Appendix A

E-gun Power Supply Circuit Diagram
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Appendix B

Transmission Efficiency of the KBr and ZnSe Optics
Figure B.1: Korth Kristalle GmbH
Appendix C

IRMPD Spectra of $V_2O_3^+$ and $V_3O_2^+$
C.1 $V_2O_3^+$

The IRMPD spectrum of $V_2O_3^+$ measured between 700 and 1400 cm$^{-1}$ is presented in Figure C.1. One absorption band is observed at 1061 cm$^{-1}$. The only dissociation channel is $VO$-loss. The width of the peak at 1061 cm$^{-1}$ is $\approx 32$ cm$^{-1}$, broader than the bandwidth of the laser which was on the order of 1% of the central laser frequency. The intensity of this peak is only 1% of the parent ion signal. This suggests a high dissociation energy, where a high number of photons is necessary for dissociation. No other bands outside this range were observed in the IRMPD spectrum.

![Figure C.1](image)

**Figure C.1:** The gas phase IRMPD spectrum of $V_2O_3^+$. The $VO_2^+$ fragment ion signal is monitored as a function of the laser frequency. The inset shows the B3LYP/TZVP structure of $V_2O_3^+$ (inset from Asmis et al.$^{39}$).

The dissociation energy $V_2O_3^+ \rightarrow VO_2^+ + VO$ was calculated by Calatayud et al.$^{40}$ by using the B3LYP functional and a value of 6.11 eV was predicted, which supports the proposed high dissociation energy of this cluster. According to this energy, 47 photons are necessary to dissociate the ion at 1061 cm$^{-1}$. 
Appendix C: IRMPD Spectra of $V_2O_3^+$ and $V_3O_2^+$

Figure C.2: Simulated IR absorption spectra based on scaled B3LYP/TZVP frequencies and relative intensities of the ground state (middle row) and an energetically low-lying isomer (top row) of $V_2O_3^+$. The lower panel shows the gas phase VPD spectrum of $V_2O_3^+ \cdot He_3$. The calculated frequencies were scaled by 0.9167 for the vanadyl modes and by 0.9832 for the $V-O-V$ modes and convoluted with a Gaussian line shape function, with a width that increases linearly with increasing frequency, in order to correct for the wavelength dependent bandwidth of FELIX. (Taken from Asmis et al.$^{39}$)
Appendix C: IRMPD Spectra of $V_2O_3^+$ and $V_3O_2^+$

Calculations and simulations of the IR spectra of two energetically low lying isomers were performed using the DFT/B3LYP approach and the TZVP basis set (collaboration with J. Sauer, Humboldt-Universität zu Berlin).\textsuperscript{39} Figure C.2 shows the lowest electronic state $^2A'$ and the first excited state $^2A''$, which is predicted 24.9 kJ/mol (0.26 eV) higher in energy.\textsuperscript{39} The IR spectra of both isomers show more than one band and both have a peak at $\approx 1040 \text{ cm}^{-1}$ which is close to the experimentally observed band in the IRMPD spectrum. In the IRMPD experiments, based on the predicted high dissociation energy, a high number of photons is required for dissociation (47 photons at experimentally observed band centered at 1061 cm$^{-1}$). In the low energy region of the spectrum an even higher number of photons is required for dissociation, hence it is not surprising that these bands cannot be observed. Furthermore, the transmitted laser pulse energy at $\approx 600 \text{ cm}^{-1}$ is reduced by $\approx 50\%$ due to the ZnSe optics, making the dissociation of the ions even more difficult. Since only one band is observed in the IRMPD spectrum, the comparison with the simulated spectra cannot attribute with certitude one of the isomers to the measured feature. For ions with such high dissociation energies, $He$ tagging helps to reduce the number of photons required for photodissociation. Thus, IR spectra measurements with the messenger atom technique should offer more information.\textsuperscript{39} In our group, the VPD spectrum of $V_2O_3^+ \cdot He_3$ was measured\textsuperscript{39} as well (see Figure C.2). The VPD spectrum reveals four bands. One of the peaks is located at 1044 cm$^{-1}$ and has the highest intensity. This band is close to the peak observed in the IRMPD spectrum located at 1061 cm$^{-1}$. The VPD spectrum shows additional three bands with lower intensities below 810 cm$^{-1}$. Comparison of the VPD and simulated spectra show a good agreement for the lowest electronic state $^2A'$. The same electronic state was predicted as the ground state by other calculations.\textsuperscript{38,40} The structure of this isomer is shown in the inset of Figure C.1. Based on the DFT calculation (collaboration with J. Sauer, Humboldt-Universität zu Berlin),\textsuperscript{39} the band at 1044 cm$^{-1}$ in the VPD spectrum is assigned to the $V = O$ mode. The other three bands are assigned to modes of the $V - O - V - O$ ring.

\textbf{C.2 $V_3O_2^+$}

The IRMPD spectrum of the $V_3O_2^+$ cation between 800 and 1450 cm$^{-1}$ is shown in Figure C.3. This IR spectrum represents the first successful experiment we performed at the FELIX facility. The spectrum reveals two absorption bands at 1185 and 1290 cm$^{-1}$. The only observed dissociation channel is $VO$-loss with the formation of the
Figure C.3: The gas phase infrared multiphoton photodissociation spectrum of the $V_3O_2^+$ cation. The $V_2O^+$ fragment ion signal is monitored as a function of the laser frequency.

A low signal of $V_2O^+$ fragment ion is observed in the trap previous to FELIX radiation, which was formed by collision induced dissociation with the He atoms during the thermalization process.

There are no prediction in the literature of the structure or simulations of the IR spectrum of this cation. The position of the bands, especially the band at 1185 cm$^{-1}$ is close to the frequency of the stretching motion of the oxo group in $V_2O_6^+$ cation (1160 cm$^{-1}$) observed in the VPD experiments performed in our group.$^{39}$ In contrast to $V_2O_6^+$, $V_3O_2^+$ is an oxygen-poor system and the presence of the oxo groups in the structure is doubtful. The second band at 1290 cm$^{-1}$ is unusually high in frequency. None of the systems presented here showed a band at so a high energy.