Stabilization of H$^+\text{--}H_2$ collision complexes between 11 and 28 K

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Formation of H$_2^+$ via association of H$^+$ with H$_2$ has been studied at low temperatures using a 22-pole radiofrequency trap. Operating at hydrogen number densities from $10^{11}$ to $10^{14}$ cm$^{-3}$, the contributions of radiative, $k_r$, and ternary, $k_3$, association have been extracted from the measured apparent binary rate coefficients, $k^* = k_r + k_3[H_2]$. Surprisingly, $k_3$ is constant between 11 and 22 K, $(2.6 \pm 0.8) \times 10^{-29}$ cm$^6$ s$^{-1}$, while radiative association decreases from $k_r(11\text{K}) = (1.6 \pm 0.3) \times 10^{-16}$ cm$^3$ s$^{-1}$ to $k_r(28\text{K}) = (5 \pm 2) \times 10^{-17}$ cm$^3$ s$^{-1}$. These results are in conflict with simple association models in which formation and stabilization of the complex are treated separately. Tentative explanations are based on the fact that, at low temperatures, only few partial waves contribute to the formation of the collision complex and that ternary association with H$_2$ may be quite inefficient because of the ‘shared proton’ structure of H$_2^+$.

Keywords: interstellar chemistry; H$^+$; H$_2^+$; association; ion traps

1. Introduction

As Oka summarized in his introductory remarks of the 2006 meeting, H$_3^+$ plays an important role in many fields ranging from astrochemistry via applications in hydrogen plasmas to fundamental aspects [1]. The combination of three protons (or deuterons) and two electrons represents a benchmark system for both understanding molecular structure and scattering dynamics. Accurate ground-state potential energy surfaces today allows us to predict low-lying rotation–vibrational states and infrared and sub-millimetre transitions with spectroscopic accuracy [2,3]. With increasing total energy, more states become accessible. The present spectroscopic activities work in an energy range where the atoms start to explore not only the triangular, but also the linear, configuration space. Here, H$_3^+$ becomes floppy and, owing to nonlinear couplings, the classical motion can become chaotic. All this and strong Coriolis coupling between rotation–vibrational states make precise ab initio calculations a challenge.

Even more complications arise if the total energy of the H$_3^+$ system reaches the dissociation limit. In this regime, specific bound or quasibound states exist, which are responsible for the pre-dissociation spectra reported by Carrington et al. [4,5].

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So far, there is no clear assignment of the observed transitions; however, there are interesting explanations [6,7]. Similar scattering states are populated in low-energy $\text{H}^+ + \text{H}_2$ collisions, leading to energy exchange, ortho–para transitions, chemical reactions (scrambling) or, the subject of this paper, to association, i.e. to continuum-bound transitions. The theoretical treatment of $\text{H}_3^+$ in the vicinity of the dissociation limit requires a potential with the correct long-range behaviour and sophisticated methods for describing the dynamics.

Addition of molecules via association is an important process for forming complex structures in many plasma environments. Radiative association plays an important role in the formation of interstellar molecules. Although under most conditions, $\text{H}_3^+$ is formed via H-atom abstraction in $\text{H}_2^+ + \text{H}_2$ collisions, association of $\text{H}^+$ with $\text{H}_2$ also plays a role under specific conditions [8]. In any case, it is of fundamental interest as the inverse process to photofragmentation. In the following, we report results for radiative association, i.e. stabilization via emission of a photon,

$$\text{H}^+ + \text{H}_2 \rightarrowarrow^k \text{H}_3^+ + h\nu,$$

and ternary association,

$$\text{H}^+ + 2\text{H}_2 \rightarrowarrow^{k_3} \text{H}_3^+ + \text{H}_2,$$  \hspace{1cm} (1.2)

where the formed complex is stabilized via collision with a third body. At the number densities $[[\text{H}_2]]$ we use in the present study, the radiative association rate coefficient $k_r$ and the ternary association rate coefficient $k_3$ contribute both significantly to the apparent binary rate coefficient,

$$k^* = k_r + k_3[[\text{H}_2]].$$  \hspace{1cm} (1.3)

For many decades, the determination of association rate coefficients has been the domain of swarm techniques operating at rather high pressures. With number densities above $10^{16}$ cm$^{-3}$ and rate coefficients of $10^{-29}$ cm$^6$ s$^{-1}$, reaction time constants were shorter than milliseCONDS and, therefore, became measurable. For reaction (1.2), Graham et al. determined a ternary rate coefficient at 300K [9], using a drift-tube mass spectrometer apparatus. Johnsen et al. extended the temperature range from room temperature down to 135K [10] and reported rate coefficients increasing from $3.0 \times 10^{-29}$ to $4.3 \times 10^{-29}$ cm$^6$ s$^{-1}$. Swarm techniques could not provide direct results for radiative association because the high densities lead to $k_3[[\text{H}_2]] \gg k_r$. This situation has changed by the development of ion-trapping techniques in the 1980s. First results for reactions (1.1) and (1.2) at 230K have been reported in Gerlich & Kaefer [11]. An early summary can be found in Gerlich & Horning [12]. Because of the high sensitivity of ion traps, one can operate at such low number densities that ternary association becomes even slower than radiative association.

In the last few years, new interest in the $\text{H}^+ + \text{H}_2$ collision system has grown, mainly owing to the fact that this fundamental three-proton two-electron system got within the reach of ‘exact’ quantum mechanical calculations (see [13,14] and references therein). Therefore, we have started a research programme to measure low-temperature rate coefficients for collisions between hydrogen ions and hydrogen atoms or molecules, including also anions. First results determined
at 11 K for ternary association, were reported recently in a conference contribution [15]. The new results cover the temperature range from 11 to 28 K and include radiative association.

2. Experiments

To study reactions (1.1) and (1.2) and to determine separately their rate coefficients, the AB-22PT instrument has been used. The principle of ion trapping and the experimental details have been described elsewhere [16]. The central part of the instrument, the 22-pole ion trap, is shown schematically in figure 1a. In the present study, normal hydrogen (one-quarter para-H$_2$ and three-quarters ortho-H$_2$) was introduced into the trap volume. A few collisions with the walls are sufficient to get the neutral gas into thermal equilibrium with the box, with the exception of the ortho–para ratio. The background pressure of the main chamber is lower than 10$^{-7}$ Pa. The level of reactive impurities in a gas leaked into the reaction volume has to be below 0.1 ppm. Impurities with the exception of HD and D$_2$ are mostly frozen out at 11 K.

The measuring procedure is based on iterative filling of the trap with a well-defined number of primary ions and analysis of the content after different times using a quadrupole mass spectrometer and micro-channel plate detector. In the present experiment, the storage times have been extended up to 30 s.

In order to test the actual conditions of the instrument, formation of He$_2^+$ dimers via the He$^+$ + 2 He reaction has been used. Although the new data shown in figure 2 are somewhat larger than the previous ion-trapping results [12], there is a good overall agreement with them and also with the analytical function extrapolating the data from Böhringer et al. [18].

Figure 1. (a) The 22-pole ion trap scheme. In the radial direction, ions are confined by the radiofrequency field, created by two sets of 11 poles (RFa and RFb) precisely mounted on opposite sides ($f = 18$ MHz, $V_0 = 19$ V for H$^+$, $V_0 = 26$ V for He$^+$). The entrance and exit electrodes (EN and EX) are used to open and close the trap with electrostatic barriers of some tens of meV. (b) Typical decrease of the relative number of trapped H$^+$ ions due to reactions with H$_2$. The number density of H$_2$ has been varied from 10$^{12}$ to 10$^{14}$ cm$^{-3}$, leading to decay time constants between many minutes and 2.5 s. (Online version in colour.)
Figure 2. Formation of He$_2^+$ dimers via the He$^+$ + 2 He reaction. Filled circles show the measured temperature dependence of $k_3(T)$ used as a thermometer in the trap, as proposed in Gerlich [17]. The inverted triangles indicate previous results obtained using a selected ion drift tube by Böhringer et al. [18] and triangles show a ring electrode trap by Gerlich, at low temperatures [12]. The dashed line extrapolates Böhringer’s fit. (Online version in colour.)

3. Results

A typical set of raw data, recorded at a 22-pole temperature of 11 K, is shown in figure 1b. In order to increase the sensitivity, a repetition period of 10 s has been chosen. About 100 H$^+$ ions have been injected each time. For better comparison of the results, the number of remaining primary ions is normalized to the initially injected ones. The number of ions in the trap has been counted at four different storage times. As can be seen from the dashed lines, $N_{H^+}$ decreases exponentially with a characteristic decay time $\tau = (k^*([H_2]))^{-1}$. The number density of H$_2$ has been varied over more than two orders of magnitude, leading to a variation of $\tau$ from 2.5 s to conditions where statistical errors limit the measurement. The rate coefficients can also be determined from the number of produced H$_3^+$ ions; however, this requires the determination of the detection efficiencies of the two different ions.

From such data, the apparent binary rate coefficient $k^*$ is determined. Figure 3 shows averages over a large set of such measurements, performed at 11 and 22 K and at H$_2$ densities as low as $4 \times 10^{11}$ cm$^{-3}$. The errors are smaller than the dot size, with the exception of the results at low densities where the bars indicate the uncertainties. For separating bi- and termolecular contributions, the data have been fitted with equation (1.3), resulting in the solid lines. Comparison of the dashed and dotted lines with the experimental results reveals that at densities below $10^{12}$ cm$^{-3}$, most products are H$_3^+$ + hv, while above $10^{13}$ cm$^{-3}$, stabilization of the H$^-$–H$_2$ collision complex with H$_2$ prevails and $k^*$ rises proportional to [H$_2$]. In accordance with expectations, the results show $k_3(11 \text{ K}) > k_3(22 \text{ K})$, while, to our surprise, the ternary rate coefficients are the same at the two temperatures.

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The results from the fits of figure 3 are plotted in figure 4 as solid circle points. In order to obtain more information on the temperature dependence of \( \text{H}_3^+ \) formation, the density has been kept constant at three different values, and the temperature has been varied between 11 and 28 K. At the low density \((9 \times 10^{11} \text{ cm}^{-3})\), the values for \( k_r \) have been determined by subtracting from the measured rate coefficients \( k^* \) the contribution from ternary association. Values for \( k_3 \) have been determined by measuring \( k^* \) at two higher densities \((8 \times 10^{12} \text{ cm}^{-3}, 1.6 \times 10^{13} \text{ cm}^{-3})\) and by subtracting the contributions from radiative association.

4. Discussion and conclusion

The basics of an empirical description of association reactions have been summarized in Gerlich & Horning [12]. It is based on the assumption that one can separate two independent sequential steps, first the formation of a long-lived complex followed by its stabilization. The collision complex is formed with a bimolecular rate coefficient \( k_c \). Assuming that there are no other product channels, this complex decays back to the reactants with a time constant \( \tau_{\text{dis}} \). Usually, a small fraction may be stabilized via emission of a photon (time constant \( \tau_r \)) or stabilized via collision with a third body. In the present study, we use only \( \text{H}_2 \) (time constant \( \tau_{\text{H}_2} \)). With these elementary processes, the overall formation of stable products can be described by the apparent second-order rate coefficient

\[
k^* = k_c \frac{1/\tau_{\text{H}_2} + 1/\tau_r}{1/\tau_{\text{dis}} + 1/\tau_{\text{H}_2} + 1/\tau_r}.
\]
A rigorous calculation of this requires, in general, a master equation approach accounting for the elementary steps that either contribute to stabilization or compete against it.

In such a model, the temperature dependence of the overall process is mainly determined by $\tau_{\text{diss}}$, while one assumes that $\tau_{\text{r}}$ and $\tau_{\text{H}_2}$ do not change much with temperature. Under such conditions, one gets the same $T$ dependence for $k_3$ and $k_r$, in contrast to our experimental observation. Here, we can give only some first hints to possible reasons. One is based on the special shape of the $\text{H}_5^+$ potential energy surface, the so-called shared proton structure [19]. Owing to this interaction, a $\text{H}_2$ approaching the $\text{H}_3^+$ collision complex slowly may pull out the proton from the collision complex instead of stabilizing it. Other explanations may be based on the fact that statistical arguments do not hold anymore at the low temperatures of our experiment. On the basis of the simple Langevin criterion using only the polarization interaction, one obtains for the total orbital angular momentum $l_m < 6$ at 10K and $l_m < 8$ at 20K. This leads to a rather low number of states accessible to the $\text{H}_3^+$ complex [6].

More theoretical and experimental work is needed to understand these scattering states of $\text{H}_3^+$. One of our aims is to go to higher temperatures for comparing our results with previous measurements. It is very important to use para-$\text{H}_2$ and to study the influence of the various nuclear spin configurations.

Finally, there are various interesting aspects of the astrophysical relevance of $\text{H}^+ + \text{H}_2$ collisions. Its role in ortho–para conversion has been reevaluated recently ([13], see also the erratum). It is an open question as to whether scattering of $\text{H}^+$ on $\text{H}_2$ is more efficient in cooling primordial gas than the $\text{H}_3^+$ molecule with its infrared active modes [20]. Another important subject is the chemical lifetime of protons in various environments. Electron transfer from atoms
(e.g. O, P, S [21,22]) competes with radiative recombination with free electrons and with neutralization in collisions with negatively charged molecules or small dust particles. Depending on the conditions and fractional abundances of the relevant targets, detailed models will predict regions where radiative association with H\textsubscript{2} is an important sink for protons and a source for excited H\textsuperscript{+}\textsubscript{3} ions.

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