Rotationally cold (> 99% J = 0) OH\(^{-}\) molecular ions in a cryogenic storage ring

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Abstract. We store a 10 keV OH\(^{-}\) ion-beam at 13.5 ± 0.5 K in one of the DESIREE storage rings. Using photodetachment thermometry we measure the effective relative photodetachment cross section at different storage times and determine the rotational temperature of the ions to be 13.4 ± 0.2 K in agreement with the macroscopic temperature. A model cross section in the threshold range taking into account the formation of excited neutral OH molecules is calculated as a function of rotational temperature in order to justify the use of the rotational thermometry method developed earlier by the group of Roland Wester at Innsbruck University in the present case. In addition, we apply a selective photodetachment technique to produce an ion beam with more than 99% of the ions in the rotational ground state. The intrinsic lifetime of the J = 1 rotational level is measured to be 145 ± 28 s.

1. Introduction

In experiments on molecular ions it would be of great advantage if all ions are populated in the same quantum state. However, most available ion sources usually produce hot ions occupying a large number of vibrational and rotational states. To relax these degrees of freedom many experiments have been performed where ions are stored in traps and storage rings. Relaxation of the vibrational degrees of freedom has been studied extensively in room temperature experiments with storage times on the order of tens of seconds. For rotational relaxation the time scales are much longer [1] and at room temperature, a large number of rotational states are occupied. Recent development in cryogenic storage techniques [2–5] allows for ion-beam storage times of hours [6] and has opened up new possibilities to study rotationally cold molecular ions.

In this work we present a study of rotational relaxation of the OH\(^{-}\) molecular ion using the photodetachment thermometry technique developed by Otto et al. [7] in one of the DESIREE storage rings. The hydroxyl anion, OH\(^{-}\), is a suitable molecular ion for photodetachment studies with its well separated rotational levels and large rotational constant \(B = 18.7354(16)\) cm\(^{-1}\) [8]. Several experiments set out to study cold OH\(^{-}\) has been performed recently. Otto et al. [7] performed photodetachment thermometry on OH\(^{-}\) stored in a 22-pole radiofrequency trap using buffer gas cooling with He. They found that the rotational temperature agreed well with...
the macroscopic temperature of their environment except at the lowest temperatures where the rotational temperature always remained higher for reasons that were not clear at the time [7]. Possible explanations for the lack of cooling to below about 20 K in the buffer gas trap was further investigated by Endres et al. [9] but again no firm conclusion was reached. Recently, Meyer et al. [10] studied the rotational relaxation of OH$^-$ in the Cryogenic Storage Ring (CSR) and found the effective radiative temperature of the blackbody field in the ring to be 15.1 ± 0.1 K although the main part of their ring was substantially colder than this. They also measured the intrinsic lifetime of the first three excited rotational levels of OH$^-$ [10].

2. Experiment
Here, we use one of the DESIREE storage rings, shown schematically in Figure 1, to study the cooling of OH$^-$ ions in a 10 keV beam. The storage rings are contained in a single cryogenically cooled chamber at 13 ± 0.5 K with a residual gas density of $10^4$ H$_2$ per cm$^3$. The OH$^-$ ions are produced in a Cesium sputter ion source, accelerated to 10 keV and mass selected by a bending magnet. A bunch of 1-10 million ions is injected into the ring. During the present experiment, a 1/e storage lifetime of approximately 10 minutes is achieved. Two laser and two detection systems are used. The first is a tunable cw Ti:Sapphire laser overlapping the ion beam collinearly in the straight section on the injection side of the ring. The neutral OH produced from photodetachment hit a glass plate emitting secondary electrons which are accelerated and detected by an MCP. The second system consists of a tunable pulsed OPO interacting perpendicularly with the ion beam on the opposite straight section. The neutral particles are detected by an Imaging Detector consisting of a triple stack MCP and phosphor screen viewed by a CMOS camera and a photomultiplier tube.

Figure 1. Schematic of one of the DESIREE storage rings. Lasers and detectors for rotational thermometry and manipulation studies are indicated.

3. Photodetachment cross section
The effective relative photodetachment cross section is modeled by [7]

$$\sigma_{\text{eff}}(E, T) \propto \sum_{J''} \sum_{J'} I(J'', J') P(J'', T)(E - \epsilon_{J'', J'})^p$$

(1)

where $E$ is the energy of the incoming photon, $J''$ is the initial rotational state of the ion, and $J'$ is the final rotational state in the neutral molecule. $I(J'', J')$ is an intensity factor for the transition $J'' \rightarrow J'$ [8, 11], $P(J'', T)$ is the population in level $J''$, $\epsilon_{J'', J'}$ is the threshold energy for the photodetachment transition, and $p = 0.28$ is an exponent for the cross section near threshold [12]. The allowed transitions are given by electric dipole selection rules $\Delta J = -3/2, -1/2, +1/2, +3/2$ for the case of OH$^-$ [8, 11]. The effective relative photodetachment cross section is dependent on the populations $P(J'', T)$ and hence the temperature $T$ of the ions. Assuming thermal equilibrium the populations $P(J'', T)$ are given by $P(J, T) \propto (2J + 1) \exp [J(J + 1)B/k_B T]$ where $k_B$ is the Boltzmann constant. Using the experimental thresholds $\epsilon_{J'', J'}$ [13], $\sigma_{\text{eff}}(E, T)$ can be modeled using Equation 1. Figure 2 shows calculated $\sigma_{\text{eff}}(E, T)$ curves for photon energies, $E$, near the electron affinity of OH for different rotational temperatures, $T$. At high $T$...
a large number of transitions to excited states in the neutral OH are contributing to $\sigma_{\text{eff}}^\text{pd}(E, T)$. As can be seen in Figure 2, $\sigma_{\text{eff}}^\text{pd}(E, T)$ is completely dominated by three transitions (from $J'' = 0, 1, 2$ to the ground state $J' = 3/2$ of OH) at $T = 15$ K.

To determine the rotational temperature of the ions we measure $\sigma_{\text{eff}}^\text{pd}(E)$ as a function of photon energy using the cw laser, correcting for the Doppler shift resulting from the collinear geometry. The experiment is repeated for different storage times as shown in Figure 3. At photon energies below 1.8137 eV the measured $\sigma_{\text{eff}}^\text{pd}(E)$ is constant which is attributed to contamination from $^{17}\text{O}^-$ in the ion beam. The differences in levels between the measurements in this energy range are due to variations in ion source conditions. Three thresholds are clearly distinguishable in the data which is consistent with the model in Figure 1. To extract the populations $P(J'')$ Equation 1 is fitted to the data using the three dominant transitions and a constant to account for the $^{17}\text{O}^-$ contamination. After 10 minutes of storage $P(0) = 93.9 \pm 0.2 \%$ and under the assumption of thermal equilibrium this corresponds to a temperature of 14.1 $\pm$ 0.2 K.

![Figure 2. Modeled $\sigma_{\text{eff}}^\text{pd}(E, T)$ for different rotational temperatures. As the temperature decreases transitions from $J'' = 0, 1, 2$ to the ground state $J' = 3/2$ dominates.](image1)

![Figure 3. Measured $\sigma_{\text{eff}}^\text{pd}(E)$ for 50, 300 and 600 s of storage. The thresholds for the dominating transitions are marked by dashed lines. The curves are fits to Equation 1.](image2)

### 4. Probing as function of time and selective photodetachment

To determine if thermal equilibrium is reached the populations need to be measured for longer times. From the measurements described above it is clear that $P(\geq 2)$ becomes negligible at long storage times, thus for this measurement it is sufficient to consider $J = 0$ and $J = 1$. Using the pulsed OPO two measurements are made, at $\lambda = 677$ nm ($E = 1.8314$ eV) and $\lambda = 679$ nm ($E = 1.8260$ eV) for photodetachment of $J \geq 0$ and $J \geq 1$ respectively. Since the form of $\sigma_{\text{eff}}^\text{pd}(E)$ is known from Equation 1 the populations $P(0)$ and $P(1)$ can be extracted. The triangles in Figure 4a show $P(1)$ as a function of storage time.

In addition to probing the rotational relaxation of the ions we also apply the cw laser at $\lambda = 679$ nm for selective photodetachment of ions with $J \geq 1$ (diamonds in Figure 4a). The result is a faster decay and a lower equilibrium population than without the depletion laser. The circles in Figure 4a show a measurement where the cw laser is turned on initially but switched off after some time causing repopulation of the $J = 1$ level due to interaction with the surrounding blackbody radiation. Figure 4b shows a similar measurement where the overlap between the laser and ion beams is better optimized resulting in a more efficient depletion. The lowest $P(1)$ in this case is $0.9 \pm 0.1 \%$ and $> 99\%$ of the ions are in the rotational ground state.
state. There is a difference in the asymptotic value of $P(1)$ between the spontaneous decay and after repopulation. This is because the cw laser induce photodetachment of $^{17}\text{O}^-$ and thus removes this beam contamination permanently. The repopulation measurement provides a better estimate of the asymptotic $P(1)$ and the final result is given by the weighted average of the two repopulation measurements of $5.1 \pm 0.3\%$, which yields a temperature of $13.4 \pm 0.2 \text{ K}$ of the stored ensemble of OH$^-$ ions. Furthermore by considering the repopulation measurements in a $13.4 \pm 0.2 \text{ K}$ blackbody radiation field, we extract the intrinsic lifetime of the $J = 1$ rotational level $A_{10}^{-1} = 145 \pm 28 \text{ s.}$ [14]

![Figure 4. Fractional population in $J = 1$ as a function of storage time. (a) Triangles: spontaneous relaxation. Diamonds: cw laser depleting $J \geq 1$. Circles: cw laser depleting $J \geq 1$ until $440$ ($380$) s, $J = 1$ repopulates due to interaction with the blackbody field. (b) A measurement with improved overlap between the cw laser and ion beam.](image)

5. Conclusions

Using photodetachment thermometry we have measured the asymptotic rotational temperature of the OH$^-$ ion beam to be $13.4 \pm 0.2 \text{ K}$, which demonstrates thermal equilibrium with the $13.5 \pm 0.5 \text{ K}$ storage ring. Using selective photodetachment we have produced an ion beam with $\geq 99\%$ of the ions in the rotational ground state. This technique will be beneficial for studies of ion interactions with photons, electrons, neutrals and other ions, as well as action spectroscopy of ions at interstellar temperatures. We measure the intrinsic lifetime of the $J = 1$ rotational level to be $145 \pm 28 \text{ s}$, which is about two standard deviations shorter than the corresponding result of Meyer et al. [10].

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