Molecular alignment of NH_3 following core electron excitation

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A multiple-ion coincidence momentum imaging spectrometer [1] is used to study the response of NH_3 to core-excitation in the vicinity of the N1s edge.

Core excitation to the 4a1 orbital (mixed valence-Rydberg character [2]), has previously been reported to result in excitation of the ammonia molecule to a dissociative core-hole state [3]. The main decay process of this state was determined to be Auger electron emission; however decay via ultra-fast dissociation on the timescale of the core-excited state was also observed to occur and was found to be enhanced as the exciting photon energy was detuned to higher energies on the repulsive potential.

In this work our main focus is to investigate fragmentation following core-excitation of NH_3 to the $N1s^{-1} \rightarrow 4a1$ state.

Upon photoexcitation the NH_3 molecule is aligned with respect to the polarisation vector of the incident radiation. If the axial recoil-approximation holds the molecular orientation before excitation is expected to be reflected in the angular distribution of the fragment ions. However, when the photon energy is detuned across the N1s → 4a1 resonance we observe a change in the alignment of the fragment ions, i.e. our experimental data suggests that changes in the geometry of NH_3 arise when the photon energy is detuned to higher photon energies away from the center resonance energy.

Here we discuss these geometric changes for the 2-body fragmentation channel NH_2^+/H^+ and the possible mechanism by which these changes occur. It has previously been observed that the dissociation process for core-excited ammonia is dependent on vibrational motion in the core-excited state [4] with both symmetric stretching, ν_1 and bending ν_2 modes playing a role. It therefore seems likely that the geometric rearrangement suggested in our data is due to such a vibrational motion accompanied with the rearrangement of a proton before fragmentation occurs.

References:
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