Probing internal excitation of trapped $O^+(^4S, ^2D, ^2P)$ ions by reaction with N_2

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When the atomic oxygen cation O^+ takes part as a reactant or a product in experimental studies, electronically exited states may play a significant role. For investigation of ion molecular reactions, a cryo-cooled radiofrequency ion trap is used. Molecular nitrogen was chosen as a monitor gas for probing a presence of long-lived excited $O^+(^2D, ^2P)$ in an ensemble of ions confined in the radiofrequency trap. The fraction of electronically excited ions was determined. The rate coefficient of the reaction of $O^+(^4S)$, the electronic ground state, with nitrogen molecule was measured at low temperatures. The reaction rate coefficient at 61 K was evaluated as $(7.5 \pm 1.5)\times10^{-12}$ cm^3 s^{-1}. It confirms an increase of the coefficient at low temperatures.

Introduction

The atomic oxygen cation O^+ plays a significant role in numerous environments such as planetary ionospheres or technological plasmas. The existence of long-lived $O^+(^2D, ^2P)$ metastable states may be important in many situations. For states $^2D_{3/2}$ and $^2D_{5/2}$ the lifetimes are in the order of hours and for states $^2P_{1/2}$ and $^2P_{3/2}$ in seconds [1]. The excited states carry electronic energy of 3.3 eV and 5.0 eV, respectively. The only exoergic channel for reaction of O^+ in ground state with N_2 is formation of NO^+ (1). The charge transfer (2) is endoergic.

$$O^+(^4S) + N_2 \rightarrow NO^+ + N, \quad \Delta H = -1.13 \text{ eV} \qquad (1)$$

$$O^+(^4S) + N_2 \rightarrow N_2^+ + O, \quad \Delta H = +1.96 \text{ eV} \qquad (2)$$

For the excited states $O^+(^2D, ^2P)$ both reactions are exoergic and for reaction (2) the rate coefficient is close to Langevin rate in the order of 10^{-10} cm^3 s^{-1} [1, 2]. The charge transfer (2) from excited O^+ ion to N_2 is dominant channel.

We used these reactions as a probe for excited states of O^+ ions confined in the radiofrequency trap. In addition we confirmed steep increase of the rate coefficient of the reaction (2) with decreasing temperature [1, 3].

Experiment

A 22-pole radiofrequency ion trap was used for this study. It was placed on a cryo-cooler in an ultra-high vacuum system. The measuring procedure was based on iterative filling of the trap with a well-defined number of primary ions O^+. They react with N_2 and the contents of the trap were analysed after chosen times by means of a quadrupole mass spectrometer with micro-channel plate detector. Additional details may be found in reference [4] and references therein. The O^+ ions were produced in separated ion source by electron impact from N_2O molecule to reduce the ratio of exited states in comparison with a production from O_2.

From the number of N_2^+ we may evaluate a fraction of exited states of O^+ as (5 ± 1)% for electron impact energy E_e = 75 eV and (10 ± 2)% for 145 eV, see Figure 1.

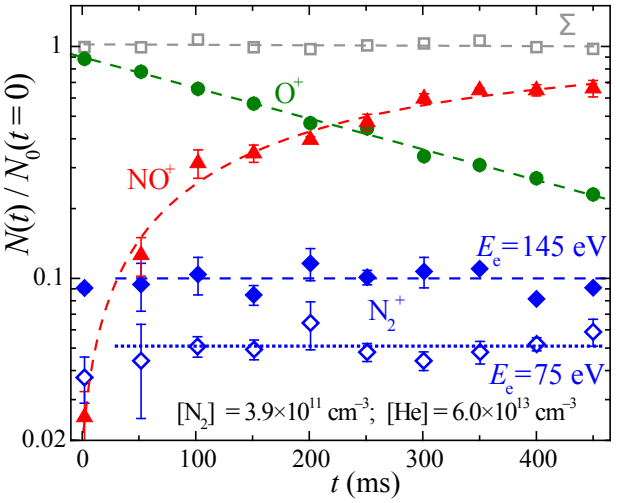

Fig. 1: Evolution of normalized number of ions in rf trap at temperature 61 K. From the increase of NO^+ we may determine the rate coefficient of the reaction (1) $(7.5 \pm 1.5)\times10^{-12}$ cm^3 s^{-1}. The number densities of the N_2 reactant and helium buffer gas are indicated in the figure.

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