

The reaction of O⁺ with HD at low temperatures

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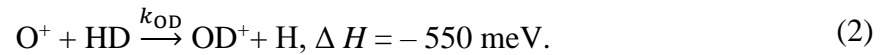
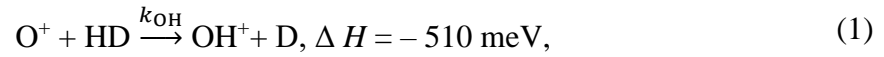
Abstract

A rate coefficient and a branching fraction of a reaction of O⁺ with HD have been studied using a 22-pole radiofrequency trap apparatus at temperatures common in interstellar clouds. Exothermic channels of production of OH⁺ and OD⁺ have been studied. Moreover, a minor endothermic channel of production of H⁺ has been observed. This article presents results of measurements of the title reaction at 26 K.

Introduction

The present study is focused on the reaction of O⁺ with HD. This reaction is a source of OH⁺ and OD⁺ in interstellar space. Ions OH⁺, H₂O⁺, and H₃O⁺ have been detected in many different interstellar media [1, 2, 3, 4]. In our group, we studied reactions leading to the origin of these ions [5, 6].

The reaction of O⁺ with HD has two exothermic channels



The total reaction rate coefficient k of both channels (1) and (2) is the sum of rate coefficients k_{OH} , k_{OD} of both channels of the reaction.

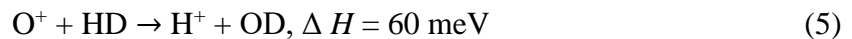
$$k = k_{\text{OH}} + k_{\text{OD}} \quad (3)$$

We define an isotopic branching fraction of OH⁺ as

$$f = k_{\text{OH}}/k. \quad (4)$$

The total reaction rate coefficient k and the isotopic branching fraction f of OH⁺ have been measured as a function of temperature using a 22-pole ion trap apparatus.

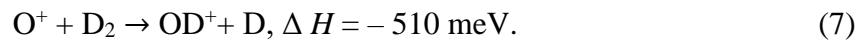
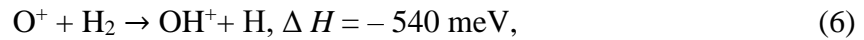
We have also considered the third additional channel [7].



Ion H⁺ can react with HD by the ternary associative reaction and produce H₂D⁺ ion. Other isotopes of H₃⁺ can be produced by the isotopic exchange of H₂D⁺.

The reactions (1) and (2) were studied theoretically and experimentally [7, 8, 9, 10]. However, these measurements were done at temperatures above 90 K [9].

For comparison, we present enthalpy of other isotopic variations of the reaction of O^+ with HD at 0 K



The reaction (6) has been studied using the 22-pole ion apparatus, results of the study of the reaction have been already published [5]. For a better understanding of the reaction process, we have decided to measure another isotopic variation of the reaction (6).

Experimental

The reaction of O^+ with HD was studied using the 22-pole radiofrequency trap apparatus. Technical details are described in [11]. The trap temperature can be stabilized at temperatures down to 10 K. We estimate a collisional temperature of this study as $T = T_{22PT} + 5 \text{ K}$ with an uncertainty of $\pm 5 \text{ K}$, T_{22PT} is the trap temperature. Discussion about the temperature of the experiment can be found in [12].

O^+ ions were produced from N_2O in an electron impact storage ion source. The ions were precooled in the storage ion source, selected by a linear quadrupole mass filter and injected into the 22-pole ion trap. The 22-pole ion trap consists of two sets of 11 rods. A radiofrequency voltage was applied to these rods. The RF voltage created an inhomogeneous radiofrequency field confining the ions in a radial direction. Potentials applied to the entrance and to the exit of the trap confined ions in an axial direction. The trap is surrounded by a copper box, which is mounted onto the cold head of the helium refrigerator with a closed-cycle. The trap was directly filled by neutral gases. Helium acts as a buffer gas and HD with the declared purity 97% acts as a neutral reactant. Number densities of He were in order 10^{13} cm^{-3} . Number densities of HD were in order from 10^{10} cm^{-3} to 10^{11} cm^{-3} . In the trap, the ions were cooled by collisions with helium and reacted with the neutral reactant. After a chosen trapping time the trap was opened, ions were selected by a quadrupole mass analyser and detected by an MCP detector. The result of a typical measurement can be seen in Figure 1.

First results

The reactions (1), (2) and (5) took place in the trap. Products of the reactions can also react and produce tertiary ions. Production of H^+ was not involved in a fit model since the low numbers of detected H^+ were negligible. The observed ion H^+ originates from the reaction (5) by the reaction of metastable O^+ .

The model which we used for describing a time evolution of ion numbers and for fitting our results is a system of differential equations:

$$\frac{dN_{O^+}}{dt} = -(r_{OH} + r_{OD})N_{O^+} \quad (8)$$

$$\frac{dN_{OH^+}}{dt} = -(r_{H_2O} + r_{OHloss})N_{OH^+} + r_{OH}N_{O^+} \quad (9)$$

$$\frac{dN_{OD^+}}{dt} = -r_{ODloss}N_{OD^+} + r_{OD}N_{O^+} \quad (10)$$

$$\frac{dN_{H_2O^+}}{dt} = -r_{H_3O}N_{H_2O^+} + r_{H_2O}N_{OH^+} \quad (11)$$

All r_{OH} , r_{OD} , r_{H_2O} , r_{OHloss} , r_{ODloss} , and r_{H_3O} are reaction rates of corresponding processes. The corresponding rate coefficients of the reactions (1) and (2) can be calculated as

$$k_{OH} = r_{OH}/[HD] \quad (12)$$

and

$$k_{OD} = r_{OD}/[HD], \quad (13)$$

respectively. $[HD]$ is the number density of neutral reactant HD. Free parameters of the model are all mentioned rates and initial numbers of ions $N_{O^+}(t=0)$, $N_{OH^+}(t=0)$, $N_{OD^+}(t=0)$, and $N_{H_2O^+}(t=0)$. As can be seen in Figure 1, other ions were observed. However, it is not necessary to involve them in the fit model for the study of reactions (1) and (2). Since ions OD^+ and H_2O^+ have the same mass number, we have to fit the total number of mass 18 ions

$$N_{18} = N_{OH^+} + N_{OD^+}. \quad (14)$$

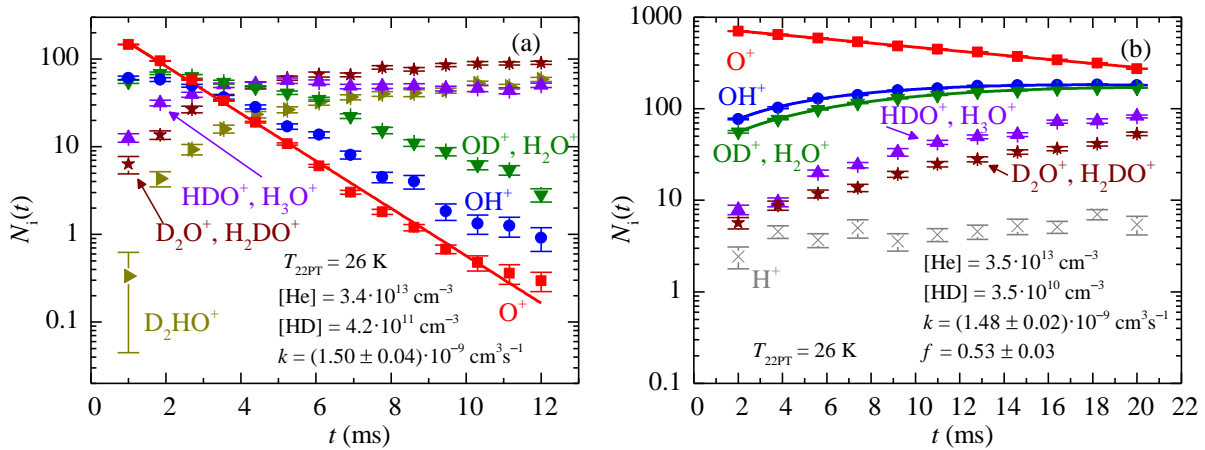


Figure 1: Example of time evolution of numbers of O^+ , OH^+ , OD^+ and H_2O^+ , HDO^+ and H_3O^+ ions at low trap temperatures. In our experiment, we are not able to distinguish ions of the same mass number from each other. Other products such as HDO^+ , H_3O^+ , D_2O^+ , H_2DO^+ , D_2HO^+ , and H^+ are not involved in the fit model. Presented errors are statistical errors from fits. The systematic uncertainty of the experiment is 20% and it is caused mainly by an uncertainty of a determination of number density of HD. (a) Measurement with a high number density of HD. By fitting a decay of O^+ we can get the total reaction rate coefficient k . (b) Measurement with a low number density of HD. The production of OH^+ and OD^+ can be observed. The total reaction rate coefficient k and also k_{OH} , k_{OD} can be determined.

From equation (8) it is obvious, that the total rate coefficient can be found out just from the evolution of N_{O^+} . Sufficiently high values of $[HD]$ are necessary for higher accuracy

of the determination of [HD] from the measured HD pressure. However, in this case, the reaction is too fast for observing the production of OH⁺ and OD⁺ ions, see Figure 1(a). Low [HD] is necessary for the determination of the branching fraction f , see Figure 1(b). By combining measurements at low and high [HD], we can obtain the total reaction rate coefficient k and the branching fraction f .

At present, we continue measuring at different temperatures. The result of our study will be a temperature dependence of the total reaction rate coefficient k and temperature dependence of the branching fraction f from measurement with lower [HD] and higher [HD], respectively.

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