(2+n) REMPI Study of Methane and Acetylene

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I hereby declare that this report is written by me and has not been handed in at part or in whole for a higher education degree.

_____________________________________

Andreas Piekarczyk
Abstract

A literature survey of multi photon ionization studies on methane was performed to create and determine the theoretical basis for first REMPI studies on methane. The failure of the performed (2+n) REMPI (n=1,2,3,...) experiment is consistent with the non-existence of REMPI studies for methane in the literature raising questions about the problems of the application of this technique for methane.

(2+n) REMPI (n=1,2,3,...) spectra were recorded for acetylene in the region between 74400 cm$^{-1}$ and 76150 cm$^{-1}$. A detailed analysis of known excited states in this region has been performed in order to determine B' values but failed at the low resolution of rotational structures in the recorded spectra. Further an analysis of the ratio of the formations processes of different molecular ion fragments was performed but lead to no clear patterns in the formation process. Further the measured power dependence of the excitation to the $3p^1\Sigma_g^+2^1$ state lead to results consistent with the theoretical expectations.

An attempt was made to determine the origin of two intense C$^+$ signals in this region giving a reasonable explanation for only one of the signals.
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(2+n) REMPI (n=1,2,3,...)

1 Theory

1.1 Resonance Enhanced Multi-Photon Ionization (REMPI)

The Resonance Enhanced Multi-Photon Ionization, short REMPI, uses one or more photons to reach an electronic excited molecular or atomic state and ionizes from this state with additional photons. The nomenclature (2+1) says that two photons are used to reach the excited state and one photon ionizes the molecule or atom. In the case of (2+1) REMPI the absorption of two photons instead of one photon of equivalent energy allows according to the selection rules the excitation into different electronic excited states compared to single-photon ionization. Compared to single-photon ionization the wavelengths are larger while the light-intensity has to be higher as well, as the absorption is a statistical process and the probability of absorbing two photons instead of one is lower. Measuring ions and ion-fragments this technique can be used to determine the quantum physical characteristics of the excited states. The energy between the ground state and the excited states are very specific and therefore characteristic for each molecule or atom which enables the use of REMPI also in analytical range. Due to the multi-photon excitation of REMPI the excitation energy to a higher electronic state can be divided by the number of photons used for excitation. Instead of one photon of 150 nm wavelength the use of light with 300 nm is possible or, by using a frequency doubling crystal, even 600 nm. As mentioned before the absorption of two photons has a lower probability and reduced therefore the signal’s intensity. The use of a frequency doubling crystal reduces the laser intensity and through this again the signal’s intensity.

1.2 Rydberg States

“An excited electronic state which is composed primarily of atomic orbitals with principal quantum numbers greater than that of the ground state and the valence excited states. Such electronic states typically have a large polarizability.”

1.3 Experimental Setup

The measurements were performed using jet cooled gas. Ions were directed into a time-of-flight tube and detected by a MCP detector to record the ion yield as a function of mass and laser radiation wavenumber to obtain two-dimensional REMPI data. Tunable excitation radiation was generated by Excimer laser-pumped dye laser systems, using a Lambda Physik COMPex 205 Excimer laser with a Coherent ScanMatePro dye laser. The C-560, C-540 and C-503 dyes were used and frequency doubling was obtained with BBO-2 crystals. The repetition rate typically was 10 Hz. The bandwidth of the dye laser beam was about 0.095 cm⁻¹. Typical laser intensity used was about 0.1-0.3 mJ/pulse. The radiation was focused into an ionization chamber between a repeller and an extractor plate. Undiluted pure CH₄ gas sample (Merck-Schuchardt OHG; purity >99.5%) and C₂H₂ (AAS Acetylene

1 IUPAC Gold Book
2.6; Linde gas) was pumped through a 500 µm pulsed nozzle from a typical total backing pressure of about 1.0 – 1.5 bar into the ionization chamber. The pressure in the ionization chamber was lower than 10⁻⁶ mbar during experiments. The nozzle was kept open for about 250 µs and the laser beam was typically fired 300 µs after opening the nozzle. Ions were extracted into a time-of-flight tube and focused onto a MCP detector, of which the signal was fed into a LeCroy 9310A, 400 MHz storage oscilloscope as a function of flight time. Average signal levels were evaluated and recorded for a fixed number of laser pulses to obtain the mass spectra. Mass spectra were typically recorded in 0.05 or 0.1 cm⁻¹ laser wave number steps. Spectral points were generally obtained by averaging over 100 pulses. The power dependence of the ion signal was determined by integrating the mass signals repeatedly and averaging over large number of pulses. The power reduction was achieved by sending the laser beam through glass lenses reducing the laser power at 8.4 % for each lens. Resulting from this power dependence measurements were performed with 91.6 %, 83.9 %, 76.9 % and 70.4 % of the original laser power at a certain wavelength. The program IGOR Pro 5.04B by WaveMatrics was used for data processing. On the working basis of recorded data available for a three dimensional graph (Figure 30), wavenumbers, ion time of flight and intensity, single masses were selected and further processed. Summing up and normalizing of neighboring mass peaks was necessary due to a shift of time of flight during each measurement caused by a shift of the laser focal point with changing wavenumbers.
2 Methane

Methane is a colorless gas and the simplest carbonic molecule having tetrahedral symmetry. The molecule with the formula CH\textsubscript{4} is well known in everyday life as town gas used for fuel, but is also a fundamental basis for chemical synthesis. Due to its simple structure and tetrahedral geometry it is ideal for studying even the quantum mechanical effects in bigger organic molecules. Methane is a component of many planetary atmospheres, in earth’s atmosphere among other things playing the role of a green house gas. On Saturn’s moon Titan exists even a methane-cycle similar to the water cycle on earth. Further it is believed that photolysis of methane is the primary step in the synthesis of higher organic molecules. For all this reasons it is necessary to understand more about and explore the higher electronic excited states of methane. The configuration of the electronic ground state of methane is the \((1a_1)^2(2a_2)^2(1t_2)^6^1A_1\) and it belongs to the point group \(T_d\).

2.1 Literature Review

Methane is due to its simplicity one of the best studied hydrocarbons and in quantum physical aspects one of the best studied organic molecules. Much work has been done on photodissociation\textsuperscript{3} and fluorescence measurement of methane to explore electronic excited states as well as calculations\textsuperscript{4}. The atmospheric importance of methane led to a strong focus on Lyman-\(\alpha\) radiation in a number of studies\textsuperscript{5,6} leaving other wavelengths unstudied. All studies have one-photon excitations as basis in common so that multi-photon studies in general unknown. In this sense it is not remarkable that no REMPI study of methane has been performed yet.

The analytical basis found in many studies is the ultraviolet absorption spectrum corresponding to the energies of electronic excited stats. The ultraviolet absorption spectrum starts at approximately \(\lambda<145\) nm\textsuperscript{7} and shows a rather diffuse increase of absorption till it reaches a maximum at about 129 nm with the first known Rydberg state with the transition \(1t_2 \rightarrow 3s(D_{2d})\)\textsuperscript{8}. Further Rydberg states are shown in Figure 1.

\textsuperscript{2} (On the formation of CH\textsubscript{4}+, CH\textsubscript{3}+, CH\textsubscript{2}+, CH\textsuperscript{+} and C\textsuperscript{+} secondary ions in methane, 1975)
\textsuperscript{3} (Explosive photodissociation of methane induced by ultrafast intense laser, 2006)
\textsuperscript{4} (Lower Rydberg series of methane: A combined coupled cluster linear response and molecular quantum defect orbital calculation, 2006)
\textsuperscript{5} (Photodissociation of methane at Lyman alpha (121.6 nm), 2008)
\textsuperscript{6} (Theoretical study of vibronic spectra and photodissociation pathways of methane, 1997)
\textsuperscript{7} (Fluorescence yield from photodissociation of CH\textsubscript{4} at 1060--1420 Å, 1983)
\textsuperscript{8} (Fluorescence yield from photodissociation of CH\textsubscript{4} at 1060--1420 Å, 1983)
The study of excited electronic states leads also to the question of the symmetry of excited states. One effect mentioned often in this context is the Jahn-Teller distortion. A weak Jahn-Teller distortion is expected for the 3pt2 Rydberg state leading to a strong vibrational enhancement. The reason for this distortion is mentioned as a mixing of the 3pt2 Rydberg state and the σ* (2t2*) orbital. Resulting from calculations it can be assumed that different favored excited states lead to different dissociation channels. The D2d geometry being energetically favored is conclusive with the lowest Rydberg state displayed in Figure 1. Further the C2v geometry is believed opening up the CH2+ and H2 fragmentation channel while a C3v geometry leads to the products CH3+ and H. Besides this two channels there are mentioned two respectively one or more fragmentation channels which are displayed in Figure 2. The shown fragments show a general problem in the determination of dissociation channels the uncertainty if fragmentations products resolve from separate pathways or if they are formed by further fragmentation of products from other channels. One approach towards the description molecular geometry and dissociation pathways was done recently on the basis of calculations showing up the possibility of a barrier less dissociation to CH2+ H2. In fact from all the possible dissociation channels shown in Figure 2 the first and the third display channels are believed to be the main ones. Figure 3 shows the correlation between methane and its dissociation products.

9 (Fluorescence yield from photodissociation of CH4 at 1060–1420 Å, 1983)
10 (Orbital picture in molecular inner-shell excited states of Rydberg-valence mixed character, 2005)
11 (Lower Rydberg series of methane: A combined coupled cluster linear response and molecular quantum defect orbital calculation, 2006)
12 (Lower Rydberg series of methane: A combined coupled cluster linear response and molecular quantum defect orbital calculation, 2006)
13 (Photodissociation of methane at Lyman alpha (121.6 nm), 2008)
14 (Photodissociation of methane: Exploring potential energy surfaces, 2006)
TABLE III. Dissociation energies (in eV) for all spin-allowed dissociation channels energetically accessible for Lyman $\alpha$ photodissociation. Experimental values are taken from Ref. 10. The electronic energies for the QZ basis set have been obtained after reoptimization of the geometry with the QZ/Ry basis. Harmonic zero-point vibrational energies are calculated using the TZ$^\ast$ basis.

<table>
<thead>
<tr>
<th>Asymptotes</th>
<th>$D_e$ (TZ$^\ast$/Ry)</th>
<th>$D_e$ (QZ/Ry)</th>
<th>$D_e$ (expt.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$($\tilde{X}^2\Sigma^\circ$)+H</td>
<td>4.35</td>
<td>4.42</td>
<td>4.48</td>
</tr>
<tr>
<td>CH$_3$(\tilde{A}^1A\tilde{i})+H</td>
<td>10.08</td>
<td>10.21</td>
<td>10.20</td>
</tr>
<tr>
<td>CH$_2$(\tilde{a}^1A\tilde{i})+H$_2$</td>
<td>4.95</td>
<td>4.99</td>
<td>5.01</td>
</tr>
<tr>
<td>CH$_2$(\tilde{b}^1B\tilde{i})+H$_2$</td>
<td>6.04</td>
<td>6.06</td>
<td>6.04</td>
</tr>
<tr>
<td>CH$_3$(\tilde{X}^2B\tilde{i})+2H</td>
<td>8.91</td>
<td>9.13</td>
<td>9.14</td>
</tr>
<tr>
<td>CH$_2$(\tilde{a}^1A\tilde{i})+2H</td>
<td>9.36</td>
<td>9.51</td>
<td>9.52</td>
</tr>
<tr>
<td>CH(CH$_3$)^2)+H$_2$+H</td>
<td>8.72</td>
<td>8.96</td>
<td>9.06</td>
</tr>
</tbody>
</table>

Figure 2\textsuperscript{15} Dissociation energies for all spin-allowed dissociations for methane

Figure 3\textsuperscript{16} Schematic overview of excited states of methane

\textsuperscript{15} (Photodissociation of methane: Exploring potential energy surfaces, 2006)
2.2 Experiment

Aim of this experiment was the scan of the region between 70400 cm\(^{-1}\) and 80000 cm\(^{-1}\) using REMPI with TOF-MS detection to determine the existence of unknown Rydberg states. The constant increase of absorption in this area combined with the rather bad resolution of absorptions spectra recorded in this area was seen as an indication for possible existence of electronic excited states in the mentioned wavenumber area. Further all described transitions between excited states are based on the spin-allowed transition on the basis of a one-photon excitation.

The detailed experimental setting is mentioned afore in the section Experimental build-up. One variant specification is the use the C-540 and C-503 laser dye, the opening time of the gas pulses of 250 µs and a delay time of 300 µs.

In progress of the measurement no signals were visible that could not be identified as the normal background of the instrument and measuring procedure. In order to achieve results a variation of parameters as delay time of the gas inlet, laser power and length of the gas pulse was performed but showed no results as well.

2.3 Conclusions

The measurements were without any results that would confirm the existence of electronic excited states in this wavenumber region. Combined with the fact that no REMPI studies of methane have been published it leads to the conclusion that either there are no electronic excited states within this region between 70400 cm\(^{-1}\) and 80000 cm\(^{-1}\) or they are not accessible to measurements using the REMPI method. This conclusion is supported by calculations\(^{17}\) matching with the absorption spectrum displayed in Figure 1.

\(^{16}\)(Explosive photodissociation of methane induced by ultrafast intense laser, 2006)
\(^{17}\)(Theoretical study of vibronic spectra and photodissociation pathways of methane, 1997)
3 Acetylene

Acetylene is colorless gas and the simplest representative in the group of alkynes. The molecule with the formula C$_2$H$_2$ is an important basis for chemical synthesis and well known to public as a gas for welding. Due to its triple-bonded carbon atoms its reactions are various and energetic rich. One further reason for the interest put in acetylene is its occurrence in space, in atmospheres of planets and comets, and the attempt to understand the formation of organic molecules. The linear molecule is centrosymmetric and belongs to the point group D$_{nh}$. Its electronic ground state is $X^1\Sigma^+_g$.

3.1 Literature Review

Acetylene is a well studied molecule and much research has been done already on photodissociation. Of special interest at this are studies of single-, two- and three-photon resonance excitation. Photodissociation is commonly found resolving form high-lying Rydberg states$^{18}$ excitation. Gerade Rydberg states are only accessible by two-photon excitation due to the strict g↔u selection for photon excitation. An excitation with one or three photons from the $^1\Sigma^+_g$ leads therefore to an ungerade state and to different photodissociation products.

3.2 Experiment

Aim of this experiment was the scan of the region between 74400 cm$^{-1}$ and 76150 cm$^{-1}$ using REMPI with TOF-MS detection. Special focus was on known excited states$^{19}$ at 74548 cm$^{-1}$, 75738 cm$^{-1}$ and 76068 cm$^{-1}$ in order to study rotational spectra of these states (Figure 4). Further a power dependence measurement was performed in order to determine the dependence of the fragmentation processes of the laser power at 76084 cm$^{-1}$. At this point it has to be mentioned that the described excited states occurred during the measurement shifted twelve wavenumbers and match the described states in more recent literature$^{20}$. The detailed experimental setting is mentioned afore in the section Experimental Setup. One variant specification is the use of the C-503 laser dye. In order to determine the B’ value of these states a calculated curve was fitted to the recorded spectra. Even though a computer based approximation of the calculated curve was not performed the attempt was made to get a rough fitting by hand. A detailed explanation of the curve fitting parameters is shown in Table 8 in the Appendix together with a list of the used curve fitting parameters.

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18 ((2+n) REMPI of acetylene: Gerade Rydberg states and photorupture channels, 2008)
19 (GERADE RYDBERG STATES OF ACETYLENE STUDIED BY MULTIPHOTON IONIZATION AND PHOTOELECTRON-SPECTROSCOPY, 1987)
20 ((2+n) REMPI of acetylene: Gerade Rydberg states and photorupture channels, 2008)
3.3 Results

3.3.1 76068 cm\(^{-1}\)

The signal at 76068 cm\(^{-1}\) corresponds to the excitation from the ground state to the 3p\(^1\)\(\Sigma^\text{g}\)\(_{2}\) state\(^{21}\). Figure 8 shows the recorded signals for the masses corresponding the ions H\(^+\), C\(^+\), CH\(^+\), C\(_2\)\(^+\), C\(_2\)H\(^+\) and C\(_2\)H\(_2\)\(^+\) in their original intensity. These are the only observed ion-masses and match with the possible fragmentation channels of acetylene. The heavily jagged structure of all signals can be seen as an indication for a rotational structure for this state but no certain B\(^{'}\) value can be distinguished due to the low resolution. Figure 9 shows the same signals after normalizing their intensities. The signal to background noise ratios of the signals is due to the transfer process not comparable in this figure.

Analyzing Figure 8 and Figure 9 shows several conspicuities. All signals have approximately the same peak shape and their maximum at the same wavenumber. The performed measurement shows a signal maximum at 76084 cm\(^{-1}\) compared to 76068\(^{22}\) cm\(^{-1}\) and matching 76085\(^{23}\) cm\(^{-1}\). In this sense from now on the signal will be named after the signal maximum according to the measurement and not the literature. On both sides of the peak all signals decrease constantly but with two different gradients. Only example is the signal for C\(_2\)H\(^+\) showing an increasing intensity for wavenumbers smaller than 76020 cm\(^{-1}\). At the same time C\(^+\) shows a decreasing intensity of approximately the same ratio. Therefore it can be assumed that their formation correlates directly. Further the C\(^+\) signal shows not only a different signal background ratios on both sides of the signal peak but also a higher background signal in general which becomes more visible in Figure 9.

In order to make the peak shape of different signals better comparable all signals were “cleaned” by subtracting the background and brought this way to the same value of background intensity. Further

\(^{21}\) (2+n) REMPI of acetylene: Gerade Rydberg states and photorupture channels, 2008
\(^{22}\) (GERADE RYDBERG STATES OF ACETYLENE STUDIED BY MULTIPHOTON IONIZATION AND PHOTOELECTRON-SPECTROSCOPY, 1987)
\(^{23}\) (2+n) REMPI of acetylene: Gerade Rydberg states and photorupture channels, 2008
the intensities of the peaks were normalized to an intensity of one. All signals were plotted together with the signal for the molecular ion $\text{C}_2\text{H}_2^+$. For easy comparability one additional curve was added showing the ratio of fragment ion intensity divided by molecular parent ion intensity. Figure 5 shows the signal for $\text{H}^+$ and $\text{C}_2\text{H}_2^+$ and their ratios which is illustrated by the violet curve. Due to the process of normalization and subtraction this curve shows two characteristics all figures have in common. Along the edges of the ion signal the signal intensity is reduced and due to fluctuations of the value can jump between positive and negative. Further a division by zero or very small values can occur causing extremely high values for the ratio curve. This explains the intense horizontal lines at the edges of the graph. The second characteristic all graphs have in commons is the value of 1 for the ratio curve at the wavenumber of the signal peak as a result from normalizing both signals to the same value for the signal peak. For a perfect match of the signal intensities the curve can be expected to be a horizontal line with the Y-value of one. Further the fragments $\text{C}_2\text{H}^+$ and $\text{C}_2^+$ were plotted in the same way together in order to determine the aforementioned correlation of both fragments. Table 1 shows a summary of these figures with a short analysis of the curve shape.

Figure 5 Illustration of the following figures showing the ratio between two different ion signals
Table 1

<table>
<thead>
<tr>
<th>Species</th>
<th>Figure</th>
<th>Description</th>
</tr>
</thead>
</table>
| $\text{H}^+/?
\text{C}_2\text{H}_2^+$ | 10      | Shows a thinner peak shape of $\text{H}^+$ ion mass signal compared to the molecular parent ion peak. The ratio curve shows increase of $\text{H}^+$ formation compared to $\text{C}_2\text{H}_2^+$ at wavenumbers than the maximum. |
| $\text{C}^+/?
\text{C}_2\text{H}_2^+$ | 11      | As mentioned before for wavenumbers smaller than 76084 cm$^{-1}$ the $\text{C}^+$ signal shows a higher Intensity. The ratio curve has “U” shape indicating a different signal shape for $\text{C}^+$ sharing the same intensity at the signal maximum. |
| $\text{CH}^+/?
\text{C}_2\text{H}_2^+$ | 12      | Shows no noticeable differences in the curve shape of both signals also indicated by the nearly horizontal curve progression. |
| $\text{C}_2^+/?
\text{C}_2\text{H}_2^+$ | 13      | Starting at approximately 76015 cm$^{-1}$ with a steep increase the signal for $\text{C}_2^+$ shows constantly a higher intensity leading to a broader peak shape than the signal for the molecular parent ion. After reaching a common intensity maximum at 76084 cm$^{-1}$ both have the same curve shape. |
| $\text{C}_2\text{H}^+/?
\text{C}_2\text{H}_2^+$ | 14      | Starting at approximately 76015 cm$^{-1}$ with a steep decrease the signal for $\text{C}_2\text{H}^+$ seems to show two local minima at approximately 76025 cm$^{-1}$ and 76035 cm$^{-1}$. The local minimum at 76035 cm$^{-1}$ appears in all spectra while the minimum at 76025 cm$^{-1}$ seem to be correlated with the forming of $\text{C}_2^+$ as aforementioned. |
| $\text{C}_2^+/?
\text{H}^+$ | 15      | The mentioned correlation of the $\text{C}_2^+$ and the $\text{C}_2\text{H}^+$ signals is visible through the steep increase of violet curve till it reaches a ratio between both signals of approximately one. The curve continues increasing slightly till 76070 cm$^{-1}$ before it starts to decrease till it reaches a Y value of one again. |

Figure 16 shows the performed curve fitting to the molecular parent ion signal in the way described in the description of the experimental setting for acetylene. The used parameters are shown in Table 2. Due to the lack of computer supported optimization of these values the estimated errors are subject to personal perception. Due to the $\Sigma$ to $\tilde{\Sigma}$ excitation $\Delta\Omega$ is equal zero.

Table 2

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Calculated value</th>
<th>Estimated error</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{B}'$ value</td>
<td>1.13</td>
<td>+/- 0.05</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>221</td>
<td>+30 / -70</td>
</tr>
<tr>
<td>Bandwidth</td>
<td>8</td>
<td>+/- 3</td>
</tr>
</tbody>
</table>

The power dependence measurement was performed at a wavenumber of 76084 cm$^{-1}$. Fig displays the processed data from one of the measurements. In the first step all data points for each ion signal were added up. Due to a different background signal with unequal distribution of positive and negative values all ion signals have been proceed individually. Resulting from the peak shape for each ion signals all data point in a signal specific window was set. From all these data points a ion-specific value was subtracted in order to make all signals values smaller zero. This value was kept a small as possible. All resulting data was added up to one point for each laser power. Table 9 in the Appendix shows the exact window range on the time of flight scale. The power reduction in the way mentioned in Experimental leads to following increments: 91.6 %, 83.9 %, 76.9 % and 70.4 % of the original laser power. All resulting values for each ion species were plotted as the natural logarithm of the intensity against the natural logarithm of the laser power Fig. To determine the slope of all curves they have
been divided in two groups of data points (Figure 6): 1-3 for the high laser powers 100-83.9 % and 3-5 for the lower laser powers 83.9-70.4 %. In each of these groups a linear regression was performed in order to determine the slope “m”. Table 3 shows the results of the performed calculations. Resulting from plotting the natural logarithm of the laser power against the natural logarithm of the intensity “m” is supposed to represent the number of photons needed for the excitation. In general the signals with the higher powers show a more constant slope compared the others. This becomes also visible in the calculated ∆m except the signal for CH⁺ which shows a higher inconstancy cause by the low signal intensity. Due to this fact a higher loading should be put to the calculated values resulting from these points.

Table 3

<table>
<thead>
<tr>
<th>Data points</th>
<th>Laser power</th>
<th>H⁺</th>
<th></th>
<th>C⁺</th>
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<th>CH⁺</th>
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<tr>
<td></td>
<td>m</td>
<td>Δm</td>
<td>m</td>
<td>Δm</td>
<td>m</td>
<td>Δm</td>
<td></td>
</tr>
<tr>
<td>1-3</td>
<td>5,467</td>
<td>0,211</td>
<td>3,212</td>
<td>0,270</td>
<td>4,388</td>
<td>0,606</td>
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<tr>
<td>3-5</td>
<td>5,805</td>
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<td>3,337</td>
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<th>Laser power</th>
<th>C₂⁺</th>
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<tr>
<td></td>
<td>m</td>
<td>Δm</td>
<td>m</td>
<td>Δm</td>
<td>m</td>
<td>Δm</td>
<td></td>
</tr>
<tr>
<td>1-3</td>
<td>3,900</td>
<td>0,199</td>
<td>2,997</td>
<td>0,138</td>
<td>3,022</td>
<td>0,076</td>
<td></td>
</tr>
<tr>
<td>3-5</td>
<td>5,480</td>
<td>0,893</td>
<td>4,551</td>
<td>0,976</td>
<td>4,546</td>
<td>0,885</td>
<td></td>
</tr>
</tbody>
</table>

Figure 6 Illustration of the performed fitting process
Figure 7 Recorded data for the power dependence measurement displayed as natural logarithm of the power against the natural logarithm of the intensity for each ion species.
Figure 8 Recorded mass spectra in their original intensity
Figure 9 Normalized mass spectra
Figure 10 $H^+ / C_2H_2^+$ signal ratio
Figure 11 $C^\text{/}C_2H_2^+$ signal ratio
Figure 12 CH⁺/C₂H₂⁺ signal ratio
Figure 13 $C_2^+ / C_2H_2^+$ signal ratio
Figure 14 $C_2H^*/C_2H_2^*$ signal ratio
Figure 15 $C_2^-/C_2H^+$ signal ratio
Figure 16 Fitted curve (blue), original signal for C$_2$H$_2^+$ (red)
3.3.2 75767 cm\(^{-1}\)

The signal at 75767 cm\(^{-1}\) corresponds to the excitation from the ground state to the 3p\(^{1}\)Σ\(^{+}\) state\(^{24}\). Again as described in the chapter before there is a slight discrepancy in the literature about the exact peak position. According to older literature\(^{25}\) the peak position is at 75767 cm\(^{-1}\) while more recent literature mentions 75760 cm\(^{-1}\). In the measurement a maximum showed up at 75763 cm\(^{-1}\). Figure 8 shows the recorded signals for the masses corresponding the ions H\(^{+}\), C\(^{+}\), CH\(^{+}\), C\(_{2}\)H\(^{+}\) and C\(_{2}\)H\(_{2}\)\(^{+}\) in their original intensity. These are the only observed ion-masses and match with the possible fragmentation channels of acetylene. The heavily jagged structure of all signals can be seen as an indication for a rotational structure for this state but no certain B' value can be distinguished due to the low resolution. Figure 9 shows the same signals after normalizing their intensities. The signal to background noise ratio of the signals is due to the transfer process not comparable in this figure.

Figure 17 shows the measured signals in their original relative intensities. Signals for C\(_{2}\)H\(_{2}\)\(^{+}\) and C\(^{+}\) seem to increase with a different gradient from the other signals indicating a different peak shape. Normalizing all signals to the same intensity shows that the crossing of lines that was visible in Figure 17 disappears in Figure 18. Instead of this it becomes visible that the signals have a different background to signal ratio. CH\(^{+}\) shows a different background to signal ratio on both sides of the peak. The same can be observed for the C' signal, but here less obvious. In general the C' signal has same as seen in 76068 cm\(^{-1}\) a high background signal compared to all other signals.

All signals were processed as aforementioned for the signals at 76068 cm\(^{-1}\) and plotted against C\(_{2}\)H\(_{2}\)\(^{+}\). Table 4 shows a summary of these figures with a short analysis of the curve shape.

**Table 4**

<table>
<thead>
<tr>
<th>(\text{H}^{+}/\text{C}_2\text{H}_2^{+})</th>
<th>Both signals show a nearly identical curve shape which is also indicated by a nearly horizontal progression of the violet curve through (Y=1).</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{C}^{+}/\text{C}_2\text{H}_2^{+})</td>
<td>Figure 20</td>
</tr>
<tr>
<td>(\text{CH}^{+}/\text{C}_2\text{H}_2^{+})</td>
<td>Figure 21</td>
</tr>
<tr>
<td>(\text{C}_2^{+}/\text{C}_2\text{H}_2^{+})</td>
<td>Figure 13</td>
</tr>
<tr>
<td>(\text{C}_2\text{H}^{+}/\text{C}_2\text{H}_2^{+})</td>
<td>Figure 23</td>
</tr>
</tbody>
</table>

\(^{24}\) ([2+n] REMPI of acetylene: Gerade Rydberg states and photorupture channels, 2008)

\(^{25}\) (GERADE RYDBERG STATES OF ACETYLENE STUDIED BY MULTIPHOTON IONIZATION AND PHOTOELECTRON-SPECTROSCOPY, 1987)
Even though literature\textsuperscript{26,27} names the excited states as being a $^1\Delta_g$ state a curve fitting is only possible using $\Delta\Omega=0$ as in a $\Sigma$ state to $\Sigma$ state transition. Comparing the peak shape with the signal at 7606 cm\textsuperscript{-1} and 74548 cm\textsuperscript{-1} the similarity to the $^1\Sigma_g^+$ becomes obvious and a $\Sigma$ states becomes more reasonable. One other possible explanation is the excitation form another state than the ground state. In the process of curve fitting this would lead due to different $\Omega$ value to the same curve behavior as in the description of a ground state to $\Sigma$ state excitation. Figure 24 shows the performed curve fitting to the molecular parent ion signal in the way described in the description of the experimental setting for acetylene. The used parameters are shown in Table 2 and as aforementioned $\Delta\Omega$ was set equal zero. Due to the lack of computer supported optimization of these values the estimated errors are subject to personal perception.

Table 5

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Calculated value</th>
<th>Estimated error</th>
</tr>
</thead>
<tbody>
<tr>
<td>B' value</td>
<td>1.144</td>
<td>+/- 0.05</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>221</td>
<td>+60 / -30</td>
</tr>
<tr>
<td>Bandwidth</td>
<td>7</td>
<td>+/- 3</td>
</tr>
</tbody>
</table>

\textsuperscript{26} (GERADE RYDBERG STATES OF ACETYLENE STUDIED BY MULTIPHOTON IONIZATION AND PHOTOELECTRON-SPECTROSCOPY, 1987)
\textsuperscript{27} (Spectroscopy and predissociation of acetylene in the np gerade Rydberg states, 2002)
Figure 17 Recorded mass spectra in their original intensity
Figure 18 Normalized mass spectra
Figure 19 $H^+/C_2H_2^+$ signal ratio
Figure 20 $C^\prime / C_2H_2^+$ signal ratio
Figure 21 CH⁺ / C₂H₂⁺ signal ratio
Figure 22. $C_2^*/C_2H_2^*$ signal ratio
Figure 23 $C_2H^+ / C_2H_2^+$ signal ratio
Figure 24 Fitted curve (blue), original signal for $\text{C}_2\text{H}_2^+$ (red)
3.3.3  74559 cm$^{-1}$

The signal at 74559 cm$^{-1}$ corresponds to the excitation from the ground state to the $3p^1\Delta_g 2^1$ state$^{28}$. Again like in the two chapters before there is a discrepancy between the literature and the measurement. The measurement shows a signal maximum at 74552 cm$^{-1}$ contrary 74559 cm$^{-1}$ in older literature$^{29}$. The only signal in this region appeared as a very broad peak for the $C_2H_2^+$ ion of approximately 100 cm$^{-1}$. The curve fitting to the recorded spectrum resulted in two different curves which are both shown due to their diversity.

Table 6 displays the values used for the curve fitting plotted in Figure 26. All detailed values for the used parameters a display in the Appendix as IIIa).

Table 7 displays the values used for the curve fitting plotted in Figure 27. All detailed values for the used parameters a display in the Appendix as IIIb).

Table 6

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Calculated value</th>
<th>Estimated error</th>
</tr>
</thead>
<tbody>
<tr>
<td>B' value</td>
<td>1.63</td>
<td>+/- 0.05</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>90</td>
<td>+/- 20</td>
</tr>
<tr>
<td>Bandwidth</td>
<td>10</td>
<td>+/- 2</td>
</tr>
</tbody>
</table>

Table 7

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Calculated value</th>
<th>Estimated error</th>
</tr>
</thead>
<tbody>
<tr>
<td>B' value</td>
<td>1.80</td>
<td>+/- 0.05</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>70</td>
<td>+/- 20</td>
</tr>
<tr>
<td>Bandwidth</td>
<td>11</td>
<td>+/- 2</td>
</tr>
</tbody>
</table>

$^{28}$ ([2+n] REMPI of acetylene: Gerade Rydberg states and photorupture channels, 2008)
$^{29}$ (GERADE RYDBERG STATES OF ACETYLENE STUDIED BY MULTIPHOTON IONIZATION AND PHOTOELECTRON-SPECTROSCOPY, 1987)
Figure 25 Recorded mass spectra in their original intensity
Figure 26 Fitted curve (blue), original signal for $C_2H_2^+$ (red)
Figure 27 Fitted curve (blue), original signal for C$_2$H$_2^+$ (red)
3.3.4 Carbon Resonance Signals

The measurement showed further two more signals that are not shown in Figure 4. These two signals were very sharp and strong signals for the mass of the C$^+$ ion at wavenumbers 75440 cm$^{-1}$ (Figure 28) and 75216 cm$^{-1}$ (Figure 29). The peak shape and the mass indicate an atomic transition for carbon being the source of these signals. A comparison with wavenumbers for electronic transition in carbon atoms leads to following results:

a) 75216 cm$^{-1}$:

There are two atomic spectral lines at 132.9578 nm and 132.9600 nm, both belonging to a $2s^22p^2 - 2s2p^3$ transition for C$^+$. Within the measurements accuracy this transition is a possible explanation for this signal. On this basis the ground state can be even specified more detailed being a $2p^3P_2$ state. In this case a two-photon excitation would take place.

A three photon excitation in this range of wavenumbers is not possible as the energy of three photons (14.03 eV) lies higher than the ionization potential of 11.26 eV.

No atomic spectral lines were found in the range between 264.5 nm and 266.5 nm therefore a one-photon excitation can be ruled out.

b) 75440 cm$^{-1}$:

No possible transitions could be found in the aforementioned database. Neither a transition for 1 photon at 265.12 nm, 2 photons at 132.56 nm nor for 3 photons at 88.37 nm can be found as a possible explanation.

---

Figure 28. Intense signal for the $\text{C}^+$ ion at 75216 cm$^{-1}$
Figure 29 Intense signal for the C$^+$ ion at 75440 cm$^{-1}$
3.4 Conclusions

The determination of the B’ values of the three states described in chapter 3.3.1-3.3.3 failed due to the low resolution of the signals recorded. No clear rotational structures were clear enough visible to identify a rotational constant B’.

The more detailed analysis of the ratios between molecular fragments and the molecular parent ion did show two different patterns. The described “U” shape of the ratio curve indicates a higher intensity of the ion fragments compared to the parent ion. The way of data processing is a major problem for further interpretation of the curve behavior as the step of normalizing the two signals is the cause of the described “U” shape. Both signals have the same value for the signal peak resulting in a ratio-curve-value of one. Moving away from this point the slope of the ratio-curve becomes more and more visible but at the same time the consistency of this curve becomes smaller the closer to the edges of the signal. Based on this there is need for a closer determination of the significance of the ratio-curve and the method of data processing applied.

An analysis of the working process with the data from the power dependence measurement 3.3.1 indicates a problem in the reduction of the uneven background-noise. The uneven structure and the change from positive to negative values makes it necessary to perform a background-noise reduction for every signal separately. With the aforementioned stronger loading on the first three data point result following numbers of photons:

<table>
<thead>
<tr>
<th>Ion</th>
<th>Number of photons</th>
</tr>
</thead>
<tbody>
<tr>
<td>H⁺</td>
<td>5</td>
</tr>
<tr>
<td>C⁺</td>
<td>3</td>
</tr>
<tr>
<td>CH⁺</td>
<td>4</td>
</tr>
<tr>
<td>C₂⁺</td>
<td>4</td>
</tr>
<tr>
<td>C₂H⁺</td>
<td>3</td>
</tr>
<tr>
<td>C₂H₂⁺</td>
<td>3</td>
</tr>
</tbody>
</table>

The process of adjusting a curve fitting by hand can be characterized as very labor-intensive and incomplete. Due to the relatively strong change of the curve with small changes of the parameters and at least two possible curves shown in 3.3 3.3.3. the existence of other possible fittings which were not found can not be ruled out.

Another question is the reproducibility of the processed data. As one example for this can be mentioned the described anomaly in the spectra of C₂⁺ and C₂H⁺ in chapter 3.3.1 towards the edges of the recorded spectrum. A comparison with other data containing the range of wavenumbers did not show this signals at all.
4 Appendix

Figure 30 Recorded 2 dimensional REMPI; 3 dimensional function

Table 8

<table>
<thead>
<tr>
<th>Position</th>
<th>Value set in calculation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Temperature (in K)</td>
<td>Variable</td>
</tr>
<tr>
<td>2. ( \Omega ) of lower state</td>
<td>0 assuming an excitation from the ground state</td>
</tr>
<tr>
<td>3. ( \Delta \Omega )</td>
<td>For excitation to ( \Sigma ) states ( \Delta \Omega = 0 ); to ( \Delta ) states ( \Delta \Omega = 2 )</td>
</tr>
<tr>
<td>4. Lower vibrational level</td>
<td>Assuming an excitation from the vibrational ground state, therefore zero</td>
</tr>
<tr>
<td>5. Higher vibrational level</td>
<td>Assuming an excitation to the vibrational ground state, therefore zero</td>
</tr>
<tr>
<td>6. ( \omega ) vibr. frequency</td>
<td>1</td>
</tr>
<tr>
<td>7. vibr. anharmonicity parameter</td>
<td>1</td>
</tr>
<tr>
<td>8. rotational constant ( B ) for upper state</td>
<td>variable</td>
</tr>
<tr>
<td>9. rotational constant ( D ) for upper state</td>
<td>1.0e-06</td>
</tr>
<tr>
<td>10. odd–even intensity ratio</td>
<td>3</td>
</tr>
</tbody>
</table>
11. purge

12. shift

13. Bandwidth for AbsorptionSpectra if Variable

14. start (ν₀ for AbsorptionSpectra if -30 Creating twice the number of data points compared to the number

15. stop (ν₁ for AbsorptionSpectra if 30

17. space (Δν for AbsorptionSpectra if 0.5

I. Make/O/N=16 InitOpt=221,0,0,0,1,1,1.13,1.0e-06,3.0,0,7,0,10,-30,30,0.05}\n
II. Make/O/N=16 InitOpt=291,0,0,0,1,1,1.144,1.0e-06,3.0,0,8,2,8,-30,30,0.05\n
III.a Make/O/N=16 InitOpt=90,0,2,0,0,1,1,1.630,1.0e-06,3.0,0,-14,0,10,-30,30,0.05\n
III.b Make/O/N=16 InitOpt=70,0,2,0,0,1,1,1.800,1.0e-06,3.0,0,-19,0,11,-30,30,0.05\n
\n\nTable 9

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>H⁺</td>
<td>62-66 μs</td>
<td></td>
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</tr>
<tr>
<td>C⁺</td>
<td>285-293 μs</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH⁺</td>
<td>298-305 μs</td>
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<tr>
<td>C₂⁺</td>
<td>415-423 μs</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₂H⁺</td>
<td>424-432 μs</td>
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<td></td>
</tr>
<tr>
<td>C₂H₂⁺</td>
<td>432-443 μs</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
5 References


