H_2-assisted ternary recombination of H_3^+ with electrons at 300 K

Petr Dohnal,[1] Peter Rubovič,[1] Ábel Kálosi,[1] Michal Hejduk,[1] Radek Plašil,[1] Rainer Johnsen,[2] and Juraj Glosík[1]

[1]*Department of Surface and Plasma Science, Faculty of Mathematics and Physics, Charles University in Prague, Prague 18000, Czech Republic*

[2]*Department of Physics and Astronomy, University of Pittsburgh, Pittsburgh, Pennsylvania 15260, USA*

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Stationary afterglow measurements in conjunction with near-infrared absorption spectroscopy show that the recombination of the H_3^+ ion with electrons in ionized gas mixtures of He, Ar, and H_2 at 300 K is strongly enhanced by neutral helium and by molecular hydrogen. The H_2-assisted ternary recombination coefficient $K_{H_2} = (8.7 \pm 1.5) \times 10^{-23}\,\mathrm{cm^6 s^{-1}}$ substantially exceeds the value measured for H_3^+ in ambient helium ($K_{He} \sim 10^{-25}\,\mathrm{cm^6\,s^{-1}}$) or predicted by the generally accepted classical theory of Bates and Khare ($\sim 10^{-27}\,\mathrm{cm^6\,s^{-1}}$) for atomic ions. Because of the extremely large value of K_{H_2} in a hydrogen plasma the ternary recombination dominates over binary recombination already at pressures above 3 Pa. This can have consequences in plasma physics, astrophysics, recombination pumped lasers, plasma spectroscopy, plasmatic technologies, etc. The ternary processes provide a plausible explanation for the discrepancies between many earlier experimental results on H_3^+ recombination. The observation that the ternary process saturates at high He and H_2 densities suggests that recombination proceeds by a two-step process: formation of a long-lived complex [with a rate coefficient $\alpha_F = (1.5 \pm 0.1) \times 10^{-7}\,\mathrm{cm^3\,s^{-1}}$] followed by collisional stabilization.

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I. INTRODUCTION

The triatomic hydrogen ion occupies a special position in molecular physics, in physical chemistry, and in astrophysics. This simple ion, whose very existence was once doubted, is now recognized as the most abundantly produced molecular ion in the universe. It not only plays a pivotal role in the molecular evolution of some interstellar clouds but also provides a tool for measuring their temperatures [1]. The recombination of the H_3^+ ion with electrons is of interest for modeling hydrogen-containing plasmas and, in part for this reason, has been studied experimentally and theoretically for over 60 years [2]. Many extensive laboratory studies have been performed to clarify the formation and destruction processes of H_3^+, in particular the recombination of H_3^+ with electrons at low temperatures [2,3]. The word "enigma" appeared frequently in publications [4] because the measured recombination rate coefficients differed by several orders of magnitude (see extended discussion in [2,3]). The principal current motivation for H_3^+ recombination studies comes from the physics and chemistry of diffuse astrophysical clouds and planetary ionospheres (see discussion in [5–7]). H_3^+ was observed spectroscopically in the laboratory in 1980 [8], but it took many years until it was detected in emission spectra from Jupiter [9], Saturn, and Uranus (see discussion in [10]), and in interstellar plasmas [11,12].

In 2001 a new theory of H_3^+ recombination was developed [13,14] and it became clear afterwards that para-H_3^+ and ortho-H_3^+ behave differently [15]. Storage rings were used in corresponding state selected studies [2]. For temperatures above 300 K the agreement between theory and the most recent storage ring experiments [16–19] is excellent but data at lower temperatures are still not quite conclusive because internal states of the recombining ions are not necessarily in thermal equilibrium [20]. It is now generally accepted that recombination of H_3^+ occurs with a binary rate coefficient of $\alpha_{bin}(300\,\mathrm{K}) \sim 6 \times 10^{-8}\,\mathrm{cm^3\,s^{-1}}$ [21]. For applications to low-density astrophysical clouds it is the binary coefficient that matters.

The fact remains that many well-executed plasma afterglow experiments gave recombination rates that were larger by factors of 3 to 4 than the theoretical and storage ring data. A better understanding was achieved after the discovery of fast helium-assisted ternary recombination of H_3^+ in afterglow plasma in a He-Ar-H_2 gas mixture [22,23]. It was then found that the ternary He-assisted recombination process

$$H_3^+ + e^- + \mathrm{He} \rightarrow \mathrm{neutrals} + \mathrm{He} \qquad (1)$$

is indeed very effective, exceeding by over two orders of magnitude (at 300 K) the value predicted by the classical treatment of Bates and Khare [24]. The much faster ternary recombination of H_3^+ has been attributed to formation of long-lived rotationally excited neutral $H_3^\#$ Rydberg molecules and subsequent collisions with helium atoms [22,23] that eventually lead to dissociation into neutral products. We note that the formation of $H_3^\#$ Rydberg states has also been invoked as a mechanism in a recombination-pumped laser in H_3^+ containing plasma [25].

The recombination of the H_3^+ ion has been studied in our laboratory for almost 15 years. During those years, several different stationary afterglow (Advanced Integrated Stationary Afterglow (AISA) [26], Stationary Afterglow with Cavity Ring Down Spectrometer (SA-CRDS) [27,28]) and flowing afterglow (Flowing Afterglow with Langmuir Probe (FALP) [29], Cryo-FALP [21,23,30]) experiments were employed to study the H_3^+ recombination process in low-temperature afterglow plasma in a He-Ar-H_2 gas mixture. The main differences are in the range of covered number densities of He and H_2, in the electron and ion densities, in the covered temperature range, in the time scale of monitored plasma decay, and in applied diagnostics (see, e.g., [23]). A broad range of the measured plasma parameters is necessary to study the dependence of the measured effective recombination rate coefficient α_{eff} on plasma parameters and eventually to determine rate coefficients for binary and ternary recombination of H_3^+ ions and their temperature dependences. This procedure is necessary

especially in the case of the H_3^+ ion, where long-lived highly excited neutral H_3 can be formed in collision of H_3^+ with electrons [22,23]. Very extensive and systematic studies are required because the afterglow plasmas are influenced also by formation and relaxation processes and also by ambipolar diffusion and these processes depend on the same parameters as the effective recombination rate coefficient.

We should mention here that in early AISA experiments (stationary afterglow with Langmuir probe and mass spectrometer [26]) we observed a rapid fall off of value of measured effective recombination rate coefficient α_{eff} at $[H_2] \ll 10^{12}\,\text{cm}^{-3}$, where newly formed H_3^+ ions undergo on average less than one collision with H_2 prior to its recombination. The mass spectra obtained during the experiment showed that H_3^+ was the dominant ion species but the internal state of the ions was not probed in the AISA experiments. We do not have a certain explanation for this observation (see discussion in [23,31]). In later experiments we used $10^{12} < [H_2] < 5 \times 10^{13}\,\text{cm}^{-3}$; the measured α_{eff} did not change with $[H_2]$ (in the context of those experiments we called it the "saturated region", see [23,31]). At these conditions the formed H_3^+ ions have many collisions with H_2 and He prior to their recombination. We found that the measured α_{eff} depends linearly on helium number density; $\alpha_{\text{eff}} = \alpha_{\text{bin}} + K_{\text{He}}[\text{He}]$ in the "saturated region." The binary rate coefficient was determined from the low-pressure limit as $\alpha_{\text{bin}} = \alpha_{\text{eff}}([\text{He}] \to 0)$. The obtained binary recombination rate coefficients are very close to the theoretically predicted value [15] and the value reported by storage ion ring CRYRING [18]. Using SA-CRDS we confirmed that H_3^+ ions in recombination dominated afterglow plasmas are in thermal equilibrium with He [32]. All these later studies were performed for $[H_2]$ higher than $10^{12}\,\text{cm}^{-3}$ but low enough to prevent formation of fast recombining H_5^+ ions.

There are good reasons to believe that hydrogen molecules should be more efficient than inert helium atoms in promoting H_3^+ recombination, and there is some earlier experimental evidence in support of this expectation [29,30,33,34]. However, the effect of H_2 has not been studied systematically and this is the first study dedicated to H_2-assisted ternary recombination.

II. EXPERIMENT

The technical details of the stationary-afterglow cavity-ring-down-spectroscopy apparatus (SA-CRDS) have been adequately described elsewhere [27]. The plasma is formed in a pulsed microwave discharge in a mixture of He, Ar, and H_2 and the densities of three rotational states of the ground vibrational state of H_3^+ during the afterglow are measured using the transitions $3\nu_2^1(2,0) \leftarrow 0\nu_2^0(1,0)$ and $3\nu_2^1(4,3) \leftarrow 0\nu_2^0(3,3)$ for ortho-H_3^+ and $3\nu_2^1(2,1) \leftarrow 0\nu_2^0(1,1)$ for para-H_3^+. Details and notation are discussed in [32,35,36]. The kinetic temperature of the ions is obtained by measuring Doppler broadening of the absorption lines and the rotational temperature is obtained from the relative populations of measured states (for details see [32]). A numerical model of the chemical kinetics is used to determine the most appropriate conditions for the experiment. A water transition at $7236.45\,\text{cm}^{-1}$ (line position taken from HITRAN database [37]) was routinely scanned to estimate the amount of H_2O impurities in the apparatus. Typically, the water vapor concentration was at a safe level of less than $5 \times 10^{10}\,\text{cm}^{-3}$ (less than 0.1 ppm of buffer gas number density).

The present experimental study focus on H_2-assisted recombination of H_3^+ ions. Ternary recombination rate coefficients were derived from the measured ion number density decays with an effective recombination rate coefficient $\alpha_{\text{eff-ion}}$ for a wide range of [He] and $[H_2]$ densities. For details on the data analysis see [32].

III. COMPLEX MODEL OF TERNARY RECOMBINATION

Ternary contributions in H_3^+ recombination can occur by formation of Rydberg molecules $H_3^{\#}$ by resonant capture of an electron into a rotationally excited Rydberg state with the formation rate coefficient α_{F}. The unstable molecule (or "complex") can decay during its lifetime by autoionization with a time constant τ_{a} or it can be "stabilized" (rendered incapable of being autoionized or being collisionally reionized) with rate coefficient k_{s_M} in a collision with a third particle M of number density [M]. Provided that the lifetime τ_{a} is much shorter than the time scale of the plasma decay, the number density ratio $[H_3^{\#}]/[H_3^+]$ can be taken as constant and the effective recombination coefficient for H_3^+ dominated plasma becomes

$$\alpha_{\text{eff-ion}} = \alpha_{\text{bin}} + \alpha_{\text{F}} \frac{k_{s_M}[\text{M}]}{1/\tau_{\text{a}} + k_{s_M}[\text{M}]}. \tag{2}$$

This model of ternary recombination is similar to that proposed in our earlier publications [22,23,30]. We introduce the three-body recombination rate coefficient K_{M} defined as $K_{\text{M}} = \alpha_{\text{F}} k_{s_M} \tau_{\text{a}}$. In the limit of small [M] (the "linear" regime) the second term of Eq. (2) reduces to $K_{\text{M}}[\text{M}]$. In the limit of large [M], the second term of Eq. (2) approaches the constant value α_{F} and the three-body recombination process is then said to "saturate." This brief discussion hides a great amount of detail. In reality, one should consider an ensemble of many complexes, and more than two steps may be required to stabilize the complexes. In the experiment both He and H_2 can act as neutral third bodies. If one assumes that both gases act on the same complexes, the product $K_{\text{M}}[\text{M}]$ can be replaced by the sum $K_{\text{H}_2}[\text{H}_2] + K_{\text{He}}[\text{He}]$. We assume these contributions to be additive. We also assume that binary and ternary recombination are purely additive. This is not necessarily true if both processes share the same initial states.

The proposed simplified recombination mechanism is summarized in Fig. 1, where k_{SHe} and k_{SH_2} are the binary rate coefficients for collisional stabilization of $H_3^{\#}$ in collisions with He and H_2, respectively. The ternary recombination rate coefficients for He- and H_2-assisted recombination

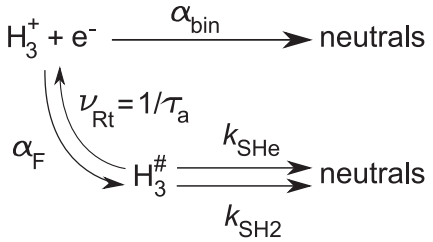

FIG. 1. The scheme of the proposed H_3^+ recombination mechanism. Used symbols are explained in the text.

(K_{He} and K_{H_2}, respectively) are introduced as $K_{He} = \alpha_F k_{SHe} \tau_a$ and $K_{H_2} = \alpha_F k_{SH_2} \tau_a$.

There is one additional recombination process that can make a contribution at high $[H_2]$: The H_3^+ ions are known to enter a chemical equilibrium with weakly bound H_5^+cluster ions that recombine very fast at 300 K ($\alpha_5 \sim 2 \times 10^{-6}\,cm^3\,s^{-1}$) [38,39]. At 300 K, the clustering equilibrium constant, defined by $[H_5^+]/[H_3^+] = K_C[H_2]$, has a value $K_C(300\,K) = 6.7 \times 10^{-19}\,cm^3$ [40]. Even at the highest H_2 concentrations ($6 \times 10^{16}\,cm^{-3}$) used in present experiments less than 4% of the H_3^+ ions are clustered.

To a good approximation, the effective recombination rate coefficient can then be written as

$$\alpha_{\text{eff-ion}} = \alpha_{\text{bin}} + \alpha_F \frac{K_{He}[He] + K_{H_2}[H_2]}{\alpha_F + K_{He}[He] + K_{H_2}[H_2]} + \alpha_5 K_C[H_2]. \quad (3)$$

A more rigorous kinetic analysis, that includes recombination of H_5^+, shows that the relative abundance of H_5^+ in recombining plasmas is smaller by about a factor of 2 than $K_C[H_2]$ and that it varies with electron density.

Equation (3) implies that $\alpha_{\text{eff-ion}}$ saturates at the value $\alpha_{\text{bin}} + \alpha_F$ if $\alpha_F \ll (K_{He}[He] + K_{H_2}[H_2])$. While in previous H_3^+ experiments [21–23,31,32] the range of [He] was too small to detect saturation, the present experiments clearly exhibit saturation (details to be given below). Also, a slight dependence on $[H_2]$ was observed in the earlier experiments [29,33,38] but it was then thought to arise from formation of fast recombining H_5^+ ions at higher $[H_2] > 10^{14}\,cm^{-3}$. However, H_5^+ formation at temperatures near 300 K does not suffice to explain the increase of the recombination rate coefficient dependent on $[H_2]$ at 300 K (with $[H_2] < 2 \times 10^{15}\,cm^{-3}$) that was also observed by Gougousi *et al.* [33]. On the other hand, Amano's [34] spectroscopic studies in a stationary afterglow experiment in pure hydrogen yielded an H_3^+ recombination rate coefficient that was independent of H_2 density, but three times larger than the currently accepted binary recombination rate coefficient [2].

IV. EXPERIMENTAL DATA AND RESULTS

Figure 2 shows typical H_3^+ decay curves measured by SA-CRDS and the calculated densities of H_3^+ and H_5^+ ions. The rate coefficients $\alpha_{\text{eff-ion}}$ are obtained by fitting the decay of the H_3^+ number densities, taken as the sum of those in the ortho and para states assuming thermal equilibrium (see discussion in [32]), or calculated from the population of the ortho-H_3^+ (1,0) state only. No substantial difference between these two evaluations was observed.

The chemical kinetics calculations solve the set of reactions as described by Plašil *et al.* [26]. Because the composition of the plasma at the end of the microwave pulse is difficult to ascertain, the calculations were performed for many sets of different initial conditions. The results of the model show that at the number densities of He, Ar, and H_2 used in present experiments the H_3^+ ion becomes the dominant ion species within 150 μs after switching off the discharge. An example is displayed in Fig. 2 for the following initial conditions in quasineutral plasma: $[H_3^+] = n_e$; $[He^m] = 1 \times 10^{11}\,cm^{-3}$, where $[He^m]$ is the number density of metastable helium

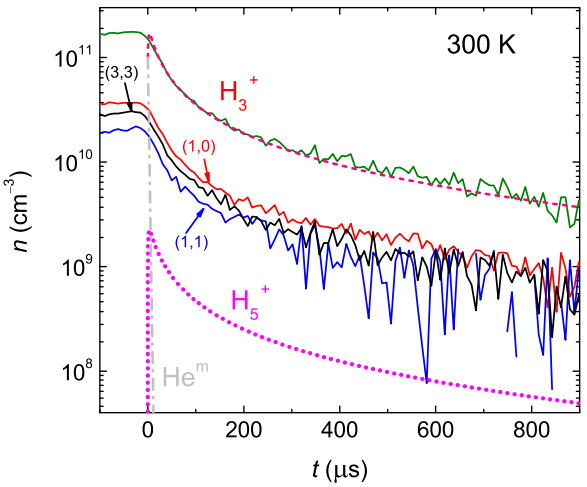

FIG. 2. (Color online) The decay curves measured for (1,0), (1,1), and (3,3) states of H_3^+ at 300 K and number densities $[He] = 8 \times 10^{17}\,cm^{-3}$, $[H_2] = 2 \times 10^{16}\,cm^{-3}$, and $[Ar] = 7 \times 10^{14}\,cm^{-3}$. The total number density of H_3^+ ions, calculated from the measured data under assumption of LTE, is shown as a full line. Calculated evolutions of the number densities of H_3^+, H_5^+, and He^m are indicated as dashed, dotted, and dash-dotted lines, respectively.

atoms. For illustration of the result of the model, the measured evolutions of the number density of (1,0), (1,1), and (3,3) states of the H_3^+ ion and of the overall number density of the H_3^+ ion are also plotted in Fig. 2. The most important reactions taking place in the formation of H_3^+ are listed in Table II of [26]. A fast decay of helium metastables He^m is given by Penning ionization with H_2 and Ar. The H_3^+ recombination rate coefficient was taken from the present data and the H_5^+recombination rate coefficient at 300 K was taken as $\alpha_5 \sim 2 \times 10^{-6}\,cm^3\,s^{-1}$ [38,39].

A large set of decay curves at 300 K, similar to those in Fig. 2, were recorded and analyzed for a wide range of $[H_2]$ and for several [He]. The dependences of $\alpha_{\text{eff-ion}}$ on $[H_2]$ at particular [He] are shown in Fig. 3. The value obtained in pure H_2 using the same experimental setup at (270 ± 5) K is also included (full diamond).

The binary rate coefficient, $\alpha_{\text{bin}}(300\,K) = 6 \times 10^{-8}\,cm^3\,s^{-1}$, is known from previous SA-CRDS and Cryo-FALP experiments [21]. To emphasize the ternary contribution we subtracted the value of α_{bin} from the measured $\alpha_{\text{eff-ion}}$ and only the difference $\alpha_{\text{eff-ion}} - \alpha_{\text{bin}}$ corresponding to the ternary contribution is shown in Fig. 3. The data clearly show that $\alpha_{\text{eff-ion}} - \alpha_{\text{bin}}$ rises with increasing $[H_2]$ up to $[H_2] \sim 10^{16}\,cm^{-3}$ and then saturates, as expected from the complex formation model [see Eq. (3)]. Two estimates of the contribution due to formation and subsequent recombination of H_5^+ ions to the overall measured recombination rate coefficient are displayed in Fig. 3. The line denoted LTE_{H_5} shows the product of $\alpha_5 K_C[H_2]$, i.e., H_5^+ is assumed to be in thermal equilibrium with H_3^+ and the $[H_5^+]/[H_3^+]$ ratio is approximated using an equilibrium constant of $K_C(300\,K) = 6.7 \times 10^{-19}\,cm^3$ [40]. A considerably smaller and more realistic contribution of H_5^+ (the line marked M_{H_5}) is obtained from our kinetic model that includes the recombination loss of H_5^+. The comparison

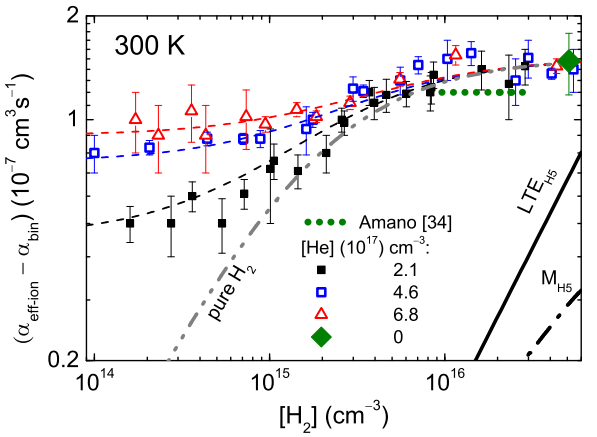

FIG. 3. (Color online) The dependencies of $(\alpha_{\text{eff-ion}} - \alpha_{\text{bin}})$ on $[H_2]$ measured at indicated [He]. Full diamond: measurements in pure H_2. Dashed lines: fits of Eq. (3) to the data, using the parameters mentioned in the text. Double-dot-dashed line: three-body recombination in pure H_2 . Solid line (LTE_{H_5}): approximate H_5^+contribution, $\alpha_5 K_C[H_2]$. Dash-dotted line (M_{H_5}): H_5^+contribution obtained from the kinetic model for $[He] = 2.1 \times 10^{17}\,cm^{-3}$. Dotted horizontal line: data obtained by Amano [34] in pure H_2 at 273 K, after subtracting $\alpha_{bin} = 6 \times 10^{-8}\,cm^3\,s^{-1}$.

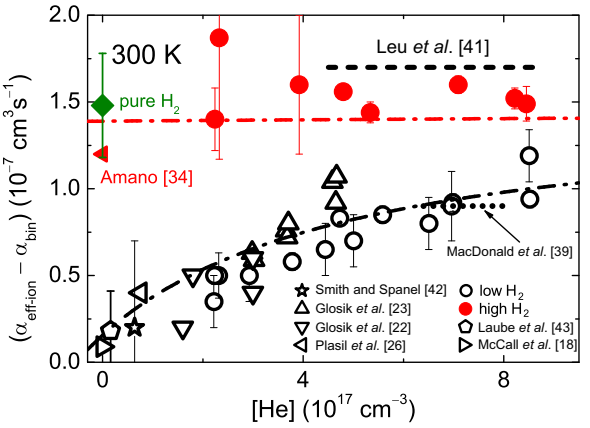

FIG. 4. (Color online) Measured dependence of $(\alpha_{\text{eff-ion}} - \alpha_{\text{bin}})$ on He number density at 300 K for $[H_2] = 2 \times 10^{14}\,cm^{-3}$ (open circles) and for $[H_2] = 2 \times 10^{16}\,cm^{-3}$ (closed circles). The values of $(\alpha_{\text{eff-ion}} - \alpha_{\text{bin}})$ measured in pure H_2 at (270 ± 5) K are denoted by full diamonds (see also Fig. 3). The values measured in other experiments [18,22,23,26,34,39,41–43] are plotted for comparison. Values indicated by open symbols were measured for $[H_2] < 5 \times 10^{14}\,cm^{-3}$. All experiments were performed with helium as a buffer gas with the exception of data in [18,34,39] where no buffer gas, pure H_2, or neon buffer gas was used, respectively. The dot-dashed lines denote values given by Eq. (3) for $[H_2] = 2 \times 10^{14}$ and $2 \times 10^{16}\,cm^{-3}$ and with parameters written in the text.

of the measured $\alpha_{\text{eff-ion}}$ with calculated contributions (LTE_{H_5} and M_{H_5}) indicates that the actual contribution due to H_5^+ formation is negligible at $[H_2] < 2 \times 10^{16}\,cm^{-3}$. We fitted the measured $\alpha_{\text{eff-ion}}$ by Eq. (3), neglecting contribution from H_5^+ formation and using $\alpha_{bin} = 6 \times 10^{-8}\,cm^3\,s^{-1}$; see the dashed lines in the Fig. 3. The inferred rate coefficients are $K_{He} = (3.3 \pm 0.7) \times 10^{-25}\,cm^6\,s^{-1}$, $K_{H_2} = (8.7 \pm 1.5) \times 10^{-23}\,cm^6\,s^{-1}$, and $\alpha_F = (1.5 \pm 0.1) \times 10^{-7}\,cm^3\,s^{-1}$. Substituting these rate constants into Eq. (3) we derived $(\alpha_{\text{eff-ion}} - \alpha_{\text{bin}})$ for the ternary recombination in pure H_2 . This gives the double-dot-dashed line labeled "pure H_2" in Fig. 3.

For comparison we also include in Fig. 3 the values obtained by Amano [34] in his spectroscopic study of H_3^+ recombination in afterglow plasma in pure H_2 at 273 K. The binary contribution has been subtracted. Amano's results agree quite well with our data, strongly suggesting that Amano measured in the saturated region.

For consistency and for comparison with previous experiments we remeasured the dependence of $\alpha_{\text{eff-ion}}$ on [He] up to $[He] = 8 \times 10^{17}\,cm^{-3}$ at a low hydrogen density, $[H_2] = 2 \times 10^{14}\,cm^{-3}$, and at 100 times higher density, $[H_2] = 2 \times 10^{16}\,cm^{-3}$. The obtained values can be seen in Fig. 4. At low $[H_2]$, $\alpha_{\text{eff-ion}}$ increases with increasing [He] and approaches saturation at very high [He]. At high $[H_2]$ $\alpha_{\text{eff-ion}}$ is nearly constant at the value α_F obtained by fitting the data in Fig. 3. The agreement of the present SA-CRDS values with those obtained in the Cryo-FALP experiment [23] is noteworthy since the electron densities in those experiments differed by more than a factor of 10. The errors in Figs. 3 and 4 are statistical errors of the fits to the time decay of $[H_3^+]$. The systematic error is estimated as 10%.

To show the difference between the helium- and hydrogen-assisted ternary recombination of the H_3^+ ion, the dependences of $\alpha_{\text{eff-ion}}$ on [He] and $[H_2]$ are plotted in Fig. 5 together

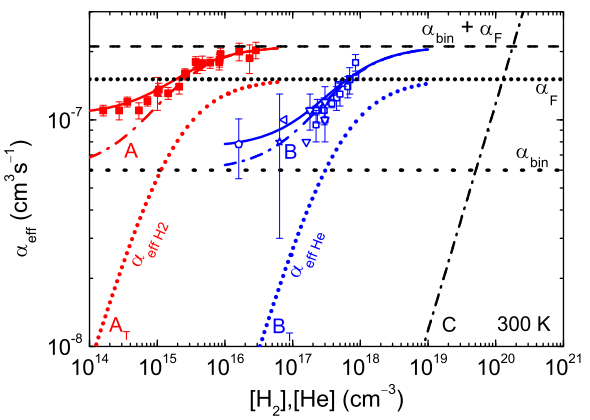

FIG. 5. (Color online) Measured dependence of the effective recombination rate coefficient on H_2 (full squares, with $[He] = 2 \times 10^{17}\,cm^{-3}$) and He number density (open squares, with $[H_2] = 2 \times 10^{14}\,cm^{-3}$) measured at 300 K. The full lines are fit to the data from Figs. 3 and 4. The horizontal dotted line shows the value of the binary recombination rate coefficient α_{bin} of H_3^+ ions at 300 K. The dashed line shows the sum $(\alpha_{bin} + \alpha_F)$, i.e., maximum rate coefficient given by the sum of contributions from binary and saturated ternary recombination. The dot-dashed lines (A, B, and C) denote the sum of α_{bin} and the contribution of the H_2-assisted process only (A), the sum of α_{bin} and the contribution of the He-assisted process only (B), and the α_{eff} arising from ternary helium-assisted recombination as predicted by the theory of Bates and Khare [24] with the ternary recombination rate coefficient of $1.2 \times 10^{-27}\,cm^6\,s^{-1}$ (C). The dotted lines denoted A_T and B_T indicate the contributions to the measured α_{eff} arising from the H_2 - and He-assisted ternary process, respectively. Values from other afterglow experiments are plotted using the same notation as in Fig. 4.

with the dependence predicted by classical Bates-Khare theory [24]. Values from other experiments are plotted using the same notation as in Fig. 4. Note the orders-of-magnitude difference between both ternary processes.

It is difficult to explain the third-body effects by accurate theoretical models. In this paper, we rationalize our observations by a highly simplified model that postulates the existence of long-lived $H_3^{\#}$ complexes, without specifying their detailed nature and the interactions that cause these complexes to eventually decay. The basic ideas are similar to those that we have described in our previous paper [30], in which we also discuss possible other three-body mechanisms.

The lifetimes of the intermediate complexes must be very large: An estimate of the three-body coefficient K_{H_2} due to H_2 is given by the product of the formation rate coefficient α_F, the complex lifetime τ_a, and the rate coefficient of stabilizing collisions $k_{S_{H_2}}$. If one takes the formation rate coefficient as $\alpha_F = 1.5 \times 10^{-7}\,\mathrm{cm^3\,s^{-1}}$, and the stabilization coefficient as $k_{S_{H_2}} = 10^{-9}\,\mathrm{cm^3\,s^{-1}}$ (a typical ion-neutral collision rate coefficient), then one needs a lifetime of $\tau_a \sim 6 \times 10^{-7}\,\mathrm{s}$ to reproduce the experimental value $K_{H_2} = (8.7 \pm 1.5) \times 10^{-23}\,\mathrm{cm^6\,s^{-1}}$ which can be obtained as $K_{H_2} = \alpha_F k_{S_{H_2}} \tau_a$. That lifetime exceeds the longest calculated [23] lifetimes of some rotational resonances ($\sim 10^{-10}\,\mathrm{s}$) by a wide margin. On the other hand, some experimental studies showed that Rydberg states of the H_3 molecule can have lifetimes exceeding $10^{-6}\,\mathrm{s}$ [44]. Previous treatments of this problem suggest that l mixing of the Rydberg electrons' angular momentum by either plasma electrons [33] or neutral particles [23,30,31] occurs and that it could enhance the complex lifetimes; l mixing of high Rydberg states with $n \gtrsim 40$ due to ambient plasma electrons is indeed an exceedingly fast process: At electron densities near $10^{11}\,\mathrm{cm^{-3}}$ mixing would occur in a time on the order of 10^{-11} to $10^{-10}\,\mathrm{s}$ for an $n = 40$ Rydberg atom [45] and increase the lifetimes by a factor of about n^2.

The experimental data show that H_2 is a much more efficient third body than helium. This suggests that complex stabilization involves reactions with the ion core, which may be rotationally and perhaps vibrationally excited, rather than with the Rydberg electron. Rydberg reactions are similar to ion-molecule reactions [46,47]. Reactions with H_2 but not He can occur by proton or H-atom exchange that reduces the energy of the complex and eventually leads to dissociation. Uy *et al.* [48] invoke this type of reaction as the principal rotational quenching mechanism in plasmas containing He and H_2.

The principal difference between He-assisted and H_2-assisted recombination can be in the interaction of the Rydberg $H_3^{\#}$ molecule with atomic He and with molecular H_2. Particularly if we have in mind the possibility of a reactive collision of $H_3^{\#}$ and H_2 followed by formation of H_5^* and its dissociation as it is described by Fermi's independent-collider model. See, e.g., recent studies of reactions of Rydberg atoms with molecules [46,47].

V. SUMMARY AND CONCLUSIONS

The cavity ring down absorption spectrometer was used to monitor *in situ* the evolution of number densities of ortho- and para-H_3^+ during the afterglow in a He-Ar-H_2 gas mixture at 300 K. From these measurements the effective recombination rate coefficient and its dependence on [He] and [H_2] were determined.

A very fast H_2-assisted ternary recombination was observed with the value of ternary recombination rate coefficient $K_{H_2} = (8.7 \pm 1.5) \times 10^{-23}\,\mathrm{cm^6\,s^{-1}}$ substantially exceeding those values measured for the same ion in ambient helium ($K_{He} \sim 10^{-25}\,\mathrm{cm^6\,s^{-1}}$) or predicted by the classical theory of Bates and Khare (with rate coefficient $\sim 10^{-27}\,\mathrm{cm^6\,s^{-1}}$) [24]. The disagreement with the Bates and Khare theory for neutral stabilized recombination of atomic ions is not surprising. In their model, the energy of Rydberg states is only reduced by Rydberg electron-atom collisions but stabilization by collision-induced predissociation, of course, is absent. The large effect of H_2 most likely explains one of the remaining discrepancies in H_3^+ recombination studies, namely, the large recombination rate coefficients measured by Amano [34].

These results are not at all the typical finding in recombination studies. As far as we know, most other molecular ions recombine largely by the binary process and the environment has little effect. The sensitivity of the H_3^+ recombination to third-body effects seems to account for many of the discrepancies between experimental studies that have been conducted and clearly demonstrates the need of further theoretical work on recombination of this simplest polyatomic ion with electrons with emphasis on formation of long-lived collisional complexes and on the influence of third particles on the overall recombination. An existence of a similar ternary process for D_3^+ ions with D_2 as the third particle is expected. We are not able to predict to what extent the H_2-assisted ternary process may have influenced recombination rates of other ions measured in plasma afterglows. The required lifetimes of the metastable Rydberg states formed in the proposed recombination process are quite long; therefore the ions recombining via direct mechanism [49] should not be affected. However, the recombination rate coefficients of some ions recombining via the indirect recombination mechanism obtained in the afterglow experiments could have been enhanced by fast ternary He- or H_2-assisted recombination. Possibly affected ions are HCO^+ and N_2H^+, as both of them recombine by the indirect mechanism [50] and the reported results of the afterglow experiments differ by almost an order of magnitude (see Fig. 2 in [51]). Moreover, the highest recombination rate coefficients for both of these ions were reported by Amano, who measured in H_2 buffer gas [34].

A fast H_2-assisted ternary recombination may directly impact models describing hydrogen plasmas and it can have consequences in plasma physics including physics of discharges, astrophysics, recombination pumped lasers, plasma spectroscopy, plasmatic technologies, etc. It can also influence processes in ionospheres of large planets with relatively high pressure of H_2, e.g., Jupiter and Jupiter-like planets, and may be important for chemistry of gas giant exoplanets.

Further measurements at different temperatures are in progress.

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