ECCL Short-Term Scientific Mission
Scientific report

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Purpose of the visit

Very recently a DEA study on penta-fluorophenylacetonitrile reported a strong signal of $[M-HF]^-$ at an energy close to 0 eV [I. Dabkowska et al. PCCP, 2009, DOI: 10.1039.b820670h]. In order to form HF from the molecule a C-F and a C-H bond must be broken. The energy required for the process is only available if the H-F bond is formed simultaneously. This remarkable reaction occurs with almost no excess energy and is only triggered by the excess charge. It is the purpose of this visit to systematically explore the mechanism of HF formation by measuring DEA to differently substituted fluorophenylacetonitrile. By studying these molecules we expect to see if the formation of $[M-HF]^-$ depends on the distance between the H and F atoms.

It is also the purpose of this visit to grant the beneficiary an experience in the field of electron attachment with standard apparatus. The beneficiary is currently working on detailed simulations concerning resolution factors in the trochoidal electron monochromator (poster will be presented at ECCL 09). This was a great opportunity to get a "hands-on feel" for the apparatus.

Work carried out

Most of the work concerned calibration of the electron monochromator (TEM) using the standard calibrant SF_6, resolving technical problems and gaining experience using this kind of experimental setup.

The molecules we focused on were *para*-fluorophenylacetonitrile and 2-chloro-6-fluoroophenylacetonitrile. The former does not have a high enough vapor pressure to be introduced into the machine through the inlet system, while the latter (a solid) has a very high vapor pressure which made it difficult to measure. Spectras were only obtained for the solid 2-chloro-6-fluorophenylacetonitrile. Those will
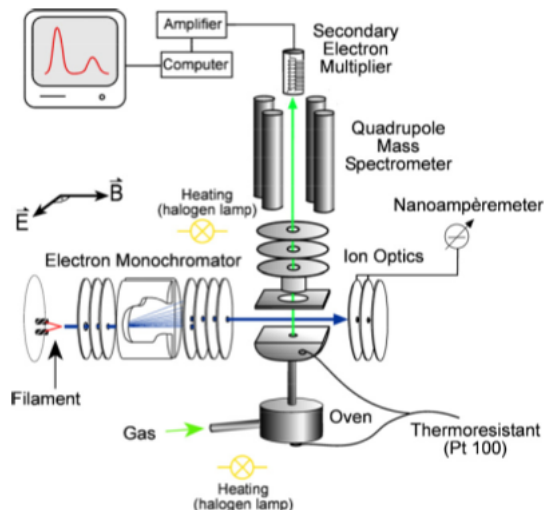
Figure 1: Schematic view of the experimental setup to study dissociative electron attachment (DEA) to gas phase molecules.

be presented here.

The experimental setup is shown in figure 1. The apparatus uses a crossed beam setup where an electron beam crosses an effusive molecular beam. The molecules are either introduced via an inlet system from outside the vacuum chamber, or in the case of solids, baked inside. After the interaction with the electron beam, the ions produced are extracted by a weak draw out field into a commercial quadrupole mass spectrometer.

Before the measurements, the apparatus was calibrated using the peak of the SF_6 resonance as a zero reference. The resolution obtained was rather bad, or in the range of 250 meV.

The resonances obtained for the solid were CN^-, $^{35}Cl^-$, $^{37}Cl^-$, $[M-78]^-$, $[M-HF]^-$ or $[M-F]^-$, M^- or $[M-H]^-$. The first three resonances mentioned are quite clear, the signal of the two Chlorine isotopes appears around 0.3 eV and is very strong whilst that of the CN^- peaks at around 6 eV. The other three however, are not so clear. Using as fixed points for calibration the following resonances; SF_6^-, SF_5^-, $^{35}Cl^-$, $^{37}Cl^-$ and CN^-, were used to fit the data by three methods. The methods are 2nd degree polynomial, least squares fit and least squares fit with a fixed zero. These gave the following masses

Table 1: Fit values

Fit Method	Mass 1 (amu)	Mass 2 (amu)	Mass 3 (amu)
2nd Poly	174	152	91
LSQ	171	151	93
LSQ-0	172	151	92
QM-values	557	491	300

As can be seen in table 1 the lowest value of the most massive fragment is 171 amu, this does not make sense, since the mass of the molecule is 169 amu. The corresponding masses of the other fragments are 151 amu, and 93 amu. The 151 amu corresponds to $[M-18]^-$ which cannot be any real fragment. If we lower the mass of each of these by 2 mass units, we arrive at 169 amu, 149 amu and 91 amu. These would then correspond to M^-, $[M-HF]^-$ and $[M-78]^-$.

By simple thermodynamics we can conclude that the electron affinity of the fragment $[M-F]^-$ has to be in the range of 5 eV in order for the C-F bond to break. The incident electron has close to zero eV and the energy of a typical C-F bond is in the range of 5 eV. We mean to calculate the electron affinity by DFT calculations. For the time being though we assume that the fragment is $[M-HF]^-$. The mass 91 (amu) can only correspond to the fragment C_5H_5CN.
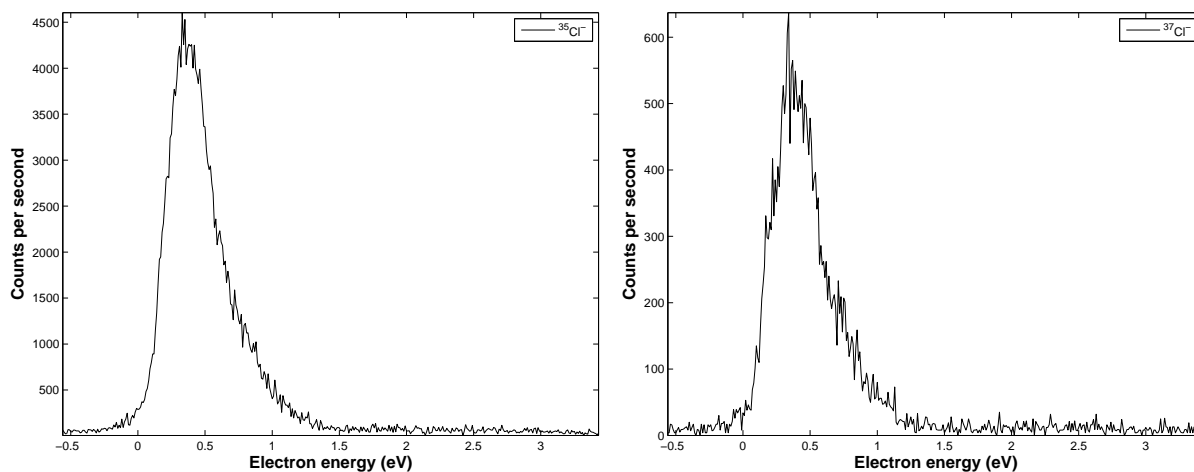
Figure 2: Left figure: the $^{35}\text{Cl}^-$ resonance, peaking at 0.3 eV. Right figure: the $^{37}\text{Cl}^-$ resonance, peaking at 0.3 eV.
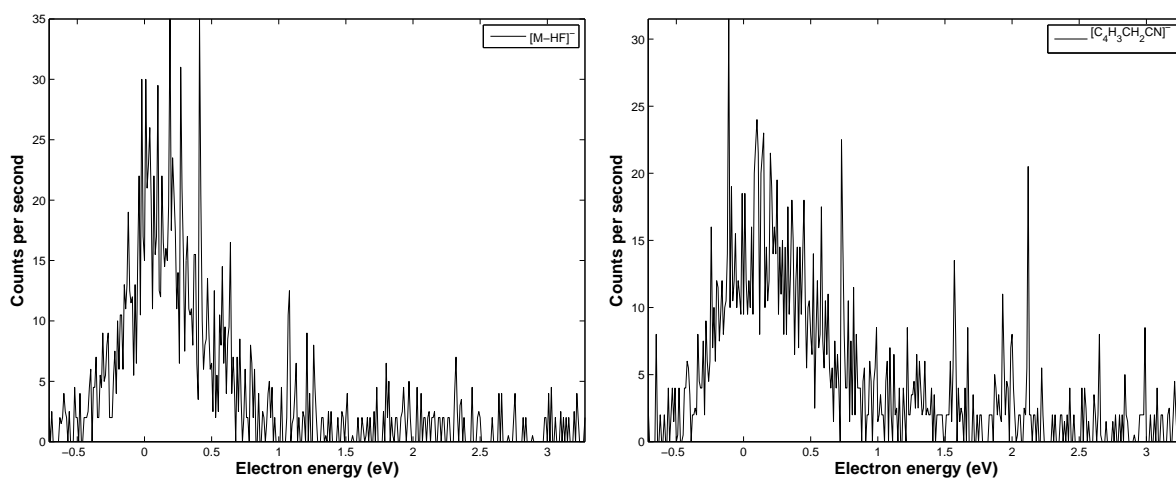

Figure 3: Left figure: the $[\text{M} - \text{HF}]^-$ resonance, peaking at 0.1 eV. Right figure: the $\text{C}_5\text{H}_5\text{CN}^-$ resonance, peaking at 0.1 eV.
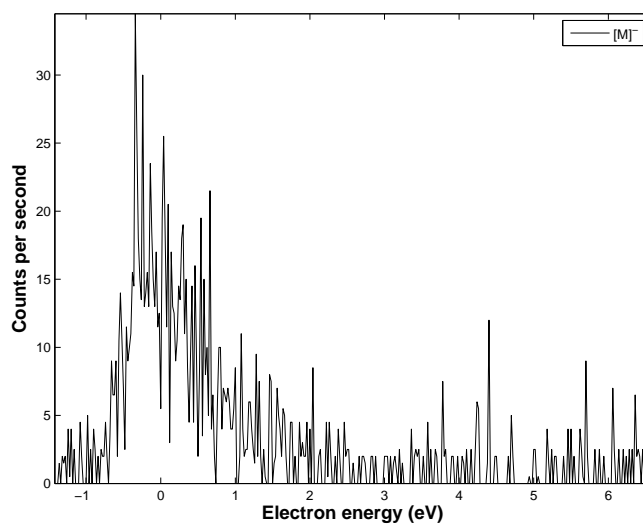

Figure 4: The M^- resonance, peaking at 0 eV.

Main results

It seems apparent that the molecule has quite a high vapor pressure which made it difficult to measure with standard techniques and that the molecule is not a good electron scavenger. However we were

able to see six different resonances, one of them which we believe to be the $[\mathrm{M} - \mathrm{HF}]^-$ resonance that we hoped to see.

Although we did not achieve to measure all the molecules we had planned, we still think this is a valid approach in understanding the mechanism and plan to continue this work at our lab in Iceland when our machines are up and running.