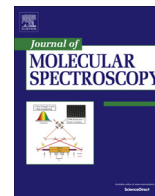




Contents lists available at ScienceDirect

Journal of Molecular Spectroscopy

journal homepage: www.elsevier.com/locate/jms



Incomplete rotational cooling in a 22-pole ion trap

E.S. Endres, G. Egger, S. Lee, O. Lakhmanskaya, M. Simpson, R. Wester*

Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, Technikerstr. 25, 6020 Innsbruck, Austria

ARTICLE INFO

Article history:

Received 27 September 2016
In revised form 12 December 2016
Accepted 19 December 2016
Available online xxxx

Keywords:

Photodetachment spectroscopy
Multipole ion trap
Buffer gas cooling
Rotational temperatures

ABSTRACT

Cryogenic 22-pole ion traps have found many applications in ion-molecule reaction kinetics and in high resolution molecular spectroscopy. For most of these applications it is important to know the translational and internal temperatures of the trapped ions. Here, we present detailed rotational state thermometry measurements over an extended temperature range for hydroxyl anions in He, HD, and H₂. The measured rotational temperatures show a termination of the thermalisation with the buffer gas around 25 K, independent of mass ratio and confinement potential of the trap. Different possible explanations for this incomplete thermalisation are discussed, among them the thermalisation of the buffer gas, room temperature blackbody radiation or warm gas entering the trap, and heating due to energy transfer from rotationally excited hydrogen molecules.

© 2016 Elsevier Inc. All rights reserved.

1. Introduction

In recent years, collisional cooling of trapped ions by buffer gas, usually consisting of a cryogenic noble gas, has been established as a standard technique to cool molecular ions in multipole traps [1]. This has opened up a diverse field of research on rate coefficients of ion-molecule reactions of astrochemical relevance [2,3], cross sections for photodetachment of interstellar ions [4,5] and high resolution molecular spectroscopy [6–9]. As sensitive spectroscopic probes laser-induced reactions [10], desorption of a tagged atom [11,12], and photodetachment [9] have been implemented. Quantum state-selected reactions have been studied at low temperatures [13] and inelastic collision rate coefficients have become accessible [14]. Furthermore, buffer gas rotational cooling has been combined with sympathetic cooling of the translational motion via laser-cooled atomic ions [15].

For experiments with trapped molecular ions, precise knowledge of the translational temperature of the ions as well as of the internal state distribution is desirable. Translational temperatures of trapped ions can be determined via high resolution spectroscopy resolving Doppler profiles. These techniques require narrow bound-bound transitions and thus are only applicable if a suitable transition and an efficient probing scheme is available [10,7]. Several simulation studies of the thermalisation process in multipole ion traps have been carried out [16–19]. Up to now experiments regularly find larger ion temperatures than predicted by simulations (see cf. [7]).

Here we present negative ion photodetachment measurements undertaken in order to investigate the thermalisation of the ions' rotational temperature and possible heating effects. This work is based on the rotational temperature diagnostics by near-threshold photodetachment that our group has demonstrated previously [20]. Precise internal state thermometry measurements of OH[−] in He and H₂, and OD[−] in HD have been carried out over a temperature range of more than 100 K. Furthermore, the rotational temperature was measured for different settings of the trapping potential. The effect of room temperature gas and of blackbody radiation entering through the openings of the trap are discussed. Finally, an indirect measurement is presented to probe the thermalisation of the buffer gas with the trap temperature.

2. Theoretical method

The excess electron of a negative ion in its internal ground state is bound with the energy of the electron affinity of the neutral molecule. If the anion is in an excited rotational state the electron binding energy is correspondingly reduced. A photon whose energy exceeds this electron binding energy can detach the electron. The total photodetachment cross section near threshold can be written as [20]:

$$\sigma_{PD}(h\nu) \propto \sum_J \frac{p(J, T)}{g_J} \left[\sum_b I_{Jb} \cdot \Theta(h\nu - \epsilon_{Jb})(h\nu - \epsilon_{Jb})^p \right]. \quad (1)$$

The outer sum is over all considered rotational states J of the anion and the inner sum over all possible transitions of the respective J level to different neutral states. $p(J, T)$ is the population of the rota-

* Corresponding author.

E-mail address: roland.wester@uibk.ac.at (R. Wester).

tional level J which weights the cross sections from each state. I_{jb} are the Hönl-London factors giving the relative transition intensities [21,22]. Θ is the Heaviside function taking only transitions above threshold into account, $h\nu$ is the photon energy and ϵ_{ji} is the energy threshold of the transition. $g_j = 2J + 1$ is the degeneracy of the rotational level which is by definition included in the Hönl-London factors and the $p(J, T)$. The degeneracy must not be considered twice and is therefore removed by explicitly dividing the population by g_j . Finally p determines the shape of the individual cross sections.

For the photodetachment of OH^- it has been shown that $p = 0.28$ works well [23]. In the experiment, photodetachment induces a loss rate for the trapped ions, k_{PD} , which is proportional to the photodetachment cross section of the anion σ_{PD} and the laser power P_L ,

$$k_{PD} \propto P_L \cdot \sigma_{PD}. \quad (2)$$

Just as the population $p(J, T)$ depends on the rotational temperature, the photodetachment cross section $\sigma_{PD}(h\nu)$ also changes with temperature. By measuring the loss rate at different transition frequencies, the rotational temperature of anions can be determined using Eq. (1).

3. Experimental setup and methods

A description of the employed 22-pole radiofrequency ion trap setup can be found in Ref. [4,20] and only a brief account is given below. The hydroxyl molecular anions are produced in a pulsed plasma discharge source from a helium-water mixture. A time of flight mass spectrometer, based on Wiley-McLaren configuration, is used for mass selection prior to loading the ions into the cryogenic 22-pole rf trap. The multipole trap creates a radial confinement potential by applying an alternating electric field on the rods. The longitudinal trapping is achieved via a constant voltage on the entrance and exit endcaps. The multipole trap features a large field free region in the radial center with a steep rising potential towards the rods. This allows an efficient trapping with little influence from perturbing external fields [24].

The trap is built inside a copper housing, which has two openings to load and unload ions. The copper housing acts as a thermal shield and is mounted on a closed-cycle refrigerator, which achieves temperatures down to about 9 K. The temperature of this thermal shield, i.e. the temperature of the trap (T_T), can be controlled between 9 K and room temperature using resistive heaters mounted at the bottom of the trap. This temperature is measured with two commercial temperature diodes with a precision below 100 mK and a typical temperature difference between the top and the bottom of the trap of one percent.

The buffer gas that is injected into the trap is expected to thermalise with the thermal shield within a few collisions and subsequently cool the trapped anions. In an ideal case the anions should reach the temperature of the buffer gas (T_{bg}) which is also equal to the temperature of the thermal shield. Due to the thermal shield and the low temperature, the buffer gas density inside the trap is higher than in the surrounding vacuum chamber. The density inside the trap is measured with a gas species-independent capacitive pressure gauge, which is held at room temperature and attached to the trap via a gas tube. This yields the pressure p_{out} , from which the density ρ inside the trap is calculated using

$$\rho = \frac{p_{out}}{k_B \cdot \sqrt{T_{out} \cdot T_T}}, \quad (3)$$

based on the ideal gas approximation in the low-density molecular flow regime. T_{out} is the ambient temperature of the setup and k_B is the Boltzmann factor.

For the measurements, the 22-pole trap is loaded with a packet of OH^- ions from the source. Buffer gas densities around $10^{13}/\text{cm}^3$ are applied, which guarantees several thousand elastic collisions and several hundred rotationally inelastic collisions per second [25,14]. Therefore steady-state conditions are reached within several milliseconds. In the trap the ions are exposed to the photodetachment laser (Sirah Matisse DR ring dye laser, employed power up to 100 mW), which probes the rotational population without perturbing it. The ions are then extracted from the trap and detected on a microchannel plate detector. Power-normalized photodetachment loss rates near threshold are obtained by repeating the measurements for different exposure times, ranging between few hundred milliseconds and several seconds, and for different laser frequencies. These rates, which range between 0.5 and 7.5 per second, are fitted to the detachment cross section described by Eq. (1), which yields the rotational temperature of the trapped ions [20]. Since the photodetachment rates are much smaller than the inelastic collision rates, the rotational populations are not significantly modified by the photodetachment laser.

4. Results

Experiments were conducted for trap temperatures between $T_T = 9$ K and 120 K. For each selected temperature T_T , internal state thermometry measurements were done to obtain the rotational temperature T_{rot} of OH^- anions in He buffer gas. The resulting rotational temperatures are plotted in Fig. 1 against the trap temperature (red circles). Above 40 K the rotational temperature follows the trap temperature with a reasonably good agreement. But below 40 K T_{rot} always remains larger than T_T and levels off at about 25 K. This represents a clear decoupling of the rotational temperature from the trap wall temperature at temperatures below 25 K. These results qualitatively confirm the results that have been found earlier by Otto et al. [20] and extend them to higher temperatures. The lowest rotational temperatures measured in the present work are slightly below the lowest temperature measured there.

To obtain more insight into this temperature decoupling we have varied the ion-to-neutral mass ratio by moving to hydrogen buffer gas. As seen in Fig. 1 (green triangles), the OH^- rotational temperature in H_2 shows an even higher rotational temperature at low buffer gas temperatures than if helium buffer gas is used. The experiments have been performed using normal- H_2 and, as discussed below, we expect these results to be influenced by rotationally excited ortho- H_2 molecules. When mixed-isotope HD buffer gas is employed instead, the rotational temperature agrees

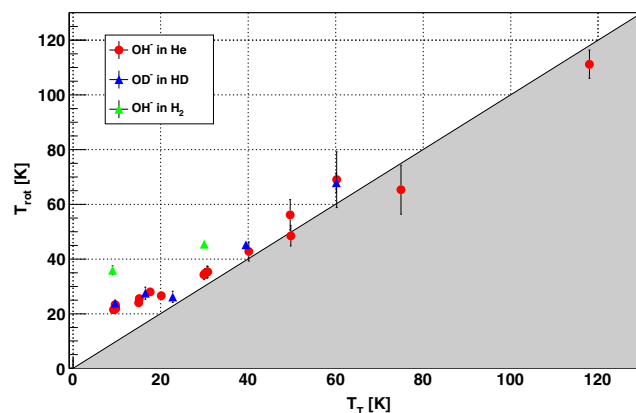


Fig. 1. Ion rotational temperature T_{rot} versus trap temperature T_T for three different neutral collision partners. The black solid line shows the ideal case for $T_{rot} = T_T$.

Download English Version:

<https://daneshyari.com/en/article/5414158>

Download Persian Version:

<https://daneshyari.com/article/5414158>

[Daneshyari.com](https://daneshyari.com)