Appendix C

DEA to isolated ketone molecules

Here, we will present spectra obtained from electron attachment experiments to 1,1,1-trifluoroacetone and hexafluoroacetone that can be compared with the cluster results. As *Oster* [69] already discussed these processes in detail the obtained ion yields will be shown without further discussion.

C.1 1,1,1-Trifluoroacetone

Reaction mechanisms leading to product formation:

$$CF_3COCH_3 \longrightarrow CF_3COCH_3^{-\#} \longrightarrow CF_3COCH_2^- + H \quad (C.1)$$

$$\longrightarrow CF_2COCH_3^- + F \quad (C.2)$$

$$\longrightarrow CF_2COCH_2^- + HF \quad (C.3)$$

$$\longrightarrow CFCOCH_3^- + F_2 \quad (C.4)$$

$$\text{or} \longrightarrow C_3F_2^- + HF + H_2O$$

$$\longrightarrow HF_2^- + CFCOCH_2 \quad (C.5)$$

$$\longrightarrow C_2H^- + CF_3H_2O \quad (C.6)$$

$$\longrightarrow HC_2O^- + CF_3H_2 \quad (C.7)$$

$$\longrightarrow F^- + CF_2COCH_3 \quad (C.8)$$

$$\longrightarrow CF_2^- + FCOCH_3 \quad (C.9)$$

$$\longrightarrow CF_3^- + COCH_3 \quad (C.10)$$

$$\longrightarrow O^- + C_3F_3H_3 \quad (C.11)$$

$$\longrightarrow OH^- + C_3F_3H_2 \quad (C.12)$$

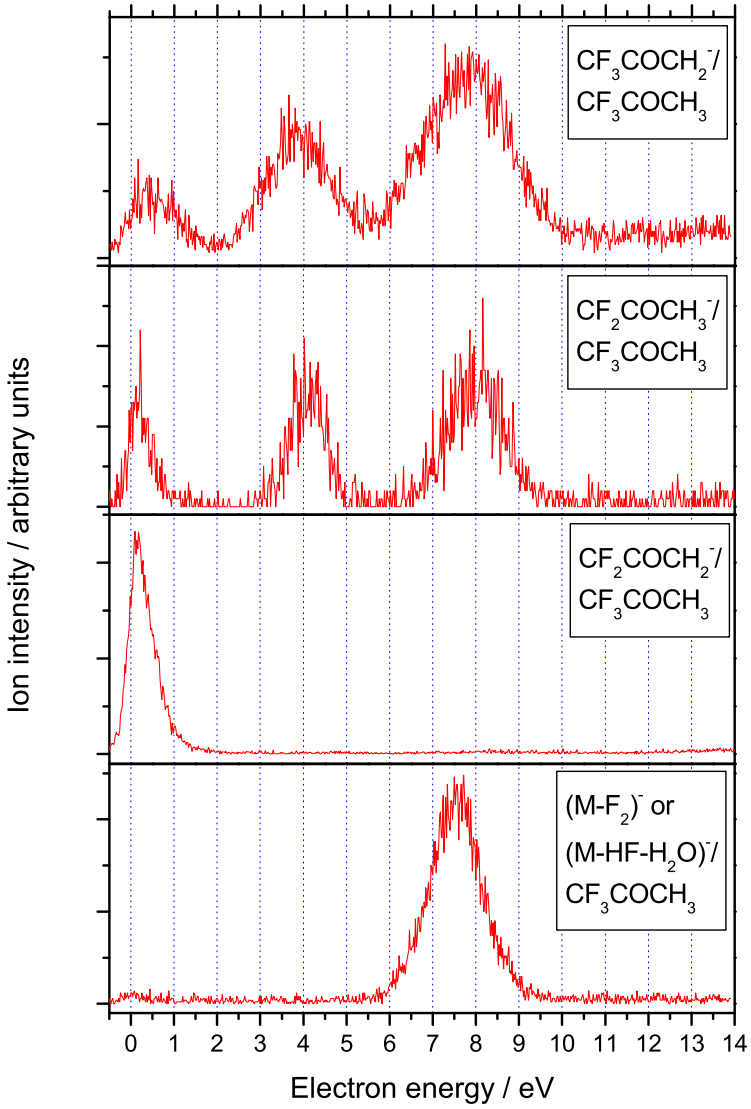

Figure C.1: Ion yield curves showing various fragments arising from electron attachment to gas phase trifluoroacetone (p=$2{\cdot}10^{-6}$ mbar, ΔE$\approx$200 meV; for (M-F_2)$^-$ / (M-HF-H_2O)$^-$: p=$1{\cdot}10^{-5}$ mbar, ΔE$\approx$240 meV)

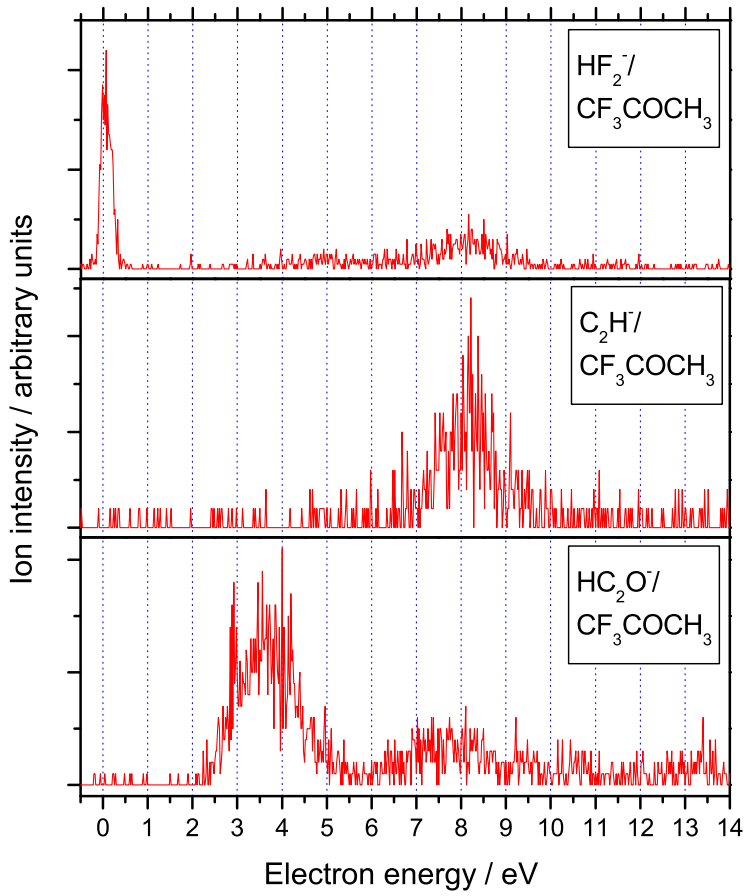

Figure C.2: Ion yield curves showing various fragments arising from electron attachment to gas phase trifluoroacetone (p=$2{\cdot}10^{-6}$ mbar, ΔE$\approx$200 meV)

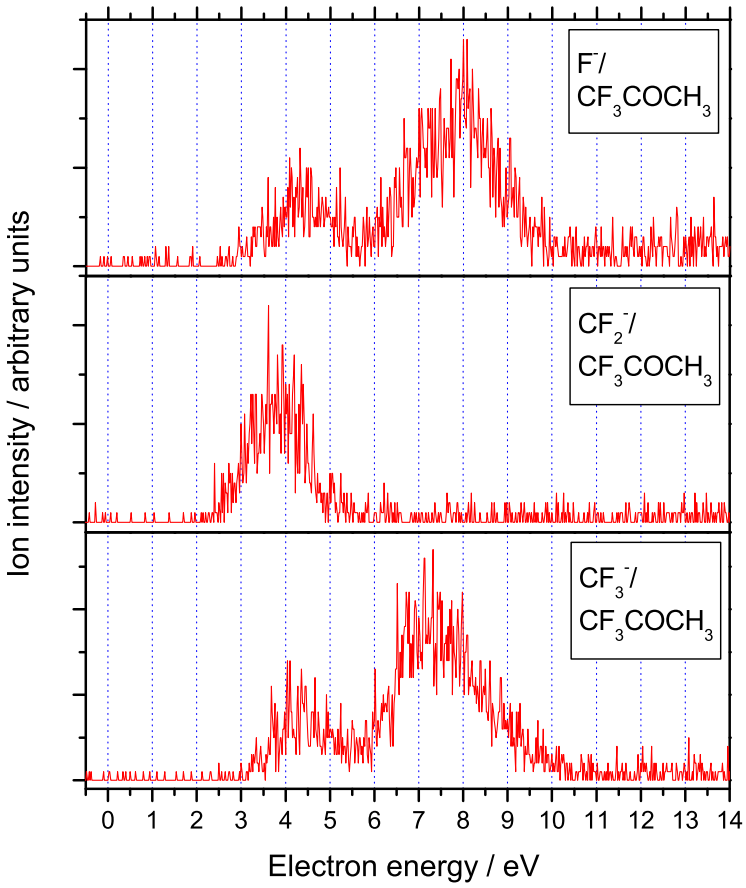

Figure C.3: Ion yield curves showing various fragments arising from electron attachment to gas phase trifluoroacetone (p=$2{\cdot}10^{-6}$ mbar, ΔE$\approx$200 meV)

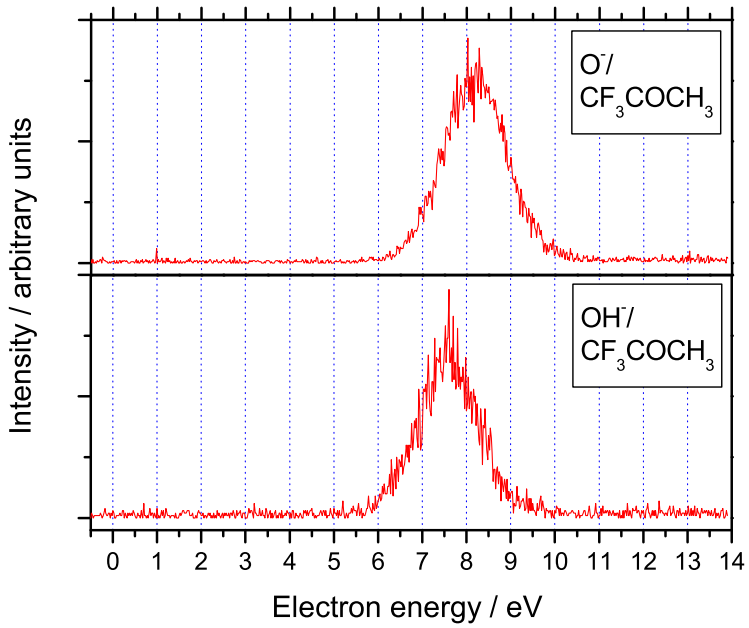

Figure C.4: Ion yield curves showing various fragments arising from electron attachment to gas phase trifluoroacetone (p=$1{\cdot}10^{-5}$ mbar, ΔE$\approx$240 meV)

C.2 Hexafluoroacetone

Reaction mechanisms leading to product formation:

$$CF_3COCF_3 \longrightarrow CF_3COCF_3^{-\#} \longrightarrow CF_3^- + CF_3CO \quad (C.13)$$
$$\longrightarrow CF_3CO^- + CF_3 \quad (C.14)$$
$$\longrightarrow CF_3COCF_3^- \quad (C.15)$$
$$\longrightarrow CF_3COCF_2^- + F \quad (C.16)$$
$$\longrightarrow F^- + CF_3COCF_2 \quad (C.17)$$
$$\longrightarrow C_3F_4^- + F_2O \quad (C.18)$$

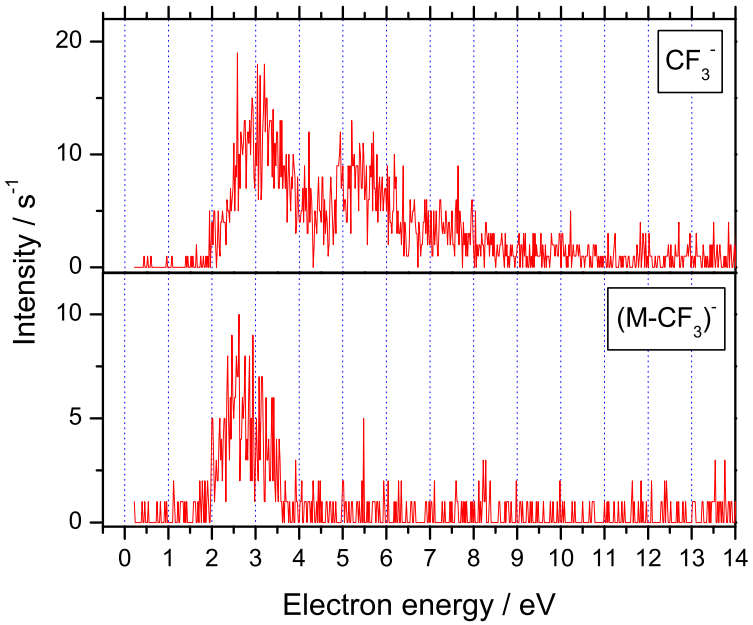

Figure C.5: Ion yield curves showing various fragments arising from electron attachment to gas phase hexafluoroacetone (p=$5{\cdot}10^{-6}$ mbar, ΔE$\approx$210 meV)

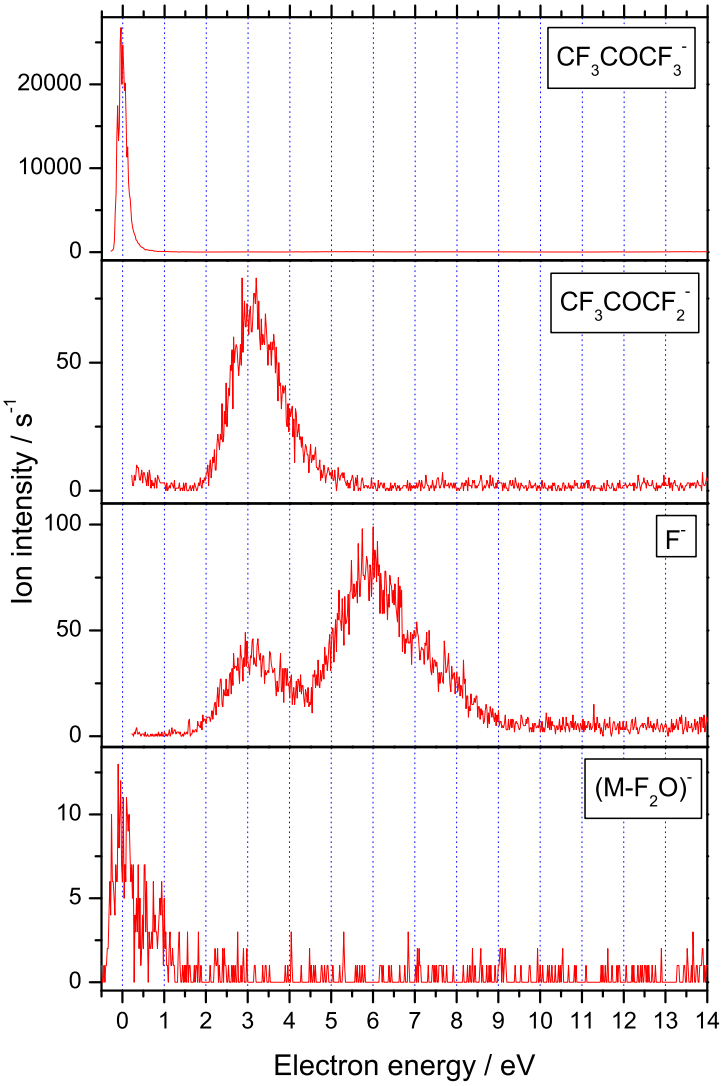

Figure C.6: Ion yield curves showing various fragments arising from electron attachment to gas phase hexafluoroacetone (p=$5{\cdot}10^{-6}$ mbar, ΔE$\approx$210 meV; the spectrum for $(M\text{-}F_2O)^-$: p=$2.4{\cdot}10^{-6}$ mbar, ΔE=180 meV)