Reactions of O\(^-\) with D\(_2\) at temperatures below 300 K

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Abstract. The reaction of O\(^-\) anions with molecular deuterium D\(_2\) has been studied experimentally using a cryogenic 22-pole radiofrequency ion trap. Two reaction channels were observed. In the associative detachment D\(_2\)O and an electron are formed and for atom transfer formation OD\(^-\) + D was observed. The rate coefficients of the reactions have been determined at temperatures below 300 K. The reaction rate coefficient \(k_1\) of the associative detachment increases with decreasing temperature from \(k_1(300 \text{ K}) = 0.5 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}\) at 300 K up to \(k_1(70 \text{ K}) = 1.2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}\) at 70 K both with 30\% overall uncertainty.

1. Introduction
Anion-neutral reactions are important for a wide range of disciplines such as astrophysics, physics of planetary atmospheres, theoretical physics, physical chemistry, ion source technology and plasma technologies. It is generally accepted, that cations and anions play an important role in the chemistry of interstellar matter. The possibility that a substantial fraction of molecular material in interstellar space might be in the form of anions was suggested by Herbst [1]. However, up to 2006, there was no general agreement about a presence of anions in interstellar space. Negative ions were thought to be unstable in this environment due to the prevalence of ultraviolet light. The detection of anions in the interstellar space is not simple. Even though more than one thousand anions are known in the laboratory, only OH\(^-\) and SH\(^-\) had measured rotational spectra before 2006 [2]. In 2006 the first negatively charged polyatomic anion, C\(_6\)H\(_-\), was identified in the molecular envelope of IRC +10216 and in the dense molecular cloud TMC-1 [3]. Recently many anions have been discovered in several interstellar environments from quiescent molecular clouds to star forming regions. Molecular anions were also detected in the coma of comet Halley where there was reported a peak in the mass spectrum that may be assigned to OH\(^-\) or O\(^-\) [4]. Models indicate that anions can have a larger abundance than free electrons in some regions shielded from UV radiation [2]. A detailed knowledge of the role of anions will be possible only when the fundamental processes involved in their formation and destruction are better understood.

The new astronomical observations stimulated experimental studies in the field of anion chemistry. Previous experimental data on anion reactions were obtained mostly in experiments that were generally limited by room temperature (see e.g. refs. [5,6] and references therein). Few experiments were carried out at temperatures down to 140 K [7]. A special type of anion reactions with neutral atom or molecule is associative detachment reactions in which neutral molecule and electron are formed. The example of fundamental and very important associative detachment reaction for evolution
in the early universe is the reaction of H\(^-\) anion with atomic H leading to the formation of H\(_2\) molecule and an electron. This reaction was recently studied in a broad temperature range including experiments down to 10 K [8,9]. Another very fundamental reaction is the reaction of O\(^-\) + H\(_2\) producing in one reaction channel neutral H\(_2\)O and electron and in second reaction channel OH\(^-\) and H. The formation of water by associative electron detachment in interstellar media was suggested by Dalgarno [10]. Studies of gas-phase processes involving vital water molecules and especially those leading to isotopic fractionation are essential for the understanding of the water formation in the Universe [11,12]. Essential are studies at low temperatures, since in interstellar media without the strong influence of UV radiation the temperature is typically below 100 K. Using ion trap experiment we have already studied the reaction of O\(^-\) with H\(_2\) and we have found a very pronounced increase of the reaction rate coefficient with decreasing temperature below 300 K [13,14]. We decided to study also a deuterium variant of this reaction for an evaluation of isotopic effect and validation of future calculations. The information about deuterated isotopologues of water may be important for an understanding of a formation of Earth-like planets [15]. The reaction of O\(^-\) with D\(_2\) has also two exothermic channels corresponding to associative detachment and deuterium atom transfer.

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\begin{align*}
    \text{O}^- + \text{D}_2 & \rightarrow \text{D}_2\text{O} + \text{e}^- , & \Delta H &= -3.65 \text{ eV} , \\
    \text{O}^- + \text{D}_2 & \rightarrow \text{OD}^- + \text{D} , & \Delta H &= -0.28 \text{ eV} .
\end{align*}
\]

We will denote the rate coefficients of these reactions as \(k_1\) and \(k_2\). The reactions were already studied at temperatures 300 K and higher [13,16]. Only the experiment of Viggiano [17] spans down to 176 K. The endoergic channel that leads to OD + D\(^-\) is not significant at temperatures below 300 K.

2. Experiment

Linear 22-pole radio-frequency ion trap (22PT) is used in the present study to measure the rate coefficient of reactions (1) and (2). Anions O\(^-\) are produced in the separated storage ions source by bombarding N\(_2\)O with electrons. The produced and accumulated anions are pulled out from the source, mass selected by the quadrupole filter and injected into the ion trap. The ions are confined in the multipole rf field and cooled in collisions with neutral helium buffer gas. The ion trap is placed on the cold head of the closed-cycle cryogenic system and it can be cooled down to the nominal temperature \(T_{22PT}\), which is adjustable in present study from \(T_{22PT} = 70\) K to 300 K. In the helium buffer there is small admixture of reactant gas, deuterium in present experiments ([D\(_2\)]/[He] < 0.01).

![Figure 1. Time dependencies of the normalised relative number of primary O\(^-\) anions and produced OD\(^-\) anions measured at nominal trap temperature \(T_{22PT} = 96\) K. By the fit of the data (full lines) the rate coefficients \(k_1\) and \(k_2\) were obtained. The dashed line indicates the calculated production of electrons in the corresponding associative detachment reactions.](image)

The pressures of the helium buffer gas and of the D\(_2\) reactant gas in the trap are measured by the calibrated spinning rotor gauge manometer. Together with data from the ionisation gauge, which is placed outside of the ion trap, the number density of D\(_2\) in the trap is determined. The general description of the used apparatus may be found in references [18] or [9]. Due to the small partial density of deuterium in the mixture, it can be assumed that anions are cooled and thermalized prior to the collision with D\(_2\). As the energy of the collision is defined primarily by the temperature of light D\(_2\),
we can assume for the present experimental configuration that collisional temperature ($T$) is not more than 10 K above the nominal trap temperature ($T_{22PT}$). Hence, we are using $T = T_{22PT} + 5$ K with the uncertainty of 5 K. For details see discussion and experimental verification in reference [19].

After a trapping time, $t$, all anions are extracted from the ion trap, analysed by the quadrupole mass filter and counted on the micro channel plate detector. Under the assumption of linearity of the detection system and taking into account mass discrimination, the relative numbers of particular ions in the trap can be obtained.

From the measured time dependencies of the relative number of primary and product anions in the ion trap, the rate coefficients of the reactions (1) and (2) are determined. The examples of the time dependencies of the measured reaction rate coefficients $k_1$ and $k_2$ at a particular temperature are calculated. For the visualisation, the time dependence of the normalised relative numbers of electrons formed in associative detachment calculated from the measured data are also shown in Figure 1 (dashed line). The normalised relative numbers of formed D$_2$O molecules is equal to that of formed electrons.

3. Results and Conclusion

The reaction rate coefficients $k_1$ and $k_2$ of associative detachment and deuterium atom transfer between O$^-$ and D$_2$ were measured for temperatures from $T_{22PT} = 70$ K up to 300 K. The temperature dependencies of the measured reaction rate coefficients $k_1$ and $k_2$ are shown in Figure 2. The present values of the reaction rate coefficients are compared with corresponding values obtained for studied reactions in previous experiments. The overall uncertainty is 30% and it is caused mainly by the uncertainty of the number density of neutral reactant. At 300 K and at 176 K both measured reaction rate coefficients agree well with values from previous experiments [13,16,17].

![Figure 2. Measured temperature dependence of the reaction rate coefficients. Panel (a): The rate coefficient $k_1$ of the reaction (1) and the Langevin rate coefficient ($k_L$) for the O$^- +$ D$_2$ collision. Panel (b): The rate coefficient $k_2$ of the reaction (2). The values from previous experiments are also depicted. Only statistical errors are indicated here. The overall uncertainty is 30%.](image)

Present studies provide data at so far unexplored temperatures below 176 K [17]. At 300 K and at 176 K both measured reaction rate coefficients agree well with data from previous experiments. At temperatures below 300 K, both measured reaction rate coefficients change the character of the temperature dependencies. The rate coefficient of the associative detachment process increases significantly with decreasing temperature from $k_2(300 \text{ K}) = 0.5 \times 10^{-9}$ cm$^3$ s$^{-1}$ at 300 K up to $k_2(70 \text{ K}) = 1.2 \times 10^{-9}$ cm$^3$ s$^{-1}$ at 70 K. The low-temperature value of $k_1$ close to the collisional reaction rate coefficient ($k_c = 1.15 \times 10^{-9}$ cm$^3$ s$^{-1}$) is indicating that nearly every collision leads to associative detachment. The rate coefficient of deuterium atom transfer is increasing with decreasing temperature from $k_2(300 \text{ K}) = 0.9 \times 10^{-11}$ cm$^3$ s$^{-1}$ at 300 K up to $k_2(70 \text{ K}) = 1.7 \times 10^{-11}$ cm$^3$ s$^{-1}$ at 70 K. Both measured temperature dependencies are similar with corresponding temperature dependencies of the rate coefficients of both channels of the reaction of O$^-$ with H$_2$ [14]. Due to this similarity, we can
assume the same explanation, i.e. the formation of long lived collisional complex (D₂O⁻) at low collision energies and transition from unreactive PES to the reactive PES owing to the conical intersection. Due to the high efficiency of this transition at low temperatures the reaction rate coefficient is close to the capture rate coefficient. Detailed studies of the reaction of O⁻ with D₂ to even lower temperatures and comparison with the reaction of O⁻ with H₂ will follow. The comparison of the reactions of O⁻ with D₂ and with H₂ may serve as the test for further theoretical calculations. A reaction of O⁻ with HD may be of interest for quantum chemistry and also for astrochemical models.

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