Transfer of a proton between H$_2$ and O$_2$

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The proton affinities of hydrogen and oxygen are very similar. Therefore, it has been discussed that the proton transfer from the omnipresent H$_3^+$ to molecular oxygen in the near thermoneutral reaction H$_3^+$ + O$_2$ $\rightleftharpoons$ O$_2$H$^+$ + H$_2$ effectively binds the interstellar oxygen in O$_2$H$^+$. In this work, the proton transfer reaction has been investigated in a low-temperature 22-pole ion trap from almost room temperature (280K) down to the lowest possible temperature limited by freeze out of oxygen gas (about 40K at a low pressure). The Arrhenius behaviour of the rate coefficient for the forward reaction shows that it is subject to an activation energy of $E_A/k = 113$ K. Thus, the forward reaction can proceed only in higher temperature molecular clouds. Applying laser-induced reactions to the given reaction (in the backward direction), a preliminary search for spectroscopic signatures of O$_2$H$^+$ in the infrared was unsuccessful, whereas the forward reaction has been successfully used to probe the population of the lowest ortho and para levels of H$_3^+$.

**Keywords:** H$_3^+$; O$_2$H$^+$; action spectroscopy; ion–molecule reaction; proton affinity; ortho/para ratio

1. Introduction

In space, H$_3^+$ is the universal proton donor to many molecules, owing to its high abundance and the low proton affinity of molecular hydrogen. This leads to common astrophysical cations such as HCO$^+$ and N$_2$H$^+$, which are readily detected in millimetre and sub-millimetre observations. As a result, protonated molecules can be taken as tracers for neutral molecules that cannot be observed owing to a missing dipole moment. For an exothermic proton transfer, the reaction is rather fast, and is often independent of temperature. Therefore, in simple cases, the abundance of the protonated molecule is just proportional to the abundance of the neutral species. While this is true for molecular nitrogen, it does not seem to be the case for molecular oxygen because previous studies [1] hint at a small endothermicity of the proton transfer reaction

$$H_3^+ + O_2 \rightarrow O_2H^+ + H_2.$$ (1.1)

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More recently, theoretical work by Widicus Weaver et al. [2] has been devoted to this reaction. This work discusses in detail the experimental finding of a nearly thermoneutral reaction with a small endothermicity to form O$_2$H$^+$ at low temperatures.

Most experiments determined the reaction rate at room temperature, using different techniques [3–5]. One measurement at 80 K has been conducted in a selected ion flow tube (SIFT) [1] experiment. In the present study, measurements in a temperature-controlled 22-pole ion trap have been carried out in the range of 40–280 K in order to characterize the proton transfer down to the lowest possible temperatures. The rate coefficient follows an Arrhenius-type behaviour for which the corresponding activation energy will be reported.

Very interestingly, the reactants H$_3^+$ and O$_2$ only populate a few rotational quantum states in low-temperature experiments and in cold cloud conditions. Therefore, the proton transfer reaction H$_3^+$ + O$_2$ will be governed only by a few state-to-state rate coefficients. It will be discussed how individual rate coefficients rule the outcome of this reaction at low temperatures.

Another interesting aspect concerns the spectroscopy of H$_3^+$ and O$_2$H$^+$. Applying the powerful technique of laser-induced reactions (LIRs) in trap experiments allows for very sensitive spectroscopy of both ions. IR spectra of O$_2$H$^+$ have been predicted by Widicus Weaver et al. [2]. Experimental data are missing to date. The situation is quite different for H$_3^+$. High-resolution spectra have been pioneered by the Oka group by investigating fundamental vibrations [6]. Recently, high-overtone spectra up to 16000 cm$^{-1}$ have been recorded by Pavanello et al. [7] in a trap experiment. There, the endothermic proton transfer to Ar is promoted by the excitation of the H$_3^+$ parent ion. These very accurate spectroscopy measurements pose a challenge to theoretical work [7]. In the present study, the endothermic proton transfer to O$_2$ is used to record fundamental ro–vibrational lines of H$_3^+$, using a home-built optical parametric oscillator (OPO) system. The aim of these measurements is to establish a route to interrogate the rotational-level population of H$_3^+$ and, thus, also the population of the two nuclear spin configurations ortho-H$_3^+$ and para-H$_3^+$.

The paper starts with a description of the trapping experiment and OPO system in §2. The kinetic measurements are described in §3, including a discussion of the results. Probing the lowest rotational states with LIR will be presented in §4. A new experimental setup allowing us to access even lower temperature conditions will be described in §5.

2. Experimental setup

(a) 22-Pole trapping apparatus

The experiments are conducted with a temperature-controlled 22-pole trapping apparatus. This apparatus has been proved to be a versatile tool to measure ion–molecule reaction rates of a number of astrophysically interesting systems in the 10–300 K temperature range [8,9]. Detailed information on the method of LIRs for recording high-resolution spectra of cold molecular ions in the trapping apparatus is given in recent studies [10–14].
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For the present study, $H_3^+$ ions are generated by electron bombardment of $H_2$ gas (Linde Gas Deutschland, grade 6.0) and collected in a radiofrequency storage ion source. The electron energy was kept at 23 eV, well above the ionization energy of $H_2$ (15.4 eV). At the beginning of each experimental cycle, a short pulse of ions is extracted from the source, mass filtered in a quadrupole mass spectrometer, and typically a few thousand $H_3^+$ ions are injected into the cold 22-pole ion trap [15] mounted on a Leybold closed-cycle helium refrigerator. On entrance, the ions are cooled down to the ambient temperature (40–280 K in this experiment) by a short intense helium pulse. In the trap, the stored ions are subjected to a cold bath of reactant $O_2$ gas (Linde Gas Deutschland, grade 2.5). The number density of oxygen gas in the trap was adjusted to $(1–6) \times 10^{10} \text{cm}^{-3}$. After a certain storage time, the ions are extracted from the trap, and either the remaining $H_3^+$ ions or the $O_2H^+$ product ions of reaction (1.1) are mass selected in the second mass filter and counted with a Daly-type detector.

(b) Reaction kinetics

For the determination of the rate of reaction (1.1), a series of experimental cycles is run in which the storage time, i.e. the reaction time, is varied between 10 and 600 ms in steps. For each storage time, either the $H_3^+$ parent or the $O_2H^+$ product ions are counted alternately, and the measurements are repeated 20 times for each datapoint to improve the statistics. This procedure is carried out at different temperatures in the 40–280 K range. The lower temperature limit is dictated by the freeze-out of molecular oxygen on the cold trap walls. At temperatures above 100 K, proton transfer reactions with residual $N_2$ and $H_2O$ are observed. As a consequence, the product ions of these parasitic reactions are recorded as well for each datapoint, and are accounted for in the analysis (see §3).

For the determination of rate coefficients, the density of oxygen is measured with a spinning rotor gauge (MKS SRG-2CE) connected directly to the inside of the 22-pole trap. As the low number densities in the trap and the vibration of the cold head prohibit the use of a spinning rotor gauge during the experiments, an ion gauge is calibrated against the spinning rotor gauge at room temperature and elevated pressures of the target gas (oxygen in this case). This procedure allows us to determine the number density with an accuracy of about 10 per cent.

(c) Laser-induced reaction spectroscopy: optical parametric oscillator system

For LIR spectroscopy, tunable continuous wave light from an OPO is sent through the axially transparent setup into the trap. To obtain a good signal-to-noise ratio, the LIR experiments are conducted at the lowest possible temperature (around 40 K), and the high power of the OPO permits one to use short storage times (typically around 300 ms). After storage, the ion cloud is extracted into the second quadrupole mass filter, selecting the generated $O_2H^+$ ions, which are finally recorded. By counting the $O_2H^+$ product ions as a function of the OPO wavelength, a spectrum of $H_3^+$ is recorded.

For the probing of the lowest rotational levels of $H_3^+$, an OPO operating in the wavelength region at around 3 μm has been used. The setup is similar to our system emitting idler radiation around the 5 μm wavelength that has been described recently in more detail [16]. Its heart is a periodically poled lithium niobate crystal (PPLN) that transforms a part of the intense and focused...
pump laser beam (Innolight MOPA series, Nd:YAG at 1064 nm wavelength, 10 W optical power) with frequency $f_p$, into the idler and signal beams obeying the conservation of photon energy $h \cdot f_p = h \cdot f_i + h \cdot f_s$. Idler and signal beams are widely tunable by choosing one of the seven poling periods and by changing the temperature (50–200°C) of the PPLN. The signal beam is kept resonant in a high-finesse ring cavity to enhance the conversion process and enable oscillation. The idler beam is the one used for the experiment with wavelengths between 2.5 and 4 μm (4000–2500 cm$^{-1}$). Its continuous fine tuning (15 GHz mode-hop free) is achieved via tuning of the pump laser. Optical powers of more than 800 mW can be reached in the idler, though it is usually limited to 200 mW in the experiments by decreasing the pump power. A narrow linewidth better than 1 MHz ($3 \times 10^{-9}$ cm$^{-1}$) has been determined for the idler radiation from an experiment with a high-finesse reference cavity [16].

For calibration purposes, frequency readouts from a high-resolution wavemeter (Bristol Instruments, model 621-A IR) are recorded simultaneously to the LIR experiment. As the emphasis of the present experiment is on the probing of the H$_3^+$ rotational population via well-documented transitions, an accurate frequency calibration with absorption cells or etalons could be omitted.

3. Thermochemical measurements and results

(a) Low-temperature reactions in the ion trap

To obtain the temperature dependence of reaction (1.1), kinetic measurements as described in §2b were performed in the temperature range from 40 to 280 K. An example for such a kinetic measurement at a temperature of 129 K is shown in figure 1a. In this experiment, about 2000 H$_3^+$ ions were injected in the trap filled with oxygen at a number density of $1.2 \times 10^{10}$ cm$^{-3}$. Inspection of figure 1a reveals an initially faster decay of H$_3^+$ followed by a slow down at longer time scales. This behaviour is partly attributed to the H$_2$ molecules leaking from the storage ion source into the trap and a subsequent back reaction of the O$_2$H$_3^+$ ions. However, the H$_2$ number density of $3.2 \times 10^7$ cm$^{-3}$, as determined from the pressure increase in the vacuum chamber is too small to explain the slow down of the H$_3^+$ decay. As will be discussed in §3b, the H$_3^+$ ensemble at 129 K is composed mainly of two components, about 50 per cent in the $(J, G) = (1, 1)$ para state reacting fast, and 50 per cent in the (1,0) ortho level with a larger endothermicity reacting at a slower rate. The solid lines in figure 1 are numerical simulations of a coupled set of rate equations for the forward and backward directions of reaction (1.1). The simulation is based on individual rate coefficients for the lowest H$_3^+$ and O$_2$ levels (as discussed in detail in §3b). For every combination of a H$_3^+$ level with an O$_2$ level, we calculated a rate coefficient that includes the specific rotational energies of H$_3^+$ and O$_2$. In the case of ortho-H$_3^+$ levels, we also include an extra endothermicity of 170 K to consider the fact that ortho-H$_3^+$ can form only ortho-H$_2$ in a reactive collision (see also §3b). To compute one overall rate coefficient for every H$_3^+$ level, we calculated a weighted average with the corresponding O$_2$ populations as weight. As an upper limit for the rate coefficients, we choose the high-temperature (300 K) value of $6.7 \times 10^{-10}$ cm$^3$ s$^{-1}$ found by Adams & Smith [1].

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Figure 1. (a) Kinetic measurements of reaction (1.1) at $T = 129\,\text{K}$ with an oxygen number density of $1.2 \times 10^{10}\,\text{cm}^{-3}$. The solid lines are numerical simulations considering only the three lowest levels of $\text{H}_3^+$ that are labelled with their quantum numbers ($J, G$). The para levels (1,1) and (2,2) react slightly faster than the ortho level (1,0). Together with the back reaction with traces of $\text{H}_2$, this leads to a non mono-exponential decay of $\text{H}_3^+$. Rate coefficients are $k_{(1,0)} = 1.6 \times 10^{-10}$, $k_{(1,1)} = 3.6 \times 10^{-10}$ and $k_{(2,2)} = 6.7 \times 10^{-10}$ (all in $\text{cm}^3\,\text{s}^{-1}$). (b) Same as (a) with $T = 49\,\text{K}$ and $\text{O}_2$ density $6.2 \times 10^{10}\,\text{cm}^{-3}$. In this case, para-$\text{H}_3^+$ reacts much faster than ortho-$\text{H}_3^+$. For long storage times, only the almost non-reactive ortho-$\text{H}_3^+$ remains in the trap and dominates the decay of $\text{H}_3^+$. At this temperature, the higher para-$\text{H}_3^+$ state (2,2) is barely populated. Rate coefficients are $k_{(1,0)} = 2.3 \times 10^{-11}$ and $k_{(1,1)} = 2.2 \times 10^{-10}$.

For the 129K simulation, the reaction rates for the (1,0) and (1,1) levels are not so much different: $k_{(1,0)} = 1.6 \times 10^{-10}$ and $k_{(1,1)} = 3.6 \times 10^{-10}\,\text{cm}^3\,\text{s}^{-1}$. Therefore, there is a smooth transition between the decay of the two parts of $\text{H}_3^+$ leading to a curve with one slope. At lower temperature values, however, the difference becomes more apparent, leading to a decay of the (1,1) fraction leaving behind
an almost unreactive (1,0) ortho fraction. This behaviour is shown in figure 1b. In this case, the temperature was 49K, and approximately 1700 H$_3^+$ ions were injected while the oxygen number density was 6.2 $\times$ 10$^{10}$ cm$^{-3}$. Owing to this behaviour, the rate coefficients at elevated temperatures are nearly equal for the two considered levels, whereas at lower temperatures, it is reasonable to derive separate rate coefficients for the two components.

In order to compare our results with previous work, we first determine a thermal rate coefficient taken from the early time decay in our measurements. At higher temperatures when both components are reacting fast, this value does not deviate from the individual rate coefficients very much. Upon reducing the temperature of the ion trap, the effective rate coefficient for the early decay decreases from 5.3 $\times$ 10$^{-10}$ cm$^3$s$^{-1}$ at 281K to 0.7 $\times$ 10$^{-10}$ cm$^3$s$^{-1}$ at 49K. Our data are summarized in figure 2 together with previously measured rate coefficients obtained with the techniques of SIFT [1,5], flowing afterglow [3], as well as with an ion cyclotron resonance (ICR) instrument [4]. An Arrhenius fit to these data yields an activation energy of $E_A/k = (113 \pm 4)$ K and a limiting high-temperature rate coefficient of $k_{lim} = 7.3 \times 10^{-10}$ cm$^3$s$^{-1}$. Comparing this high-temperature rate coefficient with the calculated Langevin collisional rate coefficient $k_c = 17.9 \times 10^{-10}$ cm$^3$s$^{-1}$ (see horizontal line in figure 2) suggests that at high temperature, roughly half of the collisions between H$_3^+$ and O$_2$ lead to a reaction. Therefore, no substantial steric hindrance is restricting the proton transfer of reaction (1.1). Assuming no barrier for the reverse reaction, the obtained value (113 $\pm$ 4) K amounts to the difference in proton affinities between H$_2$ and O$_2$.

Figure 2. Summary of measured rate coefficients for the reaction H$_3^+$ + O$_2$ → O$_2$H$^+$ + H$_2$. All previously measured rate coefficients were measured at 300K [1,3–5], with one datapoint by Adams & Smith [1] measured at liquid nitrogen temperature in a SIFT apparatus. The limiting Langevin collision rate and the Arrhenius fit of our data are also included (see text).
In general, the new data agree well with the previously measured values within the given measurement uncertainties, though the previously measured values tend to be somewhat higher. This discrepancy might be explained for methods such as with ICR by collisional heating, which can lead to higher rate coefficients for endothermic reactions. At this point, it has to be stressed that all parasitic reactions (with H$_2$O and with N$_2$) were fully accounted for in our measurements and rate simulations. In summary, the value of $\left(113 \pm 4\right)$ K serves as an average value for the difference in proton affinities of O$_2$ and H$_2$. Adams & Smith [1] extracted from their van’t Hoff plot an enthalpy for the proton transfer of $\left(0.33 \pm 0.04\right)$ kJ per mole, corresponding to about 165 K. The conversion of activation energy to an enthalpy adds some 10 K to our value (by using calculated and experimental values of the involved vibrational energies). In addition to the uncertainties in both measurements, some caution has to be exercised owing to the mentioned ortho/para composition of H$_3^+$. 

We also tried to measure the assumably fast backward reaction directly, starting with O$_2$H$^+$ produced in the storage ion source from a mixture of H$_2$ and O$_2$ gas. It turned out that the efficiency to produce O$_2$H$^+$ in our source was not sufficient for the experiments conducted here. This is likely due to the low proton affinity of O$_2$, leading to the destruction of the formed O$_2$H$^+$ immediately in collisions with H$_2$ (and also some residual N$_2$ or H$_2$O) in the source (see also §4a). Additionally, as a potential formation mechanism of O$_2$H$^+$, the collision O$^+$ + H$_2$ is non-reactive [17].

(b) Reactivity of para- and ortho-H$_3^+$

As discussed earlier, at low temperatures, the decay of H$_3^+$ due to proton transfer to O$_2$ is composed of a fast and a slow contribution. This difference is attributed to different reactivities of the two lowest ortho and para levels. In order to understand this behaviour, the internal states of H$_3^+$ and O$_2$ are depicted in figure 3. At the temperatures of the current study, only the three lowest H$_3^+$ levels, two para states $\left((J,G) = (1,1), (2,2)\right)$ and one ortho state $\left(1,0\right)$ are substantially populated. As shown in the figure, also the energy spacing of the rotational levels of the O$_2$ collision partner is quite sizable, leading to only a few rotational states taking part in the reaction. The activation energy $E_A$ shown in the diagram is the one that was derived before by our preliminary evaluation. These energetics suggest that the (2,2) para-H$_3^+$ state reacts readily at any temperature, given that the high-temperature rate coefficient is a substantial fraction of the Langevin limit. The same holds for rotationally excited O$_2$ with $N \geq 7$. As a result, it can be speculated that in a low-temperature trap experiment, only the two lowest H$_3^+$ levels are populated in the presence of O$_2$. Of these two remaining H$_3^+$ states, the $(1,0)$ ortho state (with nuclear spin $I = \frac{3}{2}$) reacts much slower because it can decompose in reaction with O$_2$ only to H$_2$ with $I = 1$, i.e. ortho-H$_2$. Formation of ortho-H$_2$ $(J = 1)$ requires some 170 K additional rotational energy with respect to the ground state para-H$_2$ $(I = 0, J = 0)$. This energy enhances the activation energy accordingly and thus leads to a substantially smaller rate coefficient for the ortho-H$_3^+$ reactant. This behaviour becomes apparent in figure 1 in the simulations given by the solid lines. The decay of the para-H$_3^+$ state determines the early time decay, while the ortho-H$_3^+$

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Figure 3. Energy level diagram for the proton transfer reaction from H$_3^+$ to O$_2$. The lowest rotational energy levels of H$_3^+$ [18] and O$_2$ [19] are shown together with the height of the activation energy $E_A$. The bar at the right-hand side depicts the translational energy $E_t$ of a room temperature supersonic molecular beam of pure O$_2$. Only the lowest states of H$_3^+$ will survive in the cold trap environment. The fine structure triplet splittings shown for O$_2$ (only fully resolved for $N = 1$) are considerably smaller than the energy spacings of the rotational levels, and have not been taken into account in the kinetics analysis.

state reacts much slower and remains as the only state in the trap. As a result, apparently only a single quantum state of H$_3^+$ is prepared in such a trap experiment.

Under high-temperature conditions in the ion source and using normal-H$_2$ (ortho to para ratio o/p = 3:1) as a precursor, the o/p ratio of the formed H$_3^+$ is 1:1 (this ratio results from the ratio of the nuclear spin degeneracies and the total number of ro–vibronic states, see e.g. table 2 in Hugo et al. [20]). Upon collision with the He atoms when entering the trap, the H$_3^+$ are cooled within their nuclear spin modifications, but leave the o/p ratio unchanged. So it is assumed that the o/p ratio at low temperatures is also close to 1:1. This ratio has been assumed for the time $t = 0$ in the simulation shown in figure 1a for 129 K. Whether the slightly lower o/p-value applied for $t = 0$ in the simulation in figure 1b is due to o/p conversion induced by collisions with O$_2$ will have to be tested at even lower temperatures in future experiments (see §5).

(c) Astrochemical implications

The present work shows that reaction (1.1) has an activation energy substantially higher than typical thermal energies of molecules in cold clouds (10 K). Thus, the formation of O$_2$H$^+$ by protonation of oxygen gas seems only feasible in molecular clouds with higher temperature or shock regions. Furthermore, the all-abundant molecular hydrogen gas will very effectively destroy the formed O$_2$H$^+$ by the presumably exothermic backward reaction. Thus, O$_2$H$^+$ as a sink for molecular oxygen in molecular clouds as discussed in Widicus Weaver et al. [2] seems unlikely.

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4. Probing the lowest levels of $\text{H}_3^+$ by laser-induced reactions

Whenever an ion–molecule reaction changes its effective rate with kinetic energy or internal excitation of either reactant, the formation rate of product ions is altered. In our trap experiments, we use this effect to enhance the product formation by light absorption of the ion, resonantly exciting specific rotational or ro–vibrational states of the ion. Scanning the frequency of the light, a spectrum of the parent ion is recorded. In the present case, we explored this light-induced reaction or LIR method for both directions of reaction (1.1), to record the spectra of both $\text{O}_2\text{H}^+$ and $\text{H}_3^+$. 

(a) Search for vibrational fingerprints of $\text{O}_2\text{H}^+$

Although $\text{H}_2$ has a higher proton affinity than $\text{O}_2$, leading to a relatively fast reaction of $\text{O}_2\text{H}^+$ with $\text{H}_2$ [1], it was hoped that internal excitation might shift the equilibrium condition, and so allow detection of fundamental vibrational bands of $\text{O}_2\text{H}^+$. To date, no spectroscopic measurements exist and only calculations [2] of the IR spectrum are available. The band origin for the $v_1$ band has been predicted to be at 3028 cm$^{-1}$, which is within the scanning range of our home-built OPO system.

As already mentioned in §3, it was nearly impossible to produce reasonable amounts of $\text{O}_2\text{H}^+$ in our storage ion source; so instead, an equilibrium situation has been generated in the trap by injecting $\text{H}_3^+$ into the trap containing $\text{O}_2$, leading to the production of $\text{O}_2\text{H}^+$. Additionally, the source pressure has been increased to leak enough $\text{H}_2$ into the trap. By adjusting the second quadrupole mass spectrometer to a mass of 3 atomic mass units, the strategy was to increase the number of detected $\text{H}_3^+$ ions following laser excitation. The OPO was scanned in the target range 3023–3055 cm$^{-1}$, but no signal change was detected. The negative result is in line with a fast back reaction, as the additional light-induced signal is probably very small. A better suited reaction scheme is needed in future experiments to record the infrared spectrum of $\text{O}_2\text{H}^+$. One possible candidate is Ar whose proton affinity is lower by some 51.9 kJmol$^{-1}$. However, it is questionable whether the approximately 3000 cm$^{-1}$ of the excited $\text{O}_2\text{H}^+$ will be sufficient to record an $\text{ArH}^+$ LIR signal. But using a seeded beam of Ar can increase the collision energy significantly and help to overcome the current limitations of having a bath of thermalized target gas (see also §5).

(b) Laser-induced reaction of $\text{H}_3^+$ in collision with $\text{O}_2$

The situation is quite different for the forward direction of reaction (1.1). Owing to its high power, the OPO system has been used to revisit the fundamental $\text{H}_3^+$ vibrations seen by Oka 30 years ago [6] with the LIR method. An example spectrum probing the lowest rotational levels of $\text{H}_3^+$ at 40 K is shown in figure 4. In addition to the transitions shown (starting from the two lowest levels (1,1) and (1,0); figure 3), also one line starting from the (2,2) level at 2762.06 cm$^{-1}$ has been probed, while that starting from the next higher (2,1) rotational level at 2762.08 cm$^{-1}$ could hardly be detected. This confirms our earlier assumption that the higher $J = 2$ levels have initial low thermal populations that are probably further depleted in collisions with $\text{O}_2$, as seen in figure 1.
Figure 4. LIR spectrum of H$_3^+$ in collisions with O$_2$ recorded with the OPO system at 40 K. Owing to the high OPO power, a short trapping time of 280 ms has been chosen. The two transitions start from the two lowest rotational levels (1,1) of para-H$_3^+$ and the 23 cm$^{-1}$ higher-lying (1,0) of ortho-H$_3^+$. For a detailed level scheme of these transitions, see fig. 2 of Kreckel [18].

Extracting level populations from LIR measurements like those shown in figure 4 is a subtle task. The LIR signal is influenced by the level population itself, but also the photon absorption process (Einstein B coefficient and spectral energy density $\rho \sim P/\Delta \nu$ of the laser), the reactivity of the excited states of the parent ions, as well as competing reactions, also play a role. For illumination times comparable or longer than those for inelastic collisions, repopulation of the pumped states by inelastic collisions has to be taken into account too. Detailed descriptions of the LIR kinetics can be found for the collision systems N$_2^+$ + Ar [21] or C$_2$H$_2^+$ + H$_2$ [22]. In figure 4, the situation appears less complicated because the LIR signals have a saturated shape, which happens when all pumped ions are converted into product ions and the signal cannot increase any further. Thus, with the high excitation rates in the current experiment (with a power of 100 mW, an excitation rate of 8700 s$^{-1}$ is estimated for the para transition), we assume in the following that the majority of the ions in the lowest rotational states have been pumped by the laser and we further assume that the excited states have an equal probability to react to the O$_2$H$^+$ LIR signal, i.e. we assume that the signals in figure 4 are proportional to the population of the probed rotational states. Therefore, this preliminary spectroscopic testing indicates that the (1,0) ortho-H$_3^+$ level has a population that is a factor of about 1.93 higher than the para (1,1) level.

As outlined in §3b, the H$_3^+$ ions are assumed to be formed in a 1:1 o/p ratio in the ion source, which is not changed by cooling the ions to 40 K by He collisions. This ratio then also holds for the two considered levels ((1,1) and (1,0)) as the population of the $J = 2$ states is negligible at the temperature of the experiment. Even if exchange between the ortho and para modifications is allowed (e.g. by collisions with O$_2$), the ratio stays close to 1:1 in the considered temperature range. Therefore, the ratio of 1.93 found in the LIR experiment is substantially higher than the 1:1 ratio of the initially cold H$_3^+$ in the two lowest states. As
shown in the kinetics section, during trapping, the \( \text{H}_3^+ \) ions are not only subject to photon excitation but also react to \( \text{O}_2 \text{H}^+ \) owing to the many collisions with the \( \text{O}_2 \) target gas. The \( \text{O}_2 \) number density in the experiment shown in figure 4 was about \( 10^{11} \text{ cm}^{-3} \). This corresponds to about 40 collisions between \( \text{H}_3^+ \) and \( \text{O}_2 \) during the 280 ms storage time. We found that the para fraction reacts much faster (without laser) than the ortho fraction. Therefore, the (1,1) para state is depleted during the LIR experiment, while this depletion is much slower for the (1,0) ortho state. As a result, the LIR signal of the ‘unreactive’ ortho species is significantly larger.

In order to more reliably derive state populations and the corresponding reaction rates, more advanced LIR experiments are planned where the cooling, the laser irradiation and the chemical probing of the states with \( \text{O}_2 \) (or Ar) will be separated in time. For that purpose, the laser and \( \text{O}_2 \) will be admitted to the trap in delayed pulses. Measuring the ratio of the (1,0) and (1,1) signals as a function of delay time will enable us to unfold inelastic processes. Most interesting are the astrophysically dominant collisions with \( \text{H}_2 \) that modify the \( o/p \) of \( \text{H}_3^+ \) \[20,23–26\].

It should be mentioned that we also searched for spectroscopic signatures of \( \text{H}_3^+ \) in the overtone range of 6097–6944 cm\(^{-1}\), similar to our previous work for \( \text{H}_2\text{D}^+ \) and \( \text{D}_2\text{H}^+ \) \[12\]. By using lists of \textit{ab initio} calculated transition values \[27,28\], three transitions in the 3\( \nu_2 \) band \[29,30\] at about 6865.7, 6877.5 and 6942.1 cm\(^{-1}\), having large Einstein \( B \) coefficients and originating from low rotational states (up to \( J = 2 \)), have been selected for the search. However, no \( \text{H}_3^+ \) line could be detected. The reasons are, on the one hand, the low laser power. For instance, the power for the transition at 6942.1 cm\(^{-1}\) starting from the (1,1) para-\( \text{H}_3^+ \) rotational level was only 0.95 mW. Additionally, for the two other transitions starting at para-\( \text{H}_3^+ \) levels with \( J = 2 \), the population at 40 K is low, as pointed out before.

5. Conclusions and future trends

In summary, the rate coefficient for proton transfer from \( \text{H}_3^+ \) to \( \text{O}_2 \) has been recorded over an extended temperature range. Owing to nuclear spin restrictions, individual endothermicities become apparent at low temperatures, manifesting themselves in a slower reaction of the ortho fraction of \( \text{H}_3^+ \). Thus, the system \( \text{H}_3^+ + \text{O}_2 \) is one of the few for which state-selective behaviour can be observed in a simple trap experiment. Besides this demonstration, this study shows that collisions with \( \text{O}_2 \) (instead of Ar) can be used in LIR to probe the population of the lowest \( \text{H}_3^+ \) rotational levels.

The possibility to prepare a single quantum state of \( \text{H}_3^+ \) (namely the lowest ortho state) calls for further trap experiments aimed at the study of state-specific reactions and inelastic processes. A dedicated, low-temperature trap experiment is currently being built to enable such sophisticated measurements. The rearranged trap setup is shown in figure 5. \( \text{H}_3^+ \) ions are produced in a storage ion source (not shown), mass selected in a first quadrupole mass filter and bent into the 22-pole ion trap. The ion trap is mounted on a 4 K cold head, and thus, \( \text{He} \) buffer gas cooling will lead to much colder \( \text{H}_3^+ \) ions. Instead of admitting the \( \text{O}_2 \) reaction gas into the trap, it will be supplied by a molecular beam. This arrangement will avoid freeze out of the reactant gas in the 22-pole trap. In addition, adjustment of the collision energy by seeding or loading of the molecular beam is possible.
Figure 5. Central part of the new-generation, low-temperature trapping apparatus. The trap can be cooled to temperatures as low as 4K. Ion bending prior to trapping enables the use of a pulsed molecular beam (O$_2$) for chemical probing of the H$_3^+$ trap contents.

Still, the number density of the beam is sufficient to act as a probing gas on a reasonable time scale. A similar trap setup operated in Prague [31] allows for enough collisions, even with atomic hydrogen, to serve the purpose of chemical probing. Also the bent arrangement will allow for a reduced H$_2$ background from the source chamber.

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