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Reactions of CO_2^+ with H, H_2 and deuterated analogues

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ABSTRACT

Combining a temperature variable 22-pole ion trap with a cold effusive beam of neutrals, rate coefficients $k(T)$ have been measured for reactions of CO_2^+ ions with H, H_2 and deuterated analogues. The neutral beam which is cooled in an accommodator to T_{ACC}, penetrates the trapped ion cloud with a well-characterized velocity distribution. The temperature of the ions, T_{22PT}, has been set to values between 15 and 300 K. Thermalization is accelerated by using helium buffer gas. For reference, some experiments have been performed with thermal target gas. For this purpose hydrogen is leaked directly into the box surrounding the trap. While collisions of CO_2^+ with H_2 lead exclusively to the protonated product HCO_2^+, collisions with H atoms form mainly HCO^+. The electron transfer channel $H^+ + CO_2$ could not be detected (<20%). Equivalent studies have been performed for deuterium. The rate coefficients for reactions with atoms are rather small. Within our relative errors of less than 15%, they do not depend on the temperature of the CO_2^+ ions nor on the velocity of the atoms ($k(T)$ lays between 4.5 and $4.7 \times 10^{-10}\ cm^3\ s^{-1}$ with H as target, and $2.2 \times 10^{-10}\ cm^3\ s^{-1}$ with D). For collisions with molecules, the reactivity increases significantly with falling temperature, reaching the Langevin values at 15 K. These results are reported as $k = \alpha\ (T/300\ K)^{\beta}$ with $\alpha = 9.5 \times 10^{-10}\ cm^3\ s^{-1}$ and $\beta = -0.15$ for H_2 and $\alpha = 4.9 \times 10^{-10}\ cm^3\ s^{-1}$ and $\beta = -0.30$ for D_2.

1. Introduction

1.1. Instruments for ion chemistry

The last decades have seen the development of many sophisticated instruments, specific tools and clever strategies for studying the interaction between ions and molecules in great detail. Techniques include crossed and merged beams, swarm methods, ion guides and traps. Many skillful methods have been invented for preparing the reactants. A recent example is the preparation of ultracold molecules via stark deceleration [1]. For extracting detailed information on the products, emerging from the collision region, the instruments are often equipped with sophisticated analytical tools; for example, ion imaging detectors allow one to map product velocity distributions. A central motivation of such activities is to understand the dynamics of elastic, inelastic and reactive collisions from first principles. For this aim, the best is to measure state-to-state differential cross-sections as a function of a variety of parameters. Another goal of studying ion chemistry is to understand (or model) thermal plasmas and charged non-equilibrium environments such as boundary layers of magnetically confined fusion plasmas or interstellar and circumstellar regions. The present needs for astrochemistry – in most cases the temperature dependence of thermal rate coefficients – have been summarized recently [2].

1.2. Cold collisions, low temperatures

A nice overview of experimental techniques used in beam scattering studies of elementary ion–molecule reactions has been given recently by Herman [3] who has strongly influenced the fields of gas phase ion chemistry and mass spectrometry over more than four decades. The “classical” ion beams were restricted to higher energies, typically above 1 eV, while, in the thermal regime, ion–molecule reactions were studied for long time predominantly by swarm and magnetic trapping techniques. The reason is that electrostatic fields are not well-suited for handling slow charged particles, especially if space charges or field distortions play a role. One of the approaches to reach low collision energies was the merged beam technique where the two reactant beams which move in the same direction, can be operated with high laboratory velocities [4]. A rather general solution is based on confining slow ions via suitable *effective potentials* created by fast oscillatory electric fields. As summarized recently in [5] this method has removed many difficulties encountered by standard electrostatic techniques. A typical application is the so-called guided ion beam method, in which a suitable electric radio frequency (rf) field is used to conduct ions through a scattering cell, filled with the neutral reaction

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partner. The results presented in this paper, also have been measured with a beam-cell arrangement; however, the roles have been changed: the neutral reactants are formed into a beam while the *target* are a few hundred ions, confined in an rf trap. In the following, the instrument will be described only briefly since the details are reported elsewhere [6].

1.3. Reactions with H and D atoms

One of our motivations to combine an ion trap with a beam of neutrals was to investigate low energy reactions between ions and radicals, especially hydrogen atoms. H-atom beams are used as targets in many experiments in fundamental physics and chemistry, including collisions with multiply charged ions, photoionization studies, or high resolution scattering experiments using crossed beams [7]. Collisions with H atoms play a central role in astrochemistry, especially in the chemistry of the early universe [8]. For example, a fundamental process is the weakly endothermic electron transfer from D to H^+, an important step in the formation of deuterated molecules in interstellar clouds. While this process is probably well enough characterized by theory [9], more complex reactions such as the H–D exchange in $H_3{}^+ + D$ certainly needs to be studied in more detail theoretically and in a low temperature experiment [10,11]. Some first measurements have been reported [4]; however not with internally cold ions as discussed in [5].

In ion chemistry, studies with atoms are rather scarce especially at energies of interest for interstellar chemistry. The older literature dealing with this subject has been reviewed by Sablier and Rolando [12]. Most ion–H atom experiments utilize swarm techniques operated at room temperature. The combination of an ion drift tube and a hydrogen atom source has provided information at higher energies [13], while a variable temperature SIFT apparatus extended the temperature range down to 120 K [14]. There has been an attempt to combine an ion cyclotron resonance cell with a hydrogen discharge source [15]; however, many complications due to H–H recombination, metastable atoms and UV photons have made it extremely hard to get reliable quantitative results from this special arrangement. The laboratory studies done since 1993 for reactions of positive and negative ions with H, N, or O atoms have been summarized very recently in a nice comprehensive review by Snow and Bierbaum [16].

1.4. $CO_2{}^+$ reacting with H or H_2

One of the first ions the reactivity of which was investigated with H atoms at thermal energies, was $CO_2{}^+$ [17]. Using a drift tube, these measurements have been extended later into the energy range between 60 and 140 meV by Tosi et al. [18]. For calibrating the atomic hydrogen density, these authors and later Scott et al. [19] have made use of the special feature that $CO_2{}^+$ produces predominantly HCO^+ in collisions with H while reactions with molecular hydrogen lead to $HCO_2{}^+$. This was one of our motivations to select this well-characterized system for calibrating and testing our new instrument. In addition, because of the importance of these reactions in connection with planetary and cometary atmospheres or interstellar clouds, we have extended the previous results towards lower temperatures.

At low collision energies, reactions of $CO_2{}^+$ with hydrogen molecules lead just to one product,

$$CO_2{}^+ + H_2 \rightarrow HCO_2{}^+ + H, \tag{1}$$

while for collision with H atoms, three channels are energetically allowed,

$$CO_2{}^+ + H \rightarrow HCO^+ + O, \tag{2}$$

$$CO_2{}^+ + H \rightarrow HOC^+ + O, \tag{2a}$$

$$CO_2{}^+ + H \rightarrow H^+ + CO_2. \tag{2b}$$

It must be mentioned that, so far, we have not yet distinguished between the two isomers formed via reactions (2) and (2a) although the relevant technique is available in instruments using ion traps [20]. In addition no products have been found from reaction (2b); however, as discussed below, we did not make use of the full sensitivity of the trap.

In contrast to the well-characterized reactions with H and H_2, the analogue processes with deuterium have been studied only in an ICR experiment [15]. In the present work we have performed detailed measurements for

$$CO_2{}^+ + D_2 \rightarrow DCO_2{}^+ + D, \tag{3}$$

$$CO_2{}^+ + D \rightarrow DCO^+ + O. \tag{4}$$

Also in reaction (4) no attempt has been made to distinguish between isomers or to detect possible traces from charge transfer.

In the following we briefly describe the experimental setup, including the hydrogen atom source and the various measuring procedures. Some remarks concerning kinematic averaging in the neutral beam-stored ion cloud arrangement are made. Various results are summarized and discussed which have been obtained with different beam arrangements.

2. Experimental

2.1. The AB-22PT

The experimental studies have been performed in the *atomic beam 22-pole ion trapping apparatus* (AB-22PT) which is shown schematically in Fig. 1. A first description and some preliminary results have been reported previously [21]. Since a detailed characterization of this new instrument is published in [6], together with a collection of typical applications, here only the most important features are summarized briefly. Concerning the basics of the rf based ion trapping technique we refer to the relevant literature [23,24]. In addition, there are several more recent applications of cryogenic rf multi-electrode traps which just have been reviewed [5,25]. Important for the present study is that the internal degrees of freedom of the $CO_2{}^+$ ions can be cooled to temperatures between 15 and 300 K and that the linear multipole is well-suited for running a molecular beam (or also a laser beam) through the trap without hitting any surface.

As indicated in Fig. 1 the instrument combines a standard ion trapping machine [26,2] with a doubly differentially pumped beam source the temperature of which can be varied. Primary ions are injected into the 22PT via an electrostatic quadrupole bender. They have been prepared in a well-established combination of a electron impact storage ion source with a quadrupole mass selector (not shown in the figure, for details see [23]). In the trap, the ions are confined in a wide near field-free environment. The typical ion volume is 1.5 cm^3. Radial confinement is achieved by an effective potential which is created by applying two opposite phases of an rf generator to the two sets of 11 electrodes. The electrostatic entrance and exit electrodes are used to control the injection and extraction procedure. Voltages of less than 100 mV are sufficient to close the trap. Analysis and detection of the ion cloud is carried out with a second quadrupole mass spectrometer and a Daly type detector [27]. For studying chemical reactions, it is sufficient to store a rather low number of ions, typically $N_0 = 1000$ primary ions are injected each time. Depending on conversion rates (relaxation, reaction, decay, etc.), they are trapped for time periods varying between ms and

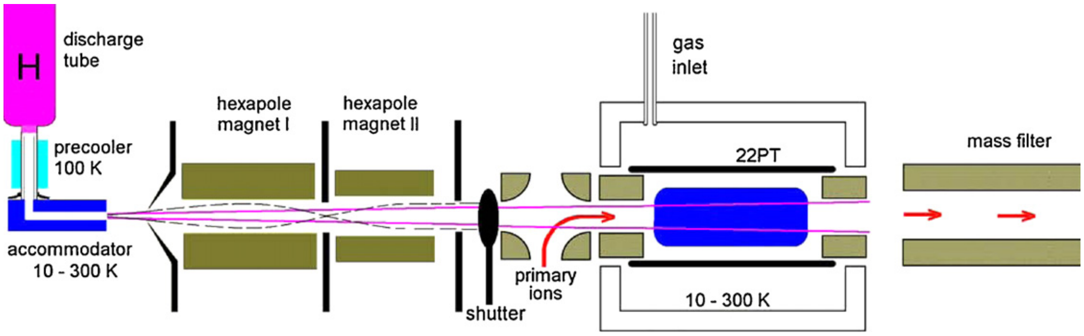

Fig. 1. Schematic diagram of the combination of an Atomic Beam (left part) with a 22-pole ion trap (AB-22PT apparatus) used for studying the interaction of a slow effusive H-atom/H_2 molecular beam with stored cold CO_2^+ ions. A short description and first results have been published previously [21]. A detailed documentation of this versatile instrument can be found elsewhere [6]. Before the primary ions enter the electrostatic quadrupole bender, they have been thermalized in a storage ion source and selected in a first quadrupole mass spectrometer (not shown, for details see [22] and [25]). The H-atoms produced in an rf discharge, are first precooled to 100 K and then thermalized to the temperature of the accommodator, T_{ACC}. For determining accurate relative rate coefficients of reactions with H and H_2, a series of measurements has been performed without the hexapole focusing magnets. This leads to straight trajectories (solid lines) for both atoms and molecules, to conservation of flux, and to a well defined overlapping region between the marked ion cloud and the neutrals (solid line) With the magnetic hexapoles in place, atoms are guided and focused, depending on their velocity. The dotted lines indicate schematically the imaging properties of the harmonic guiding field for atoms with a kinetic energy of 8.2 meV. The shutter is used for blocking the direct beam, allowing to account for reactions with background gas.

min. In general there is no loss of ions or creation of additional ones, so the total *number of ions per filling* remains constant, $\sum N_i = N_0$.

The ion trapping region is surrounded by a copper box (see Fig. 1) which is thermally connected to the cold head of a close cycle refrigerator system. Depending on the cryocooler head used, nominal temperatures as low as 3.6 K have been reached. The translational and internal degrees of freedom of the ions are coupled to the cold environment efficiently by inelastic collisions with helium buffer gas. This either can be leaked into the inner box continuously or injected as a short and intense gas pulse. The pulse is synchronized with the filling of the trap with ions. In general complete thermalization to the temperature of the surrounding walls can be achieved in a few ms. As emphasized in [5], the influence of the micro motion driven by the oscillating confining field – effects referred to as radio frequency heating – is negligible if the trap is operated properly.

2.2. *The atomic or molecular beam source*

The component dominating the otherwise well-characterized 22PT machine, is the doubly differential pumped neutral beam source. The overall geometry, defined by the accommodator, the skimmer, several apertures and the entrance and exit electrode of the trap, has been constructed in such a way that the neutrals traverse the linear multipole ion trap in axial direction without hitting any of the surfaces surrounding the interaction region. For distinguishing between the direct beam and atoms or molecules diffusing indirectly into the trap, a shutter is placed in the chamber containing the 22-pole trap (see Fig. 1).

The vacuum system consists of three differential pumping stages with nominal effective pumping speeds of 2400, 350 and 300 l/s (for hydrogen). Important details such as the conductance of the apertures in the walls separating the chambers, etc., are given in [6]. In order to be able to perform measurements with target number densities smaller than $10^8\,cm^{-3}$ an excellent vacuum is mandatory. Nonetheless, especially at elevated temperatures, we have to account for parasitic reactions of stored ions with impurities such as N_2, CO_2, H_2O.

Special emphasis has been given to the development of a well-defined, temperature variable hydrogen atom source, profiting from the variety of relevant publications. In most of our applications, we used a standard rf driven plasma source for dissociating hydrogen [22]. For slowing down the atoms emerging from the hot discharge to low velocities, cryogenic cooling has been used [28]. As indicated in Fig. 1, the hydrogen atoms pass first through a glass tube surrounded by a precooler followed by a channel in a copper block the temperature of which can be set to values between T_{ACC} = 10 and 300 K. The arrangement has been tested under a variety of conditions, using either chemical probing in the ion trap or an electron ionization source installed at the location of the 22PT (see Fig. 1). There are many descriptions and specific hints in the literature for achieving high dissociation degrees and for reducing H–H recombination on the walls of the discharge tube and the tubes, see for example [29,30]. We have found a procedure to obtain very high dissociation degrees (more than 90% at 100 K) and to keep them constant over many hours. The method which is based on coating the walls of the precooler and the accommodator with specific layers of water, is described in more detail in the thesis of Borodi [31].

The efficiency of the accommodator and the transmission features of the two hexapole magnets shown schematically in Fig. 1, have been tested by measuring velocity distributions using a chopper wheel and the already mentioned universal detector [6]. A typical time of flight distribution, recorded at T_{ACC} = 50 K, is shown in Fig. 2. Without magnets one obtains a smooth thermal distribution indicated by the dotted line, whereas specific velocity groups dominate if the two hexapoles are integrated into the machine. The

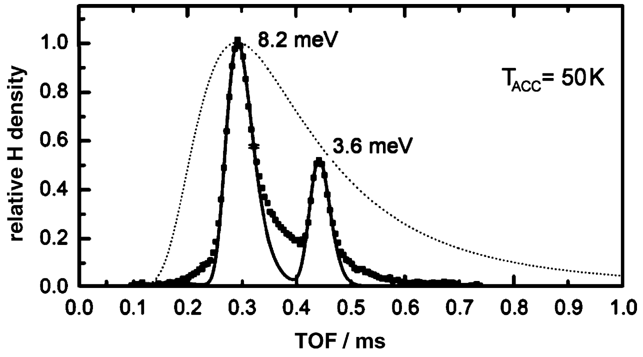

Fig. 2. Normalized time of flight distribution of H atoms measured at T_{ACC} = 50 K with an ionizer at the location of the 22-pole. Without the hexapole magnets (see Fig. 1) one obtains the thermal distribution indicated by the dotted line. The transmission features of the two hexapoles favor mainly two groups the kinetic energies of which are indicated by the two Gaussians. As illustrated by the dashed trajectory in Fig. 1 and discussed in detail in [6], the maximal transmission of H atoms is obtained for a kinetic energy of 8.2 meV.

interaction of their fields with the magnetic moment of the hydrogen atoms leads to a harmonic guiding potential and, therefore, to focusing and imaging properties. In the present case the field strength of the two different magnets and the geometry favor the transmission of atoms, having a kinetic energy of (8.2 ± 3.3) meV. With such a speed, the oscillation in transverse direction leads to about 1/2 sinus wave in the first magnet and to 1/4 wave in the second one, which is weaker and shorter. As illustrated in Fig. 1 with the dashed trajectories the result is a nearly parallel beam of atoms passing through the trap. More details and modifications for favoring slower atoms are discussed in [6].

2.3. Measuring procedure

For studying the title reaction, CO_2^+ ions have been produced by electron bombardment of carbon dioxide gas (Messer-Griesheim 2.7 purity) in a storage ion source [23]. In such a source, the long storage time and the high number density of the neutral precursor gas (>10^{-5} mbar) already leads to a significant pre-thermalization of the ions. Furthermore, the initial excitation of the ions has been kept rather low by setting the electron energy (~15 eV) just above the ionization energy of carbon dioxide (13.777 eV). After extraction of primary ions from the storage source using the pulsed exit electrode, the ions are mass selected in a quadrupole, deflected in the static quadrupole by 90° (included in Fig. 1) and injected into the trap. There they are cooled to the ambient temperature and exposed to the neutral reactant gas for a period which is varied from milliseconds to seconds or minutes. After this storage time, the trap content is extracted by opening the exit electrode, analyzed in a second quadrupole mass filter and the ions are counted. For determining reaction rate coefficients, the sequence ion formation, injection, relaxation, reaction, extraction, and analysis is repeated many times for all ions of interest. Several parameters are changed the most important being the reaction time. Others include the number density of the reactant or coolant gas, the temperature of the trap, and, especially in the results reported here, various parameters of the neutral beam.

2.4. Averaging over velocity and spatial distributions

In order to understand the potential and the limitations of the combination of a thermal ion cloud interacting with an effusive beam, one needs some basic knowledge in kinematic and spatial averaging. Some relevant hints can be found in [23]. Other special aspects, e.g., how to reach very low relative velocities or how to cool molecular ions to very low temperatures, have been discussed recently in [5] and [25].

So far, in most low temperature trapping experiments, the neutral reactants have been leaked into the box surrounding the trap (see Fig. 1), usually also together with the cooling buffer gas. Under such conditions, one can reach a thermal equilibrium at a common temperature T_{22PT} given by the surrounding walls. The measured results are thermal rate coefficients $k(T_{22PT})$. If there is some ion heating, e.g., via a parasitic low frequency components from the rf generator or other electric noise, the translational distribution of the trapped ions is no longer thermal. In such a situation it is often sufficient to approximate the motion of the ions which may be determined, for example, with laser methods, by a Maxwellian with a mean temperature, T_{ion}. As can be shown analytically [32], under such conditions one measures a thermal rate coefficients $k(T_{coll})$ with a collision temperature

$$T_{coll} = \frac{(m_{target}\,T_{ion} + m_{ion}\,T_{target})}{(m_{ion} + m_{target})}. \tag{5}$$

Another situation is a monoenergetic ion beam passing through a scattering cell containing a thermal target gas. This special case can be treated analytically, resulting in a generalized Maxwell–Boltzmann distribution [33,23]. At low beam velocities, this function approaches a normal Maxwellian with a reduced temperature

$$T_{coll} = \left\{ \frac{m_{ion}}{m_{ion} + m_{target}} \right\} T_{target}. \tag{6}$$

From a kinematic point of view, we have in the present experiment, combining a cold effusive or supersonic neutral beam with a stored ion cloud, the same situation. In reality, however, inspection of Fig. 2 reveals that the assumption of a monoenergetic beam cannot be made and a detailed analysis requires to integrate numerically (or analytically) the generalized Maxwell–Boltzmann distribution over the velocity distribution of the beam. For the rate coefficients presented in this paper, the resulting corrections are rather small since the elementary rate coefficients depend only weekly or not at all on the relative velocity. In contrast, a detailed treatment is required for the CH_5^+ + H collision system as discussed in [34]. In the following we just report the measured rate coefficients as $k(T_{22PT,}\ T_{ACC})$.

Another important aspect which is discussed in more detail in [6] is the averaging over the spatial distributions of the reactants. In a first approximation one can assume that the densities of neutrals and ions are homogeneous in the region of overlap which is indicated schematically in Fig. 1. The neutral beam diameter is typically 5 mm while, in the 22PT, the ions usually explore a cylinder with a diameter of 7–8 mm. For example, in the case of CO_2^+ ions, the 22PT has been operated with an rf amplitude $V_0 = 50$ V and a frequency $f = 16$ MHz. Using the standard definitions and formulas [23], one obtains a diameter of $2r_m = 7.2$ mm for a transverse energy $E_m = 1$ meV (8.1 mm for $E_m = 10$ meV).

3. Results

The AB-22PT apparatus has been used in various ways for studying the interaction of hydrogen atoms and molecules with cold trapped CO_2^+ ions. For obtaining reliable thermal rate coefficients for reactions (1) and (3), molecular hydrogen was leaked into the trap directly with number densities up to 10^{11} cm^{-3}. The so measured thermal rate coefficients have been used to determine in the trap the effective number density of the effusive molecular beam and together with the shutter, the molecular background. With atomic hydrogen, a series of measurements has been performed with the hexapole magnets taken out. This allows us to assume conservation of hydrogen flux, i.e., the number of H-atoms/s does not change if the discharge is switched ON. For this analysis, each H is counted independent on whether it is single or bound in a molecule. Other parameters which have been selected in various combinations are the two temperatures T_{ACC} (12–300 K) and T_{22PT} (15–300 K) and the position of the shutter which can block the direct beam. The number density of He buffer gas was always set to a few 10^{13} cm^{-3}.

For reaction (1), a typical time dependence is shown in Fig. 3 at $T_{22PT} = 15$ K using the gas inlet leaking the H_2 directly into the trap. Plotted is the number of primary and product ions, N_i, as a function of storage time. As already discussed above, the trap is usually filled with some thousand primary ions. For better statistics, the measurements are averaged over many iterations; however, the $N_i(t)$ are normalized to one iteration (*ions per filling*). Inspection shows that the number density of 1.4×10^{10} cm^{-3} is high enough for converting half of the primary CO_2^+ ions into HCO_2^+ products already after 30 ms. For evaluating such experimental data, the time dependence

Table 1
Measured reaction rate coefficients and comparison with published values.

Reaction	k[a]	α[b]	β[b]	T (K)[c]	T_{ACC} (K)	Remarks
$CO_2^+ + H_2 \rightarrow HCO_2^+ + H$	15.3					Langevin
		9.5	−0.15	15–300		this work
	8.7			300		[19] SIFT
	9.0			60–140 meV		[18] DT
	(5.8)[d]			Non-thermal		[15] ICR
$CO_2^+ + D_2 \rightarrow DCO_2^+ + D$	10.9					Langevin
		4.9	−0.30	15–300		This work
	(4.1)			Non-thermal		[15] ICR
$CO_2^+ + H \rightarrow HCO^+ + O$	19.4					Langevin
	4.7			125	300	This work[e]
	4.5			300	55	This work
	4.7			300		[19] SIFT
	2.9			60–140 meV		[18] DT
	(1.1)			Non-thermal		[15] ICR
	6			300		[17] FA
$CO_2^+ + D \rightarrow DCO^+ + O$	13.8					Langevin
	2.2			55–300	55	This work
	(0.84)			Non-thermal		[15] ICR

[a] The unit of k is 10^{-10} cm^3 s^{-1}. The errors of the absolute values for reactions with molecular target, k_1 and k_3, are estimated to be 20%, those with atomic reactants, k_2 and k_4, are 40%. Relative errors for the temperature dependence are less than 15%.

[b] The temperature dependence is approximated with $k(T) = \alpha(T_{22PT}/300\,K)^{\beta}$, the unit of α is 10^{-10} cm^3 s^{-1}. These measurements were performed with hydrogen, directly leaked into the 22-pole trap (see Fig. 1).

[c] T is either T_{22PT} or the temperature of the respective instrument. In the case of the drift tube, the mean kinetic energy is given.

[d] The number in brackets are ICR data [15] which should be take with care. For details see text.

[e] This measurement was performed using a single differential pumping stage arrangement.

of the number of stored ions, N_i, is simulated by solving numerically a system of differential equation describing the changes in the trap. Here the situation is very simple since only two channels are of importance. No other masses have been found within 3 decades, two of which are shown in the figure. The resulting rate coefficient is given in Table 1. A similar result for deuterium is shown in Fig. 4. Note that the number density, $[D_2] = 1.1 \times 10^{11}$ cm^{-3}, is ∼8 times higher leading to a faster conversion of the primary ions. Very important hints from such measurements are the mono-exponential decay of the primary ions over 2 orders of magnitude without any indication of a curvature and the convergence of the DCO_2^+ products towards the constant sum. This allows the conclusion that, within a few % accuracy, no other ions are involved.

The situation is quite different if the neutral beam is used instead of leaking the gas directly into the trap. For the measurements shown in Fig. 5 both the accommodator and the 22PT have been set to the same temperature, 55 K. The hexapole magnets have been removed from the instrument in order to get the same transmission properties for hydrogen atoms and molecules. On the left (discharge OFF), Fig. 5 shows results for reactions of CO_2^+ ions with D_2. Only some ten DCO_2^+ products are formed per filling in the time window shown. Closing the shutter (open symbols) blocks the beam and allows to determine the density of the D_2 background gas using the rate coefficients which has been determined at the same temperature of the walls of the trap, $T_{22PT} = 55$ K (see Table 1). From such measurements we obtain a mean number density of the molecu-

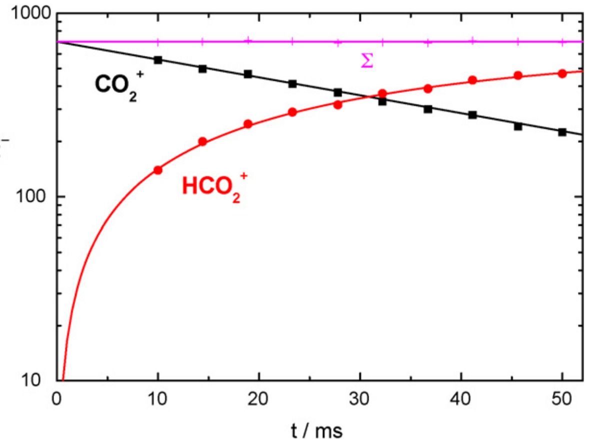

Fig. 3. Reactions of CO_2^+ ions with H_2 molecules, leaked directly into the trap at a number density of $[H_2] = 1.4 \times 10^{10}$ cm^{-3}. Plotted is the number of primary and product ions per filling, N_i, as a function of the storage time t. At each iteration, typically 700 CO_2^+ ions (full squares) are filled into the trap. For cooling the ions to $T_{22PT} = 15$ K within a few ms, He gas has been added with a number density of 4.8×10^{13} cm^{-3}. In the present example, data are evaluated after 10 ms. The number of the primary ions decreases exponentially. As can be seen from the simulation (solid lines) and the constant sum, Σ, the HCO_2^+ products grow at the same rate. No other ions have been seen within the plotted range. Rate coefficients are summarized in Table 1.

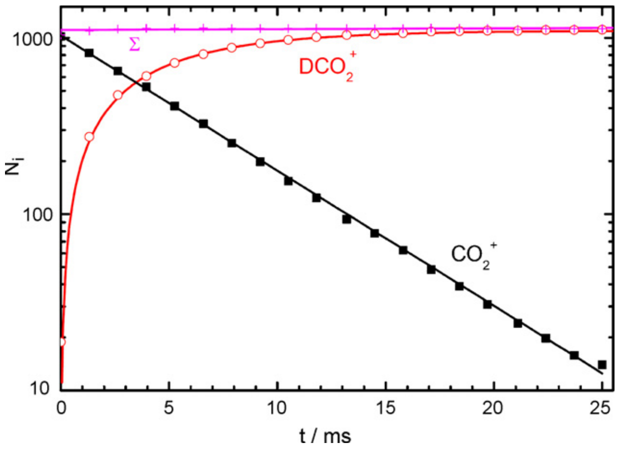

Fig. 4. Same as Fig. 3, here for deuterium. The significant higher number density ($[D_2] = 1.1 \times 10^{11}$ cm^{-3}, $T_{22PT} = 15$ K, $[He] = 4 \times 10^{13}$ cm^{-3}) allows us to follow the mono-exponentially decay over two orders of magnitude (time constant $\tau = 7.5$ ms). The solid lines are solutions of a simple rate equation system accounting just for reaction (3). The resulting rate coefficient is included in Table 1.

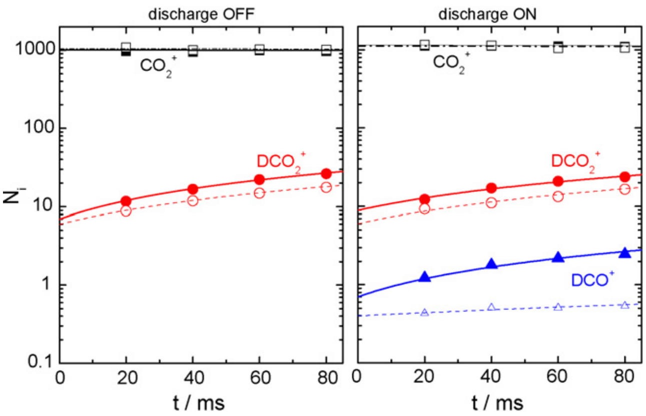

Fig. 5. Experimental results obtained without hexapole magnets. The reactions of CO_2^+ ions with the pure D_2 beam (discharge off, left panel) and with a D/D_2 mixture (discharge on, right panel) have been recorded at $T_{ACC} = 55$ K and $T_{22PT} = 55$ K. Due to the lower target density (some 10^8 cm^{-3}) the number of product ions is much smaller in comparison to Figs. 3 and 4. For subtracting the background, the shutter shown in Fig. 1 is opened (solid symbols) and closed (open symbols). The evaluation of data sets which have been taken without the magnets, is simplified due to flux conservation. The resulting rate coefficients are summarized in Table 1.

lar beam in the trap, $[D_2]_{OFF} = 1.3 \times 10^8$ cm^{-3}. As already mentioned above this mean value accounts for the fact, that the trapped ions spend about 60% of their time outside of the beam (see Fig. 1).

Switching the discharge ON (right panel) the deuterium flux consists of a D/D_2 mixture. As can be seen on the right side of Fig. 5, the fragmentation of D_2 leads to a decrease of DCO_2^+ products while the D atoms formed by dissociation produce now DCO^+ ions via reaction (4). Note that there is some minor background on mass 30, most probably caused by some background gas. Conservation of mass flux through the leak valve, the accommodator, and the trap means that one obtains for each molecule in the beam two atoms. In order to convert the flux into density in the trap one has to account for the different velocities of D and D_2. This requires division by $\sqrt{2}$, assuming that the accommodator fully thermalizes atoms and molecules to the same temperature. Accounting for these two factors, the mean number density of D atoms is obtained from

$$[D] = \sqrt{2}\,([D_2]_{OFF} - [D_2]_{ON})\,. \qquad (7)$$

Typical atom number densities measured in this way are $[D] = 10^8$ cm^{-3} corresponding to an effective dissociation degree of about 60% in the 22PT.

Such measurements have been performed at different trap and accommodator temperatures, for both hydrogen and deuterium. From a large set of data, absolute rate coefficients for reactions (2) and (4) have been determined. No significant temperature dependence has been observed between 50 and 300 K. For D, an average value of $k_4 = 2.2 \times 10^{-10}$ cm^3 s^{-1} is included in Table 1 while for reaction (2) we report two values, $k_2 = 4.5$ and 4.7×10^{-10} cm^3 s^{-1} to emphasize that these values have been measured at different combinations of T_{ACC} and T_{22PT}. For all subsequent measurements, especially with the hexapole magnets installed, these values are used as calibration standards. The errors of k_2 and k_4 are estimated to be 40% since the uncertainties of four rates enter into the evaluation. Another uncertainty is the charge transfer channel (2b); however, Scott et al. [19] reported that its contribution is smaller than 5% of the total rate coefficient. In our measurements, we have not yet searched for small amounts of ions on mass 1 or 2 which requires some effort with the quadrupole mass spectrometer. The overall charge balance of the detected ions excludes, that the charge transfer rate coefficient k_{2b} exceeds 20% of k_2.

Installing the two hexapole magnets leads to an increase of the flux of atoms. Inspection of time of flight distributions, see for example Fig. 2, allows us to estimate that, for the given geometry, an amplification factor of up to 10 can be achieved for specific velocity groups. Total averaged effective number densities of up to 3.5×10^9 cm^{-3} have been achieved. One disadvantage of the magnets is that also the molecular hydrogen background increases since the efficiency of differential pumping is reduced by the long tube like structures. Moreover, one has to account for the molecular background which is created by atom–atom recombination on walls. As a consequence flux conservation cannot be used for determining the effective number density of the atoms in the trap.

The situation is illustrated with a surprising experimental result in Fig. 6. The overall higher flux caused by guiding the atoms in the magnetic field, leads to more reactions and, already within 100 ms, to an obvious decay of the primary ions. Remarkable is the fact that the decay rate increases by a factor of 3 if the discharge is switched ON ($\tau_{ON} = 0.33$ s, $\tau_{OFF} = 1.05$ s). This is partly due to the large amount of H atoms being transferred to the trap; however, also the density of molecular hydrogen in the trap increases instead of becoming less due to dissociation. This can be seen from the larger number of HCO_2^+ products formed by reaction (1) with discharge ON. This increase of the H_2 number density in the trap is most probably caused by the fact that the loss of molecules due to fragmentation is counter-compensated by recombination. Apparently a lot of atoms collide with the surfaces surrounding the beam path. With the geometry of the beam, emerging from the magnets, and the apertures, also wall collisions in the trap cannot be ruled out. Due to the low conductance, hydrogen molecules formed inside the cooling shield (see Fig. 1) lead to a significant increase of the background of molecules.

Cryopumping can improve significantly the situation. So far, the best H/H_2 ratio in the 22PT has been achieved by operating the trap at 10 K and the accommodator at 12 K. At these conditions, an atom density of $[H] = 2.1 \times 10^8$ cm^{-3} has been obtained in the trap with a 3 times lower molecular density, $[H_2] = 7 \times 10^7$ cm^{-3}. Nonetheless, even under such conditions, the primary CO_2^+ ions still react faster with H_2 than with H, due to the larger rate coefficient. We also have performed measurements with the discharge tube placed at a much shorter distance of 8 cm to the trap by removing the differential pumping stage with the hexapole magnet. The number density achieved in this way was rather large, $[H] = 4.5 \times 10^9$ cm^{-3};

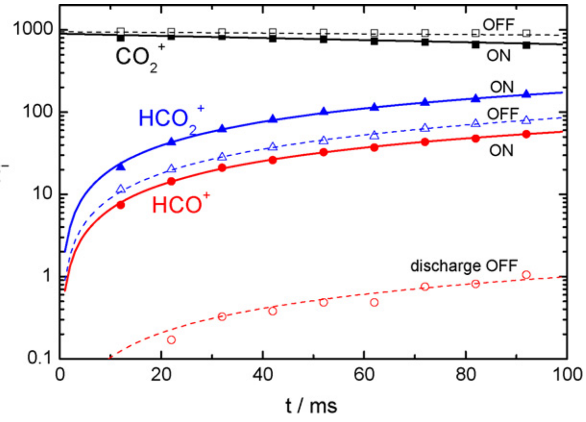

Fig. 6. Experimental results obtained with the hexapole magnets installed (see Fig. 1). The CO_2^+ ions react with an intense beam of D-atoms ($[D] = 3.4 \times 10^9$ cm^{-3}) at $T_{ACC} = 100$ K and $T_{22PT} = 100$ K. A surprising observation which is discussed in the text, is that the decline of primary ions is three times slower with the discharge switched OFF. Remarkable is also that the total number density of molecules in the trap is higher with discharge ON, $[D_2]_{ON} = 3.3 \times 10^9$ cm^{-3} than with OFF, $[D_2]_{OFF} = 1.4 \times 10^9$ cm^{-3}.

however, at the expenses of an almost 4 times larger molecular background, $[H_2] = 1.7 \times 10^{10}\,cm^{-3}$.

4. Discussions

For the first time, reactions between CO_2^+ ions and hydrogen in molecular and atomic form have been measured down to the low temperatures prevailing in dense interstellar clouds. The results are summarized in Fig. 7 and in Table 1. The errors of the absolute values for reactions with molecular target, k_1 and k_3, are estimated to be 20%, those with atomic reactants, k_2 and k_4, are 40%. Although the overall arrangement radical beam-trap is well-characterized, it cannot be completely excluded that some problems have been overlooked, especially caused by collisions of radicals with surfaces.

At room temperature the obtained rate coefficients are in reasonable overall agreement with results from previous measurements performed with different flow systems [17–19,35]. This is surprising due to the overall difficulties in determining the actual H atom concentrations in the various instruments. Reactions with H and D atoms also have been investigated with the ICR technique [15]. However, the results from this instrument deviate significantly. Not only the overall reactivity is off by a factor ~5 in the case of H atom reactions and ~3 in the case of D atom reactions but also the branching ratio is completely different, favoring the charge transfer channel (2b). Inspection of the schematic diagram of the ICR based machine (Fig. 1 in Ref. [15]) allows one to suspect that the erroneous measurements may be caused by metastable atoms, UV photons or secondary reactions involving surfaces. For example, the assumption must be questioned that all H atoms which strike a surface in the ICR cell, are lost and re-enter the gas phase as a recombined molecules.

For the molecular target, a significant temperature dependence has been observed. The data have been fitted using the function $k = \alpha(T/300\,K)^{\beta}$, a simple parameterization commonly used in reaction networks describing interstellar chemistry [36]. The fact that, at low temperatures, one reaches finally the Langevin limit (see Table 1 and Fig. 7) may be taken as an indication that, in the collision complex, time is required for dissociating the hydrogen molecule and for integrating the atom into the protonated carbon dioxide. A statistical calculation may corroborate this hypothesis.

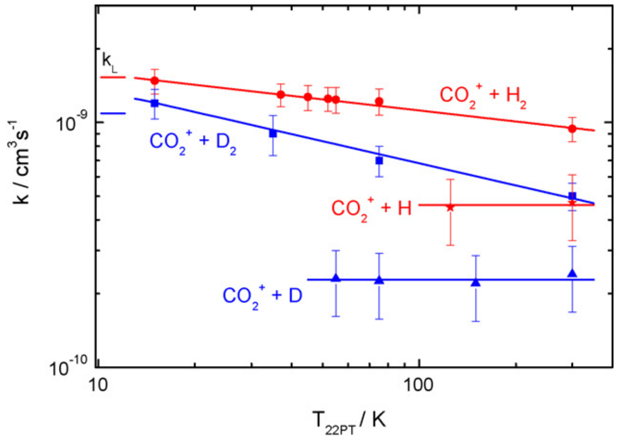

Fig. 7. Temperature dependence of rate coefficients for reactions of CO_2^+ with H, H_2, D, and D_2 (reactions (1)–(4)). The indicated overall error of the rate coefficients is explained in the text. For the reaction with hydrogen atoms, no change with temperature could be seen. With molecular reactants, the reactivity increases with falling temperature, reaching finally the Langevin limit k_L. The rate coefficients and the fitting function are given in Table 1.

For $CO_2^+ + H$ the Langevin rate coefficient is $k_L = 1.9 \times 10^{-9}\,cm^3 s^{-1}$ while reaction (2) occurs with less than 25% of the collision rate, also at low temperatures. The rate coefficient with deuterium atoms, reaction (4), is even smaller. From those collisions, which are attracted according to the Langevin prescription, only 16% react. For a system like CO_2^+ colliding with H detailed dynamical calculations on precise potential energy surfaces are feasible today. Without such information, one can only speculate. It has been stated in [19] that there seems to be a rather general rule that ion–H atom reactions have rate coefficients substantially less than the Langevin capture rate. One explanation given by Scott et al. is the influence of spin statistics. The two reactants which are doublets, interact attractively on a singlet surface while triplet surfaces may be repulsive. Other restrictions may be based on conservation of spin: reaction (2) requires the decay of a singlet HCO_2^+ intermediate into a singlet HCO^+ and triplet O atom. This is spin-forbidden. Another simple guess for H–AB + collisions in general may be that there are some steric restrictions, i.e., a reaction is rather direct and occurs only if the atom approaches the molecule from the right direction. This argument also holds for a wide temperature range due to the atom–ion mass ratio. The significant difference in the rate coefficients for H and D may be due to differences in the mobility of the two atoms or may be caused by tunneling contributions.

Another unexplained experimental observation is that the charge transfer channel (2b) is negligibly small as concluded from various authors and also from the charge balance in our trapping experiment. However, instead of entering speculations, we want to conclude the discussions by stating that a much better k_2/k_{2b} ratio can be determined with the AB-22PT instrument by optimizing the system for low masses. Related measurements have been delayed until several improvements of the setup are made, especially the integration of cryogenic pumping. With the improved sensitivity, also the two isomeric structures HOC^+ and HCO^+ can be distinguished using chemical probing [20].

5. Conclusions

Our studies of the title reaction have been motivated initially by the need to use reactions (2) and (4) for determination of the number density of hydrogen atoms directly in the trap. Such calibration standards are necessary for a beam-trap arrangement since, in contrast to the usual operation where the 22PT housing is filled with target gas with in a well-defined velocity and density distribution, the diameter of the skimmed beam is smaller than the diameter of the ion cloud in order to avoid (or reduce) collisions with the walls. For this purpose it is advantageous that the relevant rate coefficients have been found to be independent on the collision energy, which is determined by the motion of the H atoms and the rotational population of the ions.

There is a variety of other measurements which have been studied with the AB-22PT machine, including $CH^+ + H$, $CH_4^+ + H$ and $CH_5^+ + H$ [21]. Detailed publications are in preparation. A wide field of interesting research is the deuteration of hydrogenated ions in collisions with D-atoms. A system of basic interest mentioned already in the introduction is the H–D exchange in $H_3^+ + D$ collisions or other isotopic analogues. Most probably it is rather slow since it is hindered by small barriers [5]. The early merged beam studies [4] almost reached low enough collision energies; however, those experiments have been performed with internally hot H_3^+ ions. The combination of the low temperature multipole ion trap with a beam of very slow hydrogen atoms will reveal the details of the H_4^+ potential energy surface and the low energy dynamics.

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