REAGIONS OF COLD TRAPPED CH$^+$ IONS WITH SLOW H ATOMS

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ABSTRACT

The destruction of CH$^+$ ions in collisions with H atoms has been studied in a temperature-variable 22 pole ion trap (22PT) combined with a cold effusive H-atom beam. The stored ions are relaxed to temperatures of $T_{\text{22PT}} \geq 12$ K. The hydrogen atoms, produced in a radio frequency discharge, are slowed down to various temperatures of $T_{\text{ACC}} \geq 7$ K. They are formed into an effusive beam. The effective density of the hydrogen atoms in the trap as well as the H$_2$ background are determined in situ using chemical probing with CO$_2^+$. The experimental arrangement allows us not only to measure thermal rate coefficients ($T_{\text{22PT}} = T_{\text{ACC}}$), but also to extract state-specific rate coefficients $k(J,T)$ at selected translational temperatures $T_i$ for the CH$^+$ rotational states $J = 0$, 1, and 2. The measured thermal rate coefficients have a maximum at 60 K, $k = (1.2 \pm 0.5) \times 10^{-9}$ cm$^3$ s$^{-1}$. Toward higher temperatures, they fall off in accordance with previous measurements and the trend predicted by phase space theory. Toward lower temperatures, the rate coefficients decrease significantly, especially if the rotation of the ions is cooled. At the coldest conditions achieved (beam: 7.3 K; trap: 12.2 K), a value as low as $(5 \pm 3) \times 10^{-11}$ cm$^3$ s$^{-1}$ has been measured. This leads to the conclusion that non-rotating CH$^+$ is protected against attacks of H atoms. This surprising result is not yet understood. It is most probably due to quantum-dynamical effects already occurring at large distances.

Key words: astrochemistry – ISM: abundances – molecular processes

Online-only material: color figures

1. INTRODUCTION

The methylidyne cation, CH$^+$, was the first molecular ion identified in interstellar space by Douglas & Herzberg (1941). It can be observed from the ground via optical absorption lines and can provide useful information ranging from $^{12}$C/$^{13}$C ratios to the cosmic background radiation field at earlier times. Despite its abundance in a number of different interstellar environments as well as in comets (Picazzio et al. 2002), there are still many open questions concerning the formation and destruction of this fundamental ion. While standard gas-phase models predict the observed abundances of neutral CH quite well, the large column densities of CH$^+$ ions are often several orders of magnitude higher than their predictions (see Godard et al. 2009 and references therein).

In addition to electronic transitions, CH$^+$ can be traced by observing pure rotational transitions with high resolution (Cernicharo et al. 1997). Based on the accurate rest frequency of the $J = 1 \rightarrow 0$ transition (Amano 2010; Pearson & Drouin 2006), the first detection of this line has been reported recently (Falgarone et al. 2010). Precise laboratory information is needed to extract velocity distributions from the high-resolution submillimeter lines. Using the unique features of the Herschel Space Observatory, rotational lines of CH$^+$ will be reported soon from low- and high-temperature environments. Especially interesting, also in combination with the state-specific results reported in the present contribution, are the rotational transitions $1 \rightarrow 0$ and $2 \rightarrow 1$.

As discussed by Black (1998), CH$^+$ is a member of a special class of reactive molecular ions, which are destroyed efficiently with electrons and with the most abundant neutral species, H and H$_2$. In order to compensate for its short chemical lifetime, non-thermal conditions are postulated for its production based on shocks, carbon grain erosion, UV irradiation near young stellar objects, or another heating mechanism (Duley et al. 1992; Godard et al. 2009). A recent publication discusses in detail the role of vibrationally excited H$_2$(v > 0), which has, in collisions with C$,^+$ significant influence on the abundances of CH$^+$ and other hydrocarbons (Agundez et al. 2010). The dilemma is that this ion is also abundantly found in the cold neutral medium. Therefore, one has to find other mechanisms that either prevent the destruction via reactions or lead to additional formation of the methylidyne cation, especially at low temperatures.

There are interesting new attempts to resolve this puzzle. An overview of experimental results obtained at selected temperatures for CH$^+ (x = 0–5)$ colliding with hydrogen atoms, molecules, and isotopic variants has been reported by Gerlich et al. (2011). To gain further insight into the chemical and physical conditions of those regions of the interstellar medium (ISM) where CH$^+$ is abundant, the methylidyne cation has been observed together with the methyl cation CH$_3^+$ (Indriolo et al. 2010). In the same study, various processes have been discussed and used in a simple model for linking these two species. For correlating the wealth of new data on rotational populations of CH$^+(J)$ with their environment, more experimental and theoretical efforts are needed, especially to provide state-specific rate coefficients.

There are a variety of gas-phase processes leading to CH$^+$ (Williams 1992). Theoretical predictions for radiative association,

$$C^+ + H \rightarrow CH^+ + h\nu,$$

have led to the conclusion that this reaction is too slow to contribute sufficiently (Graff et al. 1983). Recent calculations, however, indicate an increase in the rate coefficient at very low temperatures due to resonances (Barinovs & van Hemert 2006). As briefly mentioned in the conclusions, more accurate calculations and especially first measurements are urgently

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needed. If reaction (1) really can contribute to the production of CH\(^+\) at low temperatures, the rate coefficients are within the reach of our apparatus.

A very early discussion of the production of interstellar CH\(^+\) via

\[
\text{C}^+ + \text{H}_2 \rightarrow \text{CH}^+ + \text{H}
\]  

(2)

has been published by Stecher & Williams (1972). Since this reaction is endoergic by 0.393 eV (4560 K, see below), formation of CH\(^+\) in the ISM is restricted to regions where high kinetic energies occur or where a considerable amount of rotationally (J > 6) or vibrationally (v > 0) excited H\(_2\) molecules are present, e.g., in shock waves (Elitzur & Watson 1978) or higher layers of circumstellar envelopes (Herpin et al. 2002). Indeed, a correlation between the abundance of excited H\(_2\) and CH\(^+\) has been detected in diffuse clouds (Lambert & Danks 1986).

Several analytical expressions have been proposed over the years to describe the temperature dependence of the rate coefficient for reaction (2). Some of them have been derived from detailed measurements of cross sections in the threshold region using the guided ion beam technique (Ervin & Armentrout 1984; Gerlich 1986). Recommended for astrochemical models are state-specific thermal rate coefficients based on detailed experiments and statistical calculations (Gerlich et al. 1987). These results are reported as k(T,J) using Arrhenius-type functions. A detailed comparison with thermal rate coefficients measured in a high-temperature flowing afterglow apparatus from 400 to 1300 K (Hierl et al. 1997) supports the validity of these functions. Quite recently, this information has been put into astrochemical models (Agundez et al. 2010).

At low temperatures, such as in dark interstellar clouds, the only process of hydrocarbon ion formation from C\(^+\), regarded as important, is the radiative association process:

\[
\text{C}^+ + \text{H}_2 \rightarrow \text{CH}^+_2 + h\nu.
\]  

(3)

This reaction has been studied using various theoretical approaches. Relevant references and a discussion of various experimental aspects can be found in Gerlich & Horning (1992). Reliable rate coefficients for reaction (3), measured in a low-temperature ion trap, have been reported in Gerlich (1994). The experiment, performed at a trap temperature of 10 K, has revealed a significant difference for collisions with n-H\(_2\) (6.8 ± 0.9)×10\(^{-16}\) cm\(^3\) s\(^{-1}\) and with p-H\(_2\) (1.7 ± 0.2)×10\(^{-15}\) cm\(^3\) s\(^{-1}\).

As already indicated above, the number of interstellar CH\(^+\) ions is significantly reduced via reactions with other abundant interstellar species. Hydrogen abstraction in collisions with H\(_2\) is fast (Gerlich et al. 2011). Dissociative electron–ion recombination has been summarized in Larsson & Orel (2008). Given the ubiquity of H atoms in space, the reverse process of reaction (2),

\[
\text{CH}^+ + \text{H} \rightarrow \text{C}^+ + \text{H}_2,
\]  

(4)

deserves special attention. The situation until 1984 has been discussed in Federer et al. (1984). It was accepted that at 100 K, reaction (4) is slow, k = 2 × 10\(^{-12}\) cm\(^3\) s\(^{-1}\). Based on detailed balance considerations, Chesnavig et al. (1984) predicted that the rate coefficient for reaction (4) should approach the Langevin limit at low temperatures. In line with this are results obtained with the selected-ion-flow drift tube (SIFDT) technique (Federer et al. 1984, 1985). In the UMIST database, a temperature-independent rate coefficient of 7.5 × 10\(^{-10}\) cm\(^3\) s\(^{-1}\) is used (Woodall et al. 2007).

While most experimental studies for reactions (2) and (4) are several decades old, the CH\(_2^+\) ion, its potential energy surface, and the dynamics of reactions (2) and (4) have attracted many theoreticians in recent years (Stoecklin & Halvick 2005; Halvick et al. 2007; Warmbier & Schneider 2011). Figure 1 shows some features of the potential energy surface connecting the CH\(^+\) + H\(_2\) reactants with the C\(^+\) + H\(_2\) products via the deeply bound CH\(_2^+\) intermediate. For a more complete correlation diagram, see Ervin & Armentrout (1986). Some details of the potential energy surfaces will be mentioned in the discussion section. For reactions at thermal or subthermal energies, it is usually assumed that higher lying potential energy surfaces can be neglected. In our experiment, the CH\(^+\) ions are cooled to the X'\(^1\Sigma^+\) ground state and, depending on the temperature of the trap, only a few rotational states are populated (see Table 1). As shown in the right part of Figure 1, the product ion is either C\(^+\)\(^2\)P\(_{1/2}\) or C\(^+\)\(^2\)P\(_{3/2}\). The exoergicity of reaction (4) is sufficient to create H\(_2\) molecules with rotational states up to J = 6. Excitation of C\(^+\)\(^2\)P\(_{3/2}\) requires only 7.863 meV. As indicated by the dashed line, slight deviations from the collinear approach of the reactants, i.e., H–CH\(^+\) or CH\(^+\)–H, lead to barriers. They are small but may influence collisions in the

### Table 1

<table>
<thead>
<tr>
<th>J</th>
<th>E (meV)</th>
<th>5 K</th>
<th>12.2 K</th>
<th>20 K</th>
<th>30 K</th>
<th>40 K</th>
<th>50 K</th>
<th>100 K</th>
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<td>0</td>
<td>0.0</td>
<td>99.9</td>
<td>89.9</td>
<td>70.6</td>
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<td>10.1</td>
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<td>41.9</td>
<td>46.5</td>
<td>47.1</td>
<td>37.6</td>
</tr>
<tr>
<td>2</td>
<td>10.4</td>
<td>0.9</td>
<td>4.8</td>
<td>10.5</td>
<td>15.8</td>
<td>28.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>20.7</td>
<td>0.1</td>
<td>0.7</td>
<td>2.0</td>
<td>11.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>34.5</td>
<td>0.1</td>
<td>3.1</td>
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</tr>
<tr>
<td>5</td>
<td>51.7</td>
<td>0.5</td>
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<td></td>
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<tr>
<td>6</td>
<td>72.2</td>
<td>0.1</td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

Note. CH\(^+\) rotational constants (Carrington & Ramsay 1982): B = 13.9302 cm\(^{-1}\), D = 0.0014 cm\(^{-1}\).
Fig. 2. Schematic diagram of the AB-22PT. This instrument has been developed to expose trapped ions to an effusive beam of slow H or D atoms (Borodi et al. 2009; Gerlich et al. 2011). Primary ions (here CH\(^+\)) are continuously generated by electron bombardment in an RF storage ion source (not shown), mass filtered, and injected into the ion trap via the indicated electrostatic quadrupole bender. After variable storage times the ions are extracted from the trap, mass analyzed in a QPMS, and counted. This process is repeated and averaged over many iterations.

(A color version of this figure is available in the online journal.)

meV range. When the intermediate is bent by more than a few degrees (C\(_2\)s symmetry), the strongly bound CH\(_2^+\) intermediate is accessible on a monotonously falling potential energy surface.

2. EXPERIMENTAL DETAILS

As discussed in more detail by Gerlich et al. (2011), there have been so far only a few experimental studies of reactions between ions and H atoms and none at temperatures relevant for low-temperature astrochemistry. Initial results for reaction (4) have been obtained in an SIFDT operated at 300 K (Federer et al. 1984). A significant step forward has been the use of ion traps for astrochemical applications (Gerlich 1994, 1995) and, later, the combination with effusive or supersonic beam sources. Figure 2 shows schematically the Atomic Beam 22 Pole Trap Apparatus (AB-22PT) instrument used in the present study. An overview of the apparatus and a brief summary of the low-temperature ion trapping technique has been given recently (Gerlich 2008; Gerlich & Borodi 2009).

In the present study, CH\(^+\) ions are produced in a storage ion source via electron bombardment of methane. They are mass filtered and injected into the 22PT via an electrostatic quadrupole bender. There they are confined in the wide nearly field-free effective potential created by the inhomogeneous radio frequency (RF) field. The trap is surrounded by a copper box, mounted onto the cold head of a closed-cycle He refrigerator (Leybold RGD 210, lowest temperature 10 K). For analysis, primary and product ions are extracted, mass analyzed in a quadrupole mass spectrometer (QPMS), and counted. Large differential pumping capacity is provided using several turbomolecular pumps.

The stored ions are exposed to an effusive, skimmed, and doubly differentially pumped beam of cold H atoms. The production of the H-atom beam and various experimental tests have been reported recently (Borodi et al. 2009). To determine the effective number density of H and H\(_2\), chemical probing with stored CO\(_2^+\) ions is applied. The beam is cooled with an accommodator connected to a cold head. Additional information on the H-atom beam source can be found in Gerlich & Borodi (2009) and Gerlich et al. (2011). Specific technical aspects are collected in the thesis of G. Borodi (Borodi 2008). Note that, in the present study, the focusing hexapole magnets have been taken out to jet thermal velocity distributions.

For the first time, a 7.1 K H-atom beam has been produced with sufficient flux, using a Sumitomo SRDK-101E cold head to cool the accommodator. Figure 3 shows a normalized time of flight (TOF) distribution. The minor difference between the temperature of the accommodator (\(T_{\text{ACC}} = (6.0 \pm 0.3)\) K) and that of the Maxwellian fit (\(T_{\text{FIT}} = (7.1 \pm 0.4)\) K) is most probably due to the low thermal conductivity of the PTFE layer. The minor but significant differences between the experimental points and the fit between 4 and 7 ms are discussed in the text.

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\[
\begin{align*}
T_{\text{ACC}} & = (6.0 \pm 0.3)\text{ K} \\
T_{\text{FIT}} & = (7.1 \pm 0.4)\text{ K}
\end{align*}
\]

of flight (TOF) distribution. The minor difference between the temperature of the accommodator (\(T_{\text{ACC}} = (6.0 \pm 0.3)\) K) and that of the Maxwellian fit (\(T_{\text{FIT}} = (7.1 \pm 0.4)\) K) is most probably due to the low thermal conductivity of the polytetrafluoroethylene (PTFE) layer used for reducing H–H recombination on surfaces. It is interesting to note that, between 4 and 7 ms, there is a small but significant difference between the experimental points and the best fit. Although the operating conditions (nozzle, pressure, flux) are typical for an effusive beam source, the cross sections for slow H–H collisions are apparently so huge that slow atoms are “pulled” toward the mean velocity of the beam. This does not influence the present results; however, it is a problem if one intends to use, via TOF selection, the slow Boltzmann tail to prepare sub-K ions (Gerlich & Borodi 2009). At an accommodator temperature of 61 K, TOF calibration revealed a beam temperature of 62 K.

The translational and internal degrees of freedom of the stored ions are coupled to the cold environment by inelastic collisions with helium buffer gas. Important for the present study is that \(T_{\text{22PT}}\) determines the population of just a few rotational states of CH\(^+\). As can be seen in Table 1, close to 95% of the molecules
are in the rotational ground state at 10 K, while at 100 K, states up to \( J = 7 \) are populated. Due to the mass ratio, the translational temperature is the mass-weighted average \( T_t = (m_{\text{ion}} T_{\text{neut}} + m_{\text{neut}} T_{\text{ion}})/(m_{\text{ion}} + m_{\text{neut}}) \). Cooling or heating of CH\(^+\) via the blackbody radiation from the surrounding cold shield is negligible under the conditions (storage time, buffer gas density) of the experiment.

3. RESULTS

The basic procedures of typical trapping experiments (filling the trap, cooling, reacting, extracting, and analyzing) have been described often. A detailed discussion of the competition between reactions of CH\(^+\) with H and H\(_2\) and secondary reactions leading finally to CH\(_3\) can be found in Gerlich et al. (2011; see especially Figure 3). To illustrate the situation with the weak but very cold 7.1 K H-atom beam, Figure 4 shows the temporal evolution of ions, starting with 700 CH\(^+\) and some background on the masses 12, 14, and 15 u. The relevant parameters are given in the figure caption.

Inspection of the count rate occurring on mass 12 reveals that there is a very small background when there are no H atoms in the hydrogen beam (i.e., the RF discharge is switched OFF), about 0.06 counts per filling. Within the statistical error smaller than the size of the symbols used in the plot, there is no change in the time window shown. When the discharge is ON, a few additional C\(^+\) ions are formed. Since the injected CH\(^+\) is initially hot and therefore reacts more efficiently with H, the number of C\(^+\) ions (0.02) is already larger than the background at 20 ms; however, within this time, the primary ions are cooled to the temperature of the trap. From the subsequent increase of C\(^+\) (1.4 ions s\(^{-1}\)), the number of primary ions, and the effective number density of H, one already obtains a reliable estimate of the rate coefficient for reaction (4), \( k = 5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} \).

For a more detailed evaluation, the temporal evolution of the number of stored ions, \( N_i(t) \), is modeled by numerically solving a system of differential equations simulating the interactions in the trap. Analyzing possible errors leads to a final result of \( (5 \pm 4) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} \).

This result is included in Figure 5 as an open circle. It has been measured under the coldest conditions presently achievable in our instrument (beam: 7.3 K; trap 12.2 K). This figure also presents new measurements (filled circles) for the temperature range from 30 K to 100 K. These data, which have been obtained under thermal conditions, i.e., for \( T_{\text{ACC}} = T_{22\text{PT}} \), show a maximum of \( (1.2 \pm 0.5) \times 10^{-9} \text{ cm}^3 \text{ s}^{-1} \) at 60 K and a steep fall-off toward lower temperatures. In accordance with previous discussions (Gerlich et al. 2011), all experimental data above 60 K, obtained with different methods, roughly follow the trend predicted by phase space theory (PST; Halvick et al. 2007). For astrochemical applications, between 100 and 1000 K it is recommended to use the temperature-dependent function

\[
k = 7.84 \times 10^{-10} \left(\frac{T}{300 \text{ K}}\right)^{-0.22} \text{ cm}^3 \text{ s}^{-1},
\]
and rotational energy, Figures 6 and 7 present additional data. Both figures report results measured as a function of the temperature of the ion trap, \( T_{22PT} \), while the temperatures of the beam, \( T_{ACC} \), are kept fixed at \( T_{ACC} = 61 \, \text{K} \) (Figure 6) and \( T_{ACC} = 9 \, \text{K} \) (Figure 7). The corresponding translational temperatures \( T_t \) are plotted as the upper scale. As explained in Gerlich et al. (2011), the translational temperature (or in other words, the temperature of the Maxwellian, describing the distribution of the velocities in the center-of-mass frame) is the mass-weighted average of the two temperatures of the reactants. This result is exact, provided the ion distribution is a three-dimensional Maxwellian and the effusive beam is a one-dimensional Maxwellian in all directions of its angular distribution.

Figure 6 shows data for three separate runs. Measurements have been performed during cooling down the trap (solid squares) and warming it up (open squares). A third set of data (small triangles) has been accumulated on another day. Within the scatter of the data, mainly due to instabilities of the neutral beam, the steep dependence on the ion temperature is obviously reproduced. For comparison and also for routine calibration of the scatter of the data, mainly due to instabilities of the neutral squares) and warming it up (open squares). A third set of data have been performed during cooling down the trap (solid squares) and warming it up (open squares). A third set of data have been performed during cooling down the trap. The results plotted as triangles have been measured on a different day. It is obvious that the overall trend is reproduced. For comparison and calibration, rate coefficients for the reaction \( \text{CO}_2^+ + \text{H} \rightarrow \text{HCO}^0 + \text{O} \) have always been measured in between (filled big triangles connected with the dashed line). They are known to be independent of the trap temperature, \( k = 5 \times 10^{-10} \, \text{cm}^3 \, \text{s}^{-1} \) (Borodi et al. 2009). The dashed line is the result from a weighted average of state-specific rate coefficients (see the text).

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4. DISCUSSIONS

How can one explain the surprising observations presented in Figures 5–7? From a theoretical point of view, one has to remember that the reaction is exothermic and that there is general agreement that the potential energy surface is attractive almost everywhere. Concerning the experiment, one has to keep in mind that interpretations are rather uncomplicated because translational energy is primarily determined by the H atoms, i.e., via \( T_{ACC} \), while \( T_{22PT} \) almost exclusively changes the population of the rotational states of \( \text{CH}^+ \). There are a few obvious experimental facts. From Figure 6, one can conclude that rotational excitation of \( \text{CH}^+ \) reactants significantly accelerates the formation of \( \text{C}^+ + \text{H}_2 \) since at \( T_{ACC} = 61 \, \text{K} \) there is no significant variation in translational temperature (see \( T_t \), upper scale). As can be seen from Table 1, two-thirds of the trapped ions are already rotationally excited at 50 K, while at the lowest ion temperature, 12.2 K, 10% are left in the first rotational state, with all other ions in the ground state. Therefore, one is tempted to deduce that, at low collision energies, \( \text{CH}^+ (J = 0) \) does not react at all. Comparing Figures 6 and 7, which show results for different H-atom velocities but over the same range of the temperature of the ion trap, reveals that translational energy also plays a role in promoting the reaction. Looking at Figure 7 one may speculate that, around \( T_t = 11 \, \text{K} \), there is an indication of a threshold in the translational energy dependence.

A more quantitative evaluation of the data must be based on elementary state-to-state rate coefficients or cross sections, \( k_{ij} = g g_i f_j (g) \), where \( g \) is the relative velocity of the collision, i.e., \( E_i = \mu / 2 \, g^2 \), and the global quantum numbers \( i \) and \( f \) account, in our energy range, only for initial and final rotational states, and perhaps nuclear spin and fine structure. Figure 1 illustrates that the exothermicity allows one to produce rotationally excited \( \text{H}_2 \) states up to \( J = 6 \). Therefore, it is reasonable to assume that there are no stringent restrictions due to nuclear spin: the two H atoms approaching each other most probably form para- and ortho-\( \text{H}_2 \) according to the statistical weights of the total nuclear spin, i.e., 1:3. There are no obvious propensity rules for forming \( \text{C}^+ \) in the \( ^2P_{1/2} \) or \( ^2P_{3/2} \) states. Therefore, we make the following

![Figure 6](image-url)  
**Figure 6.** Test of reproducibility and comparison with the calibration reaction. All data points have been measured with the hydrogen beam operated at \( T_{ACC} = 61 \, \text{K} \). Three data sets are shown as a function of the trap temperature, \( T_{22PT} \). The temperature scale on top gives the translational temperature \( T_t \). The data shown as solid squares have been obtained during the cool-down phase; open squares have been obtained during warming. The results plotted as triangles have been measured on a different day. It is obvious that the overall trend is reproduced. For comparison and calibration, rate coefficients for the reaction \( \text{CO}_2^+ + \text{H} \rightarrow \text{HCO}^0 + \text{O} \) have always been measured in between (filled big triangles connected with the dashed line). As reported in Borodi et al. (2009), \( \text{HCO}^+ \) ions are exclusively produced in collisions with H atoms, with a temperature-independent rate coefficient of \( k = 5 \times 10^{-10} \, \text{cm}^3 \, \text{s}^{-1} \) (Borodi et al. 2009). The dashed line is the result from a weighted average of state-specific rate coefficients (see the text).

(A color version of this figure is available in the online journal.)

![Figure 7](image-url)  
**Figure 7.** Rate coefficients for the reaction \( \text{CH}^+ + \text{H} \rightarrow \text{C}^+ + \text{H}_2 \), measured as a function of the trap temperature \( T_{22PT} \) for \( T_{ACC} = 9 \, \text{K} \). The temperature scale on top gives the translational temperature \( T_t \). The different symbols represent different data sets recorded at different times. The dashed line is the result from a weighted average of state-specific rate coefficients (see the text).

(A color version of this figure is available in the online journal.)
simple ansatz for the state-specific rate coefficients, $k_i = \sum k_{ij} = k(J, T_i)$ for $J = 0$–2, mainly to illustrate the general trend:

$$k(J = 0; \ T_i)/10^{-9} \ cm^3 \ s^{-1} = 0.05 + 0.1 (T_i - 9 \ K)/50 \ K, \eqno{(6a)}$$

$$k(J = 1; \ T_i)/10^{-9} \ cm^3 \ s^{-1} = 0.1 + 1 (T_i - 9 \ K)/50 \ K, \eqno{(6b)}$$

and

$$k(J = 2; \ T_i)/10^{-9} \ cm^3 \ s^{-1} = 1.2 + 0.8 ((T_i - 9 \ K)/50 \ K)^2. \eqno{(6c)}$$

For the two lowest rotational states a linear increase with $T_i$ is assumed while for $J = 2$ a quadratic dependence has been chosen. For $J \geq 3$, the experimental results are not sensitive in the present temperature range. The simulations are performed with constant rate coefficients:

$$k(J \geq 3; \ T_i)/10^{-9} \ cm^3 \ s^{-1} = 1.5. \eqno{(6d)}$$

The predictions based on these functions are shown as short-dashed lines in Figures 5–7. It is obvious that they do not lead to an optimum fit of the experimental data; however, more would be an overinterpretation of these first low-temperature results. Looking at Figure 5 reveals that the measured thermal rate coefficients show an even steeper dependence on $T$. This could be due to the fact that $J = 0$ reacts even less than assumed in Equation (6a) or that there is really a threshold in the $E_r$ dependence as already speculated in combination with Figure 7. Inspection of Figure 6 indicates that $J = 2$ may be more reactive at $T_i > 60 \ K$ than predicted by Equation (6c).

So far, no attempt has been made to use functions that also include the high temperature range shown in Figure 5. The rate coefficient reaches a maximum at $T = 60 \ K$ followed by a slow decay toward higher temperatures. The dash-dotted line has been mentioned above in the results section (see Equation 5).

The (HCH)$^+$ system has been the subject of numerous theoretical and experimental efforts. Detailed studies have been performed to characterize the ground state structure of the methylene cation, CH$_2^+$, and to predict and observe its spectrum (see Solomonik & Yachmenev 2008 and references therein). Using pulsed-field-ionization zero-kinetic-energy photoelectron spectroscopy, the rotational structure of the ground state has been determined in detail (Willitsch & Merkt 2003). A thorough discussion of the Renner effect, which couples the ground electronic state, $^2A_1$, and the first excited electronic state, $^5B_1$, can be found in Bunker et al. (2007). The exothermicity for reaction (4), (0.3932 ± 0.0001) eV, is based on the measured dissociation energy of CH$_2^+$, $D_0 = (4.0849 ± 0.0001)$ eV (Hechtfischer et al. 2002), and the corresponding value for H$_2$, $D_0 = (4.47807 ± 0.00001)$ eV.

In order to understand the large distance behavior of the CH$^+$ + H interaction, it is necessary to get potential energy surfaces in the asymptotic range with sub-meV accuracy. Early calculations (Sakai et al. 1981; Jaquet & Staemmler 1982) have been extended recently by Stockelk & Halvick (2005). In all results the ground state surface is found to be attractive everywhere apart from the two linear (H–CH)$^+$ and (H–H)$^+$ configurations and their surroundings. A few stationary points of the reaction path leading from the $^1\Sigma$ methylidyne cation and the $^2S$ hydrogen atom to the $^2P$ carbon ion and the $^1\Sigma^+$ molecular hydrogen are indicated in Figure 1. The barrier close to the linear configuration is predicted to be 113 meV high; however, it vanishes when the CH$_2^+$ ion is bent, and a few degrees are already sufficient (Warmbier & Schneider 2011). Nonetheless, the details of the potential energy surface in the environment of these barriers may be of importance.

Using the picture of classical trajectories, it seems to be obvious that in most collisions the attractive slope is followed and that the reactants form the 4.8 eV bound CH$_2^+$ intermediate, a typical example for capture. Close coupling of all degrees of freedom and long lifetimes will lead to scrambling of the phase space, and it seems to be reasonable to predict the decay of this intermediate complex toward products or back to reactants with statistical methods. The result is that, in the temperature range of the present experiment, the reaction rate coefficient gets close to the capture rate coefficient (see PST in Figure 5).

In order to avoid capture, there must already be something occurring at great distances. This idea is also corroborated by the reaction of CH$^+$ with D leading with equal probability to C$^+$ + HD and CD$^+$ + H, contradicting any statistical model (Gerlich et al. 2011). Is it possible that one finds dynamical restrictions if one accounts in detail for the centrifugal repulsion due to the orbital angular momentum of the relative motion, $I^2$? Simply using the charge-induced dipole potential for the long-range attraction, partial waves up to $l_{max} = 7$ can contribute to the reaction at $E_r = 1$ meV; for higher $l$, the approaching H atom is repelled at large distances. These limits, however, do not lead to any obvious explanation for the change in reactivity below 50 K. Therefore, one has to look in more detail at the influence of the rotational state of the CH$^+$ ion. Is it possible that, for $J = 0$, the wave of the approaching H atom feels the two rather high barriers such that a major part gets reflected? It may be that the results reported in Stockelk & Halvick (2005), which are based on the RIOSA-NIP method, provide good results for the non-rotating diatom. In general, this method is known to underestimate the reactivity because it neglects the reorientation during the approach of the attacking atom toward the molecule.

5. CONCLUSIONS

In this contribution we report first results for the title reaction at temperatures below 50 K using the combination of an ion trap with an effusive H-atom beam. Such instruments (see also Yuan et al. 2011) allow one not only to study ion chemistry over a wide temperature range, but also to get state-specific information needed to describe non-equilibrium conditions of interstellar molecular clouds. In Gerlich et al. (2011), several experimental improvements are mentioned for increasing the selectivity and the sensitivity of the present setup. It is important to get a more stable cold H-atom beam and to reduce the H$_2$ background, e.g., by using cryo-pumping.

The special feature of such an instrument is that one has separate control over the internal temperature of the reactants and the translational velocity using a temperature-variable ion trap and a cold effusive or supersonic beam of atoms, radicals, or molecules. Following in more detail the reactivity of the initially injected ions, i.e., the competition between relaxation and reaction, one can get additional information (see Figure 4). To actually extract state-specific rate coefficients, excitation schemes with photons are preferred (e.g., laser-induced reactions). In the present case, a direct proof of the unexpected rotational dependence is to excite CH$^+$($J = 0$) ions directly using millimeter-wave radiation (Amano 2010). Extensions to $^{13}$CH$^+$ or $^{12}$CD$^+$ are certainly interesting.

Although the (HCH)$^+$ system is one of the simplest three-atom three-electron systems involving one $p$ electron, many questions remain unanswered. The interpretation of our experimental
results needs better quantum-mechanical calculations. It also
may be necessary to account for excited potential energy
surfaces, e.g., for the coupling between the \(^2A_1\) and the \(^2B_1\) states (Bunker et al. 2007). So far, all calculations have been based on
a global, single-valued potential energy surface. An additional
experiment of fundamental interest is to study in the trap the
rotational excitation or relaxation of \(CH^+\) in collisions with an
effusive or supersonic beam of helium atoms and to compare
them to close-coupling calculations (Hammani et al. 2009).

As summarized in the introduction, we do not yet know
the mechanisms leading to the \(CH^+\) abundances observed in
space. So far, most astrochemical models use, in many cases
quite successfully, thermal rate constants, perhaps with one
parameter describing the temperature dependence. In the case of
\(CH^+\), one needs more insight into all related chemical and
physical processes. An example illustrating this is the statement
of Herzberg one can find in *Spectra of Diatomic Molecules*
(1950) concerning CN and also \(CH^+\): “From the intensity ratio of the lines with \(J = 0\) and \(J = 1\) a rotational temperature of 2.3 K follows which has of course only a very restricted meaning.”

Obviously the \(CH^+\) ions are sufficiently decoupled from the
follows which has of course only a very restricted meaning.

(1950) concerning CN and also \(CH^+\):”

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