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Chemical synthesis in acetonitrile containing discharges. Insights from photoionization experiments with synchrotron radiation

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Acetonitrile, $\text{CH}_3\text{CN}$, has been observed in several extraterrestrial environments: the envelope of carbon rich stars, dense interstellar clouds, comets and the atmosphere of Titan, the largest moon of Saturn. On Earth the major natural source of acetonitrile is biomass burning. Due to its widespread use as a solvent, the ion chemistry of acetonitrile has been the subject of extensive investigations. Understanding the ion chemistry in gaseous discharges is in fact crucial, inter alia, for decoding mass spectra and for developing new MS methodologies.
It has been assumed for a while that ionization of acetonitrile produces ions with the same atomic connectivity $\text{CH}_3\text{CN}^+$. However, recent studies have shown that the most stable structure of the acetonitrile radical cation is $\text{CH}_2\text{CNH}^+$.
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In high pressure discharges the situation is further complicated since reactive processes have to be taken into account!

$\text{CH}_3\text{CN}^+ \quad m/z \ 41$
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We have studied the photo-induced ion chemistry of acetonitrile by using tuneable synchrotron radiation in the VUV region, detecting primary photo-ions and secondary ionic products deriving from self-reactions at thermal collision energies. The idea is to compare appearance energies of the different product ions. This allows us to distinguish ions that are directly produced by photoionization from those generated by ion-molecule reactions. Related thermochemistry calculations permit to gain further
A) Photon beam
B) Octopole ion guide
C) Deflector
D) Quadrupole mass spectrometer
Circular Polarisation beamline at ELETTRA (Trieste, Italy)
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Circular Polarisation beamline at ELETTRA (Trieste, Italy)
<table>
<thead>
<tr>
<th>m/z</th>
<th>Ion formula</th>
<th>Experimental appearance energy (eV)</th>
<th>Literature appearance energy (eV)</th>
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</thead>
<tbody>
<tr>
<td>40</td>
<td>C₂H₂N⁺</td>
<td>13.95±0.05</td>
<td>13.94±0.02</td>
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<tr>
<td>41</td>
<td>C₂H₃N⁺</td>
<td>12.18±0.05</td>
<td>12.201±0.02</td>
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<tr>
<td>42</td>
<td>CH₃CNH⁺</td>
<td>12.18±0.05</td>
<td></td>
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<tr>
<td>54</td>
<td>C₃H₄N⁺</td>
<td>14.48±0.05</td>
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<tr>
<td>81</td>
<td>C₄H₅N₂⁺</td>
<td>13.96±0.05</td>
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<tr>
<td>82</td>
<td>C₄H₆N₂⁺</td>
<td>12.16±0.05</td>
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<tr>
<td>83</td>
<td>C₄H₇N₂⁺</td>
<td>12.15±0.05</td>
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<tr>
<td>95</td>
<td>C₅H₇N₂⁺</td>
<td>14.45±0.05</td>
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<tr>
<td>122</td>
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<td>13.97±0.05</td>
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<tr>
<td>123</td>
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<td>124</td>
<td>C₆H₁₀N₃⁺</td>
<td>12.15±0.10</td>
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</table>
Ab initio calculations permit to infer structural information.
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<table>
<thead>
<tr>
<th>Reaction</th>
<th>ΔE (eV) ( \text{G3} )</th>
<th>ΔE (eV) ( \text{Experimental} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CH}_3\text{CN}^+ \rightarrow \text{c-C}_2\text{H}_2\text{N}^+ + \text{H} )</td>
<td>1.75</td>
<td>1.77</td>
</tr>
<tr>
<td>( \text{CH}_3\text{CN}^+ \rightarrow \text{CH}_2\text{CN}^+ + \text{H} )</td>
<td>2.22</td>
<td></td>
</tr>
<tr>
<td>( \text{CH}_3\text{CN}^+ \rightarrow \text{CH}_2\text{NC}^+ + \text{H} )</td>
<td>2.64</td>
<td></td>
</tr>
</tbody>
</table>
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ΔE (eV)  G3  ΔE (eV)
CH₃CN⁺ → c-C₂H₂N⁺ + H  1.75  1.77
CH₃CN⁺ → CH₂CN⁺ + H  2.22
CH₃CN⁺ → CH₂NC⁺ + H  2.64
Pictorial view of the geometries for the stable isomers of the dimer C₄H₆N₂⁺ observed at m/z 82, reported in order of increasing energy (A lowest L highest).
Conclusions:

we have measured the appearance energies of various ions resulting from the photoionization of gaseous acetonitrile by using tunable synchrotron radiation in the VUV region.
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Special thanks to my coworkers:

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