THERMAL PROPERTIES OF CLUSTERS AND MOLECULES

- Experiments on evaporation, thermionic emission, and radiative cooling

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THERMAL PROPERTIES OF CLUSTERS AND MOLECULES
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ABSTRACT

This thesis presents experiments performed on clusters and molecules, where the three channels of unimolecular decay have been studied. Evaporation from protonated and negatively charged water cluster have yielded size dependent heat capacities, where the smallest sizes with fewer than 21 molecules show a heat capacity similar to bulk ice whereas clusters with molecules between 21 and 300 have a heat capacity in between that of ice and liquid water. The increase in heat capacity per added molecule in the cluster indicates that the intramolecular degrees of freedom are frozen at the temperatures in the experiment ($T \approx 160$ K). Experiments on small mixed water-ammonia clusters resulted in relative evaporation fractions for sizes between a total of three to eleven molecules, and 16 molecules. The clusters were found to evaporate predominantly water molecules except for clusters containing six or more ammonia molecules. Relative evaporation rates for $\text{D}_2\text{O}$, HDO, and $\text{H}_2\text{O}$ were measured for $\text{NH}_4^+(\text{H}_2\text{O})_4$ with zero to six deuteriums interchanged with the hydrogens. The relative rates were found to be $1 : 0.71 : 0.56$.

Absolute time-dependent cooling rates for hot $\text{C}_{60}^-$ were obtained in an electrostatic storage ring with single photon absorption experiment. The cooling of the molecule could be divided into a thermionic emission part and a radiative part, where the crossover between the two occurred at 5 ms, after which radiation was shown to be the dominant cooling channel. The spontaneous decay profiles were used to extract decay parameters of the large organic anion zinc phthalocyanine (ZnPc). Numerical simulations of the decay process show good agreement with measurements, using parameters derived from an analytical approximation also used for fullerenes. Photoabsorption experiments were performed on the much smaller $\text{C}_5^-$, showing the presence of strong radiative cooling. The cooling rate was determined by the dependence of the photoinduced neutralization yield vs. photon energy and laser firing time.

Keywords: water clusters, fullerenes, unimolecular decay, evaporation, thermionic emission, radiative decay, cooling rates, heat capacities