Complex formation and internal proton-transfer of hydroxyl-hydrogen anion complexes at low temperature

Daniel Hauser¹, Olga Lakhmanskaya¹, Seunghyun Lee¹, Štěpán Roučka² and Roland Wester¹

¹ Institute for Ion Physics and Applied Physics, University of Innsbruck, Technikerstraße 5, 6020 Innsbruck, Austria
² Department of Surface and Plasma Science, Charles University in Prague, V Holešovičkách 2, 108 00 Prague, Czech Republic

E-mail: roland.wester@uibk.ac.at

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Abstract

We have studied the three-body complex formation rate of the hydroxyl anion with molecular hydrogen at low temperatures. The formed cluster is found to quickly undergo internal proton transfer to a hydrogen anion–water complex. This is probed by photodetachment spectroscopy, which clearly distinguishes the two isomeric structures. The product cluster is the only isomer found to be stably formed at the temperature and densities employed in the experiment. The cluster then binds an additional hydrogen molecule by a second three-body collision, which appears at a rate comparable to the first formation process. This is followed by a rapid growth to larger clusters.

1. Introduction

The field of cold molecules has caught increasing attention during the last decades, as it creates new opportunities for studies of the dipole moment of the electron [1, 2] or possible change of the fine-structure constant [3–5]. It also made it possible to perform new precision spectroscopy experiments [6–11], and study collision [12–14] and reaction dynamics [15–21] of molecules at low temperatures. Optical pumping and sympathetic and buffer gas cooling are the most common approaches to create cold molecules, spanning a temperature range from the ultracold regime to several kelvin. Optical pumping has been employed for selected molecules to cool translational and internal degrees of freedom [22–27]. During recent years, also Sisyphus, evaporative, and direct laser cooling of several neutral molecules could be demonstrated [28–30]. Sympathetic cooling of molecular ions in a coulomb crystal has proven to be efficient to cool translational and vibrational degrees of freedom, even to ultracold temperatures [23, 31]. Recently, the combination of ion–ion sympathetic translational cooling and buffer gas rotational cooling of molecular ions in a coulomb crystal has been demonstrated [14].

Only neutral buffer gas cooling is currently applicable for the translational degrees of freedom of negatively charged ions. This is because the majority of anionic systems do not provide any electronically excited states; therefore, bound–bound spectroscopy of molecular anions is usually limited to rovibrational transitions and photon scattering rates that are too small to be used for optical cooling. Bound-free spectroscopy such as resonance enhanced multi-photon dissociation or photodetachment spectroscopy has been established to quantify the quantum state populations of molecular ions [6, 14, 32]. The use of photodetachment to produce rovibrational ground state populations of molecular anions by means of depletion of rovibrational excited states has recently been proposed [33]. To study high-precision spectra of cold molecular ions in ion traps, the technique of laser-induced inhibition of cluster growth (LIICG) has been developed [34, 35]. Also for negative ions, pure rotational cw-Thz spectroscopy has been demonstrated in ion traps for OH⁻ and OD⁻ [11, 36]. The discovery of the first molecular anions in space created the need for more spectroscopy and reaction experiments on cold molecular anions [37]. Some star-forming regions and planetary atmospheres can even exhibit densities that bring three-body processes into play [38–40].

Several ion trap experiments have been carried out to study the cold chemistry of anions with neutrals at low temperatures down to about 10 K [16, 21, 42]. Recently chemical reactions and also inelastic collisions of the
hydroxyl negative ion at temperatures below 20 K have been performed [33, 43]. The reaction of OH \(-\) with molecular hydrogen proceeds via the HO\(_3\)\(^-\) intermediate complex. This complex was first discovered in 1982 and then studied extensively (see reference [44] and references therein). A large number of formation and destruction mechanisms of this complex have been identified [44]. Also a detailed photoelectron spectroscopy study has been performed [45, 46]. In this work, the three-body formation rate of ODD DO DD\(_2\) 3 ++→ +− − is measured at 20 K collision temperature. This extends previous work done on the three-body formation of HO\(_3\)\(^-\) at 88 K to even lower temperatures [44]. Furthermore, we present a scheme to identify the isomeric structure of the formed complex. The fully deuterated system is chosen to suppress unwanted H/D-exchange reactions, as discussed below.

2. Methods

The experiments are carried out in a cryogenic rf ion trap experiment that has been described previously [21, 32, 47]. A schematic drawing of the setup is shown in figure 1. Argon is used as a carrier gas to transport a mixture of heavy water vapour, mixed with regular water impurities, into the pulsed ion source by means of a self-built piezo valve. A pulsed plasma discharge that is ignited across the supersonically expanding gas mixture subsequently generates a cloud of OD\(^-\) and also OH\(^-\) ions, which are extracted by a Wiley–McLaren mass spectrometer (blue pulse in the inset). Ion optics and a static quadrupole bender focus the ions into a 22-pole ion trap. The trap is cooled to a temperature of 8.5 K.

While entering the 22-pole ion trap, the ions are decelerated by a static voltage offset and further cooled by collisions with the buffer gas, D\(_2\), which is thermalized to the temperature of the trap. Due to radiofrequency heating, the relevant temperature of the ion–neutral collision system is slightly higher than the trap temperature [48, 49]. Recent measurements of the OH\(^-\)-He system yielded a rotational temperature of 20 K [32]. This is also assumed to be the relevant relative collision temperature in this work. Normal–D\(_2\), composed of both para and ortho hyperfine states, is used at densities between \(10^{13}–10^{14}\) cm\(^{-3}\).

After a certain trapping time the remaining ions are extracted into the reflectron time-of-flight mass spectrometer. The ions are detected by a multi-channel-plate (MCP) detector, and their corresponding time of flight is measured. The time evolution of an ion is calculated by integration of the MCP detector signal at various trapping times. The ions can be reflected once by the reflectron mirror 1 (RM\(_1\), single-reflection mode) or multiply cycled by switching on reflectron mirror 2 (RM\(_2\), multi-reflection mode) to increase the mass resolution [32, 50]. Two different experiments are performed:
Cluster reactions: parent and product ions are extracted after a trapping time $\tau$ in order to measure their ion time evolution (green pulse in the inset in figure 1).

Photodetachment studies: the same measurement procedure is performed as in the cluster reaction experiment. If the trapping time exceeds $\tau_0 = 7$ s, a laser shutter (LS) is opened, which drives the photodetachment reaction $X^- + h\nu \rightarrow X + e^- (E_{\text{kin}})$ (red pulse in the inset in figure 1). Again the time evolution of the ion signal is measured.

The photodetachment spectroscopy is performed by a cw ring cavity laser (Sirah Matisse DR) at a photon energy of $\lambda^{-1} = 14658.511$ cm$^{-1}$ with laser powers ranging from (200–670) mW. Details about the density calibration of D$_2$ can be found elsewhere [32, 33, 41]. By monitoring the composition of the introduced reactant gas D$_2$ with the Pfeiffer PrismaPlus$^{\text{TM}}$ QMG 220 residual gas analyzer, one can exclude any three-body process connected to gas impurities.

3. Results and discussion

3.1. Complex formation

The three-body formation rate coefficient for the anionic reaction system

$$\text{OD}^- + \text{D}_2 + \text{D}_2 \rightarrow \text{OD}_3^- + \text{D}_2$$

has been measured at a relative temperature of about 20 K. Note that reaction studies of mixed isotopic composition are inconclusive due to the isotope exchange reactions

$$\text{OD}^- + \text{H}_2 \rightarrow \text{OH}^- + \text{HD}$$

$$\text{OH}^- + \text{HD} \rightarrow \text{OD}^- + \text{H}_2.$$  

Both reactions have rate coefficients [43] that lead to reaction time scales between 0.1–20 s$^{-1}$ for the conditions in our experiment. These time scales exceed the three-body formation rates of OH$^-$ and ODH$_2^-$, which would convolute both formation rates and thereby complicate the analysis significantly. However, the isotopic substitution reaction of OH$^-$ with D$_2$ helps convert all initially produced unwanted OH$^-$ anions into OD$^-$. Figure 2 shows the measured time evolution of OD$^-$, OD$_3^-$, and larger hydroxyl-hydrogen clusters OD$^-$$_{2n+1}$ as a function of storage time in the trap. These data are acquired in single-reflection mode (see above). The ion cluster signal is a sum of at least six different ions with masses heavier than 40 amu and summed up to give the total cluster signal. The inset in the upper right corner shows a zoom into the ion signal for short trapping times up to one second.

By monitoring the composition of the introduced reactant gas D$_2$ with the Pfeiffer PrismaPlus$^{\text{TM}}$ QMG 220 residual gas analyzer, one can exclude any three-body process connected to gas impurities.

Figure 2. Time evolution of OD$^-$, OD$_3^-$, and cluster ion signal as a function of trapping time measured in single-reflection mode. At least six different ions with masses heavier than 40 amu are detected and summed up to give the total cluster signal. The inset in the upper right corner shows a zoom into the ion signal for short trapping times up to one second.
Here, \( k_1 \) represents the three-body loss rate of \( \text{OD}^- \), which is equal to the formation rate of \( \text{OD}_3^- \), and \( k_2 \) is the loss rate of the \( \text{OD}_3^- \) cluster. The solution of equation (5) is a biexponential function of the form

\[
\left[ \text{OD}_3^- \right](t) = A \cdot \left( e^{-k_1 t} - e^{-k_2 t} \right),
\]

which is fitted to the ion cluster data in figure 2 for storage times above 1 s to exclude the initial thermalization phase. In figure 3 the obtained loss rates are plotted versus \( \text{D}_2 \) density.

As a first step a second-order polynomial is fitted to the data with no restrictions on the fitting parameters. Statistical analysis showed that linear contributions to the reaction rate coefficient are zero within the \( 1\sigma \) error. This shows that a three-body collision (see equation (1)) is responsible for the loss of \( \text{OD}^- \). Hence, only a quadratic and an offset term are considered for fitting the data in figure 3. The results are shown in table 1, together with their statistical accuracies. The overall systematic accuracy due to the \( \text{D}_2 \) density calibration is estimated to be 10\%, twice the accuracy of the absolute density measurement. The offset values correspond to the background loss due to evaporation from the ion trap [51].

For the three-body formation of \( \text{H}_3^+ \) in normal-\( \text{H}_2 \) a very similar rate has recently been measured [52] at the same temperature, although the system is characterized by a much stronger attractive interaction than the present one. It seems that the larger density of internal states in the present system and the weaker interaction roughly compensate in their opposing influences on the three-body rate coefficient. The three-body reaction rate coefficient of \( \text{OD}^- \) at 20 K is larger by more than a factor of three when compared to measurements done on the \( \text{H}_3\text{O}^- \) system at 88 K [44]. Such information is not only useful for understanding the growth of ionic clusters, e.g., in denser regions of the interstellar medium; it also allows us to assess under which conditions a system can be studied by the spectroscopic technique of LIICG [34].

### 3.2. Photodetachment study of the isomeric structure of \( \text{OD}_3^- \)

The \( \text{OD}_3^- \) collision complex enters via the \( \text{OD}^-(\text{D}_2) \) channel and is then stabilized by a subsequent collision with a second \( \text{D}_2 \) molecule. Figure 4 shows a one-dimensional cut through the potential energy surface for the \( \text{H}_3\text{O}^- \) system [46], which would also be applicable to the fully deuterated system when neglecting zero-point energy (ZPE) effects. Two different isomeric structures are found as minima on the surface, labeled configurations 1

![Figure 3. Dependence of the loss rate of the \( \text{OD}^- \) and \( \text{OD}_3^- \) ions as a function of deuterium density in the 22-pole ion trap. The solid lines are fits to a quadratic density dependence; the resulting fit parameters are listed in table 1.](image-url)
and 3. They are separated by a barrier of 0.077 eV (without ZPE correction). The ground and first excited vibrational levels of the H$_3$O$^-$ system are found to be localized in configuration 3, while the second excited vibrational level mainly lives in configuration 1 [46]. Vibrational levels have not yet been calculated for the DO$_3$$^-$ system. It is therefore not known if a localized excited vibrational state can exist in the potential minimum of the isomeric configuration 1.

The two isomeric complexes of OD$_3^-$ are characterized by different electron affinities of 2.05 eV and 1.5 eV, respectively [45, 46]. Photodetachment spectroscopy at a photon energy of 1.82 eV can only detach the OD$_3^-$ isomer (configuration 3). This scheme has been used to probe the isomeric structure of the ion.

Figure 5 shows the time evolution of the ions in the 22-pole ion trap including photodetachment, which starts 7 s after loading the ions into the 22-pole ion trap. The inset shows a zoom into the storage times when the photodetachment takes place. The red triangles show the OD$_3^-$ cluster evolution, which rapidly decays to zero due to the photodetachment process. The blue circles mark the OD$^-$ ion evolution, which remains unaffected by the photodetachment.
the barrier between the two isomers significantly, collision-induced isomerization seems unlikely for a barrier height of about 77 meV at the collision temperature of 20 K in the 22-pole ion trap. Further high-level quantum dynamic calculations would be required to clarify if any stable vibrational localized state in isomeric configuration 1 exists and which process is responsible for the formation of the D(3D2O) complex.

4. Conclusion

Ternary rate coefficients for the formation of negative cluster ions have been presented at a temperature of 20 K for the first two steps of the formation of OD−2n+1 clusters. The two complexes OD3 and OD5 form with similar rate coefficients. A very similar rate has also recently been measured for the three-body formation of H3+ in normal–H2. Larger anion clusters grow more rapidly and were not analyzed in the present study.

By employing isomer-specific photodetachment we could show that the OD5 complex forms in the D(3D2O) isomeric structure by undergoing internal proton transfer either directly upon formation or within a few seconds of storage. In the latter case isomerization must occur by collisional activation or by tunneling. Our results show how cold molecular ions of growing structural complexity can be studied using cryogenic ion traps. The spectroscopic probing technique shows promise for application also to other polyatomic or cluster anions.

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