td>2</td>
</tr>
<tr>
<td>$^1\Sigma_u^+$</td>
<td>8.63</td>
<td>7.1</td>
<td>7.02</td>
<td>23</td>
<td>1</td>
</tr>
<tr>
<td>$^1\Delta_u$</td>
<td>7.66</td>
<td>6.0</td>
<td>6.09</td>
<td>26</td>
<td>1</td>
</tr>
<tr>
<td>$^1\Sigma_u^+$</td>
<td>6.33</td>
<td>5.2</td>
<td>5.3</td>
<td>19</td>
<td>2</td>
</tr>
</tbody>
</table>

values of the vertical energies for the three doublet excited states are presented in Table III.

We have the carbon molecule and a pair of hydrogen atoms as DR products. The two H atoms in their $^2S$ ground states give the molecular states $^1\Sigma_u^+$ and $^3\Sigma_u^+$ (as for a H$_2$ molecule). To be able to assign the dissociated molecular states for C$_2$H$_2$ we have calculated the vertical energies for the C$_2$ molecule at the same CAS level. In Table IV the first six excited states are shown. They are in good agreement with the observed values [19]. Combining the states of H + H and C$_2$, one gets the number of dissociation limits of acetylene C$_2$H$_2$. As one can see, the $^1\Sigma_u^+$ and $^3\Sigma_u^+$ states converge to the same dissociation limit C$_2$(C$_2$H$_2$) + 2H($^1\Sigma_u^+$, $^3\Sigma_u^+$). This result agrees well with the fact that a combination of the spins of the two separated hydrogen atoms can produce either singlet or triplet degenerate states of the radical pair.

The vertical splitting between the ground singlet and first triplet states of C$_2$ molecule is quite small and is equal to 0.12 eV [19], while our theoretical LR MCSCF method gives 0.4 eV, an overestimate by a factor of 3. On the other hand, our LR calculations of the C$_2$H$_2$ molecule; the two lowest states in C$_2$, (Fig. 3). The discrepancy in the energy gap $^1\Sigma_u^+ - ^1\Pi_u$ between our result and the known experimental value (see Tables IV and V) can be explained in terms of the C–C bond lengths. All the singlet states PECs were calculated along the $^1\Sigma_u^+$ reaction coordinate and all the triplet states PECs were calculated along the $^3\Sigma_u^+$ reaction coordinate. Thus, for example, the lowest dissociation limit C$_2$(C$_2$H$_2$) + 2H is calculated at the C–C bond length of the C$_2$(C$_2$H$_2$) equilibrium. Because of that, the energy gap between two limits is overestimated, since it corresponds to the vertical excitation of the C$_2$ molecule, being perturbed by H...H radical pair environment.

The singlet and triplet states PECs of the $^1\Sigma_u^+$ symmetry have a very similar behaviour, in spite of the fact that the reaction coordinates are quite different with respect to the C–C bond lengths, (see Fig. 1). In order to simplify the discussion later in this work and to summarize the results described above, we state that:

(i) a combination of the two H atoms in their $^2S$ ground states gives the molecular states $^1\Sigma_u^+$ and $^3\Sigma_u^+$ (as for a H$_2$ molecule);

![Fig. 3. Electronic states of $\Pi_u$ symmetry, calculated by LR MCSCF method. Solid curves are the ground states of C$_2$H$_2$ and C$_2$H$_2$. $^1\Sigma_u^+$, and also the $^1\Pi_u$ state which is involved in the DR process. Dash curves are singlet and triplet excited states.](image)

Table III. Vertical electronic excitation energies for the doublet states of acetylene ion, as calculated by LR MCSCF method.

<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>$^1\Sigma_u^+$</td>
<td>7.55</td>
<td>9.4</td>
<td>25</td>
</tr>
<tr>
<td>$^1\Pi_u$</td>
<td>6.1</td>
<td>6.85</td>
<td>12</td>
</tr>
<tr>
<td>$^1\Sigma_u^+$</td>
<td>5.67</td>
<td>6.75</td>
<td>19</td>
</tr>
<tr>
<td>$^1\Pi_u$</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Table IV. Vertical electronic excitation energies for the singlet and triplet states of C$_2$ molecule, as calculated by LR MCSCF method.

<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>$^1\Pi_u$</td>
<td>2.5</td>
<td>2.25</td>
<td>11</td>
</tr>
<tr>
<td>$^1\Pi_u^+$</td>
<td>1.65</td>
<td>1.5</td>
<td>10</td>
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<td>$^1\Pi_u$</td>
<td>1.04</td>
<td>1.26</td>
<td>21</td>
</tr>
<tr>
<td>$^1\Sigma_u^+$</td>
<td>0.75</td>
<td>0.8</td>
<td>7</td>
</tr>
<tr>
<td>$^1\Pi_u$</td>
<td>0.12</td>
<td>0.4</td>
<td>&gt;200</td>
</tr>
<tr>
<td>$^1\Sigma_u^+$</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
(ii) the lowest $1^3\Sigma_+^+$ and $3^3\Sigma_u^+$ states of C$_2$H$_2$ molecule correlate with the dissociation limit
\[ C_2(1^3\Sigma_+^+) + 2H(3^3\Sigma_u^+) ; \]  
for 2H in combination with the ground state of C$_2$ molecule;
(iii) for the same reason the $1^3\Pi_u$ and $1^3\Pi_g$ states of C$_2$H$_2$ molecule can correlate with the dissociation limit
\[ C_2(3^3\Pi_u) + 2H(1^3\Sigma_+^+ , 3^3\Sigma_u^+) ; \]  
for example, $1^3\Pi_u$ state can lead to $C_2(3^3\Pi_u) + 2H(3^3\Sigma_u^+)$ dissociation limit;
(iv) the geometry optimisation of the lowest singlet and triplet state PECs leads to the same lowest dissociation limit with the same C–C bond lengths in the C$_2$ molecule;
(v) the discrepancy in the energy gap $1^1\Sigma_+^+ - 1^3\Pi_u$ between our result and the known value (Tables IV and V) can be explained in terms of the C–C bond lengths: since the C–C bond in the $1^3\Pi_u$ state is longer than the C–C bond in the $1^1\Sigma_+^+$ state, the vertical excitation energy for the transition is larger than the adiabatic energy; this discrepancy cannot influence our qualitative calculations.

It is known that the bond lengths are quite different for the different states of C$_2$H$_2$ or C$_2$ molecules, [12,19]. We have calculated the bond distances, angles and energies for most of the excited states in C$_2$H$_2$. Such set of optimised values for the lowest states of acetylene molecule is shown in Table V; qualitative consequences of these differences are taken into account in the following discussion of the DR mechanism.

### Table V. C–C and C–H bond lengths for the excited singlet and triplet states of a linear C$_2$H$_2$.

<table>
<thead>
<tr>
<th>State</th>
<th>R(CC), Å</th>
<th>R(CH), Å</th>
<th>&lt;HCC</th>
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<tr>
<td>$2^1\Sigma_u^+$</td>
<td>1.313</td>
<td>1.0756</td>
<td>180°</td>
</tr>
<tr>
<td>$1^1\Sigma_u^+$</td>
<td>1.3421</td>
<td>1.0745</td>
<td>180°</td>
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<tr>
<td>$3^1\Pi_u$</td>
<td>1.4101</td>
<td>1.0884</td>
<td>180°</td>
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<tr>
<td>$2^1\Pi_u$</td>
<td>1.413</td>
<td>1.087</td>
<td>180°</td>
</tr>
<tr>
<td>$1^1\Pi_g$</td>
<td>1.2796</td>
<td>1.1227</td>
<td>180°</td>
</tr>
<tr>
<td>$1^1\Delta_u$</td>
<td>1.4279</td>
<td>1.0785</td>
<td>180°</td>
</tr>
<tr>
<td>$1^1\Sigma_g^+$</td>
<td>1.5334</td>
<td>1.0758</td>
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<td>$2^1\Pi_g$</td>
<td>1.2637</td>
<td>1.1269</td>
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<tr>
<td>$1^1\Delta_g$</td>
<td>1.2649</td>
<td>1.0731</td>
<td>180°</td>
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As follows from Table V, some excited states have a clear trend for C–C bond dissociation. For example, the $3^1\Sigma_u^+$ states are characterized by a very long C–C bond, (about 1.5 Å). The doubly excited configurations prevail in these states and their analysis indicate that they can dissociate to the two CH radicals. The same is true for the $2^1\Sigma_u^+$ and partly for the $1^1\Delta_u$ states. All these states are very unfavourable in the three-body breakup, Eq. (2). Thus one can understand qualitatively the competition between channels, Eq. (2) and Eq. (3), accounting the positions of all these states in the vertical spectrum, (Table I).

4. Discussion and comparison with the DR experiment

From the observed experimental data [2–7] one can find the obvious correlation between the branching ratio in the three-body channels and the values of the released kinetic energy. For example, the probability for H$_2$O$^+$ to dissociate into the O + H + H channel is 71% with released energy of 3.1 eV [2,7]; for H$_2$O$^+$ into the OH + H + H is 67% with KER = 1.3 eV [3]; for CH$_2$ into the C + H + H is 63% with KER = 2.3 eV [5]; for C$_2$H$_2$ into the C$_2$H + H + H is 59% with KER = 1.07 eV [23], etc. On the other hand, the KER in the C$_2$ + H + H channel for C$_2$H$_2$ (30%) and in the NH$_2$ + H + H channel for NH$_2$H$_2^+$ (21%) is almost negligible, 0.2 eV and 0.1 eV correspondingly. One can see that the dissociation goes more efficiently along the three-body pathways if more KER is available in the DR process [7].

Ab initio calculations from this work might give us important information about the presence or absence of some possible mechanisms for the three-body C$_2$ + H + H channel. Our calculations show that the $1^3\Pi_u$ state is one of the possible candidates for the three-body dissociation of the ion–electron recombination process; (shown as a solid line in Fig. 3). When the ion captures a free electron the rapid dissociation process starts via the repulsive $1^3\Pi_u$ state, which crosses the ionic state at the vibrational level $v = 0$. The dissociation continues along this surface and through the parallel symmetric CH-stretching exits to the dissociation limits of the neutral fragments, Eqs. (8), which is very close in energy to their ground states limit, Eq. (7) (statement (iii)). In addition, these two final states cannot be distinguished with a standard detector technique such as a surface barrier detector (SBD), which were used in our experiments at the CRYRING facility [6,26].

The “picture” is very qualitative and it cannot be interpreted in terms of the real thermochemical values, e.g., because the energy gap in the limits is overestimated (statement (v)). One has to consider that the reaction coordinates are the same for all triplet states, which differ from that for the singlet states. This means that for the different triplet states the DR potentials would differ from the simple picture (Fig. 3) taking into account that, in reality, each state has its own particular reaction coordinates (see Table V).

Another, but less possible, candidate for the three-body DR channel is the $3^3\Pi_g$ state (Fig. 7). It has a shallow, shifted minimum, at a prolongated CH distance. This minimum is not far from the ionic equilibrium. One has to note that our ionic curve is calculated with the MCSCF method, and gives an equilibrium energy which is lower than the experimental ionisation potential [20]. The shallow minimum of the $3^3\Pi_g$ state is produced by an avoided crossing with the $2^3\Pi_g$ state. Indeed, this crossing produces a very asymmetrical funnel. After the electron capture, the neutral system can come to this $3^3\Pi_g$ potential state and,

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moving along this PES it can easily relax through the funnel to the lower $2^3\Pi_g$ state PES and then dissociate to the singlet limit state $C_2(^1\Sigma_u^+)+2\text{H} (^3\Sigma_u^+)$, produced by two triplet products.

An important result of our study is that other states that have been calculated do not fit the simultaneous three-body break-up (Figs. 4–6, 8). Consider, for example, $^1,^3\Sigma_u^+$ excited states (Fig. 5). All these states, singlet and triplet, have very high energy barriers with respect to the simultaneous CH-bond breaking. Since all possible excited states have been considered in the important energy region, we can calculate that the number of possible candidates for three-body break-up is limited to the states of $^3\Pi_u$ and $^1\Pi_g$ symmetries. The $^3\Delta_s$ state (Fig. 4) has a shallow minimum with very long C–H bond length: $r_e(\text{C–H}) + \Delta r(\text{C–H}) = 2.1\text{Å}$. This weakly bound complex H...C...H can serve as an intermediate state in the concerted dissociation, (Eq. (3)), but it is not accessible by direct DR process.

In order to perform definite calculations about DR mechanisms a molecular dynamics calculations in the PES are needed.

5. Conclusion

This work presents ab initio calculations, performed by the MCSCF linear response method with augmented pVDZ-basis set for qualitative interpretation of the DR reaction $C_2\text{H}^+ + e \rightarrow C_2 + 2\text{H}$. All the computed vertical excitation energies are in agreement with the previous calculations and experimental data for acetylene [12].

A search for highly excited valence and Rydberg states of different symmetries give us a chance to find some of the doubly excited states, which lead to the $C_2 + 2\text{H}$ dissociation limit. Among the important conclusions, we have found that the $^1\Sigma_u^+$ and $^3\Sigma_u^+$ states of the 2H radical pair in combination with the ground state of the $C_2$ molecule gives the same dissociation limit $C_2(^1\Sigma_u^+)+2\text{H} (^3\Sigma_u^+, ^1\Sigma_u^+)$ limit. Thus the geometry optimisation of the lowest singlet and triplet state PECs leads to the same limit with the same C–C bond lengths in the $C_2$ molecule.
Two possible PEC’s candidates have been proposed for the three-body break-up $C_2 + H + H$: the $1^3\Pi_u$ and $3^3\Pi_g$ potential surfaces are found to be accessible and involved in the dissociation into the $C_2(1^3\Sigma_g^+) + 2H(1^3\Sigma_g^+, 3^3\Sigma_u^+)$ or $C_2(3^3\Pi_u) + 2H(3^3\Sigma_u^+)$ channels, respectively, where the neutral products are in their ground electronic states or very close to them. Most of the excited states that we have calculated do not fit the simultaneous three-body break-up, e.g., they have too large energy barriers to prevent three-body dissociation.

One also has to remember that our results present a rather qualitative interpretation and cannot be described in terms of the real thermochemical values. The picture can be modified by taking into account the fact that most of the excited states have their own reaction coordinates. The state-averaged MCSCF calculations might improve vertical excitation energies over the LR MCSCF approach. However, the importance of the present work is obvious for a better understanding of the physics of the dissociative recombination process of neutral and ionic species. For about thirty excited states PES have been calculated along the dissociation reaction coordinates, optimised for the lowest triplet excited state ($1^3\Sigma_u^+$) of acetylene.

Reaction coordinates for the ground states of acetylene and of its ion are also optimised for comparison with linear symmetry constrains.

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