Binary and ternary recombination of D_3^+ ions with electrons in He-D_2 plasma

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An experimental study is reported about the recombination of D_3^+ ions with electrons in a low-temperature plasma (200–300 K) consisting of He with a small admixture of D_2. At several temperatures, the pressure dependence of the apparent binary recombination rate coefficient (α_{eff}) was measured over a broad range of helium pressures (200–2000 Pa). The binary and ternary recombination rate coefficients were obtained from measured pressure dependences of α_{eff}. The binary recombination rate coefficient obtained $\alpha_{bin}(300\ \text{K}) = (2.7 \pm 0.9) \times 10^{-8}\ \text{cm}^3\ \text{s}^{-1}$ is in agreement with recent theory. The ternary recombination rate coefficient obtained is $K_{He}(300\ \text{K}) = (1.8 \pm 0.6) \times 10^{-25}\ \text{cm}^6\ \text{s}^{-1}$. In analogy with the recently described process of helium-assisted ternary recombination of H_3^+ ions, it is suggested that the ternary helium-assisted recombination of D_3^+ ions proceeds through the formation of a neutral long-lived highly excited Rydberg molecule D_3 followed by a collision with a He atom.

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I. INTRODUCTION

The interaction of electrons with H_3^+ and D_3^+ ions has fundamental importance for plasma physics, physical chemistry, astrophysics, spectroscopy, and for quantum theory (see, for instance, the following reviews [1–7]). Up until the year 2001, theory had predicted a very slow recombination rate for H_3^+ and D_3^+ ions and there were large discrepancies between values of the recombination rate coefficients measured in different experiments and also between experiments and theory. The situation changed in 2001 when Jahn-Teller coupling was included in the theory of H_3^+ and D_3^+ recombination [8]. After further refinement the cross sections and the rate coefficients for H_3^+ and D_3^+ recombination were calculated in 2003 [9]. The most recent theoretical values obtained for the rate coefficients of dissociative recombination for H_3^+ and D_3^+ are $\alpha_{H_3^+}(300\ \text{K}) = 5.6 \times 10^{-8}\ \text{cm}^3\ \text{s}^{-1}$ and $\alpha_{D_3^+}(300\ \text{K}) = 4 \times 10^{-8}\ \text{cm}^3\ \text{s}^{-1}$, respectively [10,11]. For H_3^+ ions, better agreement between theoretical and measured cross sections was obtained when rotationally cold H_3^+ ions were used in the storage ring experiments [12,13]. There are, however, no storage ring data with rotationally cold D_3^+ ions up to now. Plasma experiments with neither ion give such straightforward agreement with theory. In our previous studies of H_3^+ and D_3^+ recombination in an afterglow plasma (the stationary afterglow—AISA experiment in Prague), we observed the dependence of measured recombination rate coefficients on the hydrogen and deuterium densities, respectively [14–16]. The actual measurements were carried out in 200–2000 Pa of He with a small admixture of H_2 or D_2. The experimental hydrogen and deuterium densities varied from $5 \times 10^{10}\ \text{cm}^{-3}$ up to $\approx 5 \times 10^{15}\ \text{cm}^{-3}$. In the course of those studies, we realized that the dependence on hydrogen or deuterium density is caused by a multistep recombination process in He-H_2 and He-D_2 plasmas. To stress this fact, the symbol α_{eff} was used to denote the measured "effective" recombination rate coefficients. We also measured the dependence of both recombination rate coefficients on temperature and on the He buffer gas pressure.

In the experiments with an H_3^+-dominated plasma in He buffer gas, we observed a linear dependence of the measured α_{eff} on the helium density [17]. We interpreted these results by assuming that the observed recombination process in He buffered plasma has two parallel channels: binary and ternary. The rate coefficients of both processes were extracted from those measurements [18]. In order to provide a rudimentary theoretical description of this recombination process, we have calculated the lifetimes of neutral H_3^* formed in collisions of H_3^+ ions with electrons (the delay time Δt in the $H_3^+ + e^-$ collision, in the sense introduced by Smith [19]). The theory shows that the delay time depends on collision energy and, moreover, it is state sensitive, e.g., at collision energies $\approx 150\ \text{cm}^{-1}$ the delay time can be $\Delta t \approx 100$ ps for para H_3^+, whereas for ortho H_3^+, in contrast, only short-lived H_3^* states with $\Delta t < 3$ ps are formed. During the delay time, the H_3^* molecule formed in $H_3^+ + e^-$ collision can collide with a helium atom. The calculated delay time was used to estimate the ternary recombination rate coefficient. These calculations assumed that l-changing collisions of H_3^* with helium atoms are important. It was further assumed that the colliding particles have a relative velocity distribution corresponding to thermal equilibrium at the given temperature and that the rate coefficient for l-changing collisions is constant $k^l = 2.3 \times 10^{-8}\ \text{cm}^3\ \text{s}^{-1}$ (for more information, see Refs. [17,18]). Because the delay time is state sensitive, we obtained different ternary rate coefficients for ortho and para H_3^+ ions.

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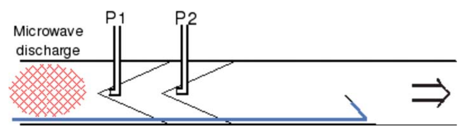

FIG. 1. (Color online) FALP experiment. The buffer gas (He) flows through the discharge region (left side) toward the pump (right side). Ar is added via port P1 to form an Ar^+-dominated plasma. Via port P2 deuterium is added to form the D_3^+-dominated plasma. The Langmuir probe is movable from the position of port P2 up to the end of the flow tube. The buffer gas velocity gives the relation between the position in the flow tube and the decay time.

Naturally, following the observation of this ternary process in an H_3^+-dominated afterglow plasma, we have begun to explore similar phenomena in a D_3^+-dominated plasma. Here we report the results of an experimental study of the recombination in D_3^+-dominated plasma in He-D_2 at temperatures 200–300 K. For discussions of the results of previous relevant studies of D_3^+ recombination in a plasma environment, see Refs. [3,4,16,20].

II. EXPERIMENTS

In the present study, we have used the flowing afterglow (FALP) apparatus. Some data obtained in our previous Advanced Integrated Stationary Afterglow (AISA) [3,16] and FALP [21,22] experiments are also discussed. The apparatus AISA was described previously [3] and will not be repeated here. We only briefly mention FALP (for further details, see, e.g., [5,21,23]).

In the FALP experiment (see Fig. 1), a helium carrier or buffer gas is flowing with high velocity along the flow tube (5 cm in diameter; 100 cm long). A plasma is formed in the upstream glass section of the flow tube (on the left side) in a microwave discharge in pure He. The initially formed plasma contains He^+ ions, helium metastables (He^m), and electrons [21,22,24]. The flowing buffer gas carries the plasma from the discharge region along the flow tube. The evolution and composition of the afterglow plasma along the flow tube can be influenced by the addition of reactant gases to the buffer gas via entry ports P1 and P2.

In the present experiments, Ar is injected via port P1 and in a sequence of reactions, an Ar^+-dominated plasma is formed; for a discussion of this system, see Refs. [3,4]. The plasma then flows along the flow tube for 35 ms. To this already relaxed plasma [25], deuterium is introduced and in a sequence of ion-molecule reactions a D_3^+-dominated plasma is formed (for details of its formation, see Refs. [3,16,21]). The D_3^+ ions formed in this manner recombine with electrons, and the density of charged particles (ions and electrons) decreases (decays) along the flow tube. The electron density is measured with a Langmuir probe [26]. From the electron-density decay, the recombination rate coefficient for D_3^+ ions can be obtained. In the data analysis, we assume that after the D_3^+-dominated plasma is formed, the recombination process during the plasma decay (along the flow tube) can be described by a single value of the rate coefficient (α_{eff}). Basically, the recombination rate coefficient α_{eff} is extracted under the assumption that the plasma decay can be described by the balance equation,

$$\frac{dn_e}{dt} = -\alpha_{\mathrm{eff}} n_e n_+ - \frac{n_e}{\tau_D} = -\alpha_{\mathrm{eff}} n_e^2 - \frac{n_e}{\tau_D}, \qquad (1)$$

where n_e and n_+ are the electron and ion densities, respectively. The constant τ_D characterizes the losses due to ambipolar diffusion. The afterglow plasma is quasineutral, i.e., $n_e = n_+$. The details of the data analysis have been described in our previous publications (see, e.g., notably Ref. [22]). The present experiments use helium densities [He] in the range $\approx 1-6\times10^{17}$ cm^{-3} and deuterium densities $[D_2]$ in the range $\approx 10^{11}-10^{15}$ cm^{-3}. If we consider that the typical lifetime for a D_3^+ ion, after formation and prior to its recombination, is ≈ 5 ms, then within this time the D_3^+ ion will experience on average several "state changing collisions" in order to form a population of internal states corresponding to the temperature of the buffer gas. Particularly important are collisions with D_2 because only they can change the nuclear-spin state of the ions (para, ortho, or meta ratio), which is coupled with rotational excitation. If we assume that the rate coefficients for para (p), ortho (o), and meta (m) transitions are $\approx 2\times10^{-10}$ $cm^3\,s^{-1}$ (see the discussion for H_3^+ ions in Refs. [27,28]), then we obtain for the average number N of the state changing collisions per ion: $N<1$ for $[D_2] < 10^{12}$ cm^{-3} and $N>1$ for $[D_2] > 10^{12}$ cm^{-3}.

In the present experiments, the decay of the afterglow plasma has been studied at $[D_2] > 10^{12}$ cm^{-3}, i.e., in conditions where we can expect the para, ortho, and meta concentrations to be in equilibrium. In fact, the dependence of the recombination rate coefficients α_{eff} on $[D_2]$ has been measured over a broad range of deuterium densities, in order to clearly distinguish the conditions where D_3^+ ions are in equilibrium and where α_{eff} is not dependent on $[D_2]$.

In the present experimental arrangement (with decay times up to 50 ms), we can measure recombination rate coefficients as small as 1×10^{-8} $cm^3\,s^{-1}$, and the accuracy of the measured rate coefficients is approximately $\pm 30\%$.

III. RESULTS

The decay of the afterglow plasma in a He-Ar-D_2 mixture has been monitored at different temperatures (200–300 K) and over a broad range of helium and deuterium densities. The effective recombination rate coefficients obtained are observed to depend on temperature and on the densities of both gases $\alpha_{\mathrm{eff}} = \alpha_{\mathrm{eff}}(T,[D_2],[He])$; this indicates that the observed "deionization process" cannot be pure binary dissociative recombination (the subscript "eff" is intended to reflect this fact). Examples of decay curves measured at 250 K are plotted in Fig. 2. From these decay curves, the effective recombination rate coefficients were calculated using the advanced analysis [22]. The plasma decay in the very early afterglow (having decay times <10 ms) is influenced by the formation of the D_3^+-dominated plasma, but this is accounted for in the advanced analysis [22]. Also plotted is the decay curve measured in the He-Ar afterglow dominated by Ar^+ ions in otherwise identical conditions. The recombination of atomic Ar^+ ions can be neglected and the decay of plasma is

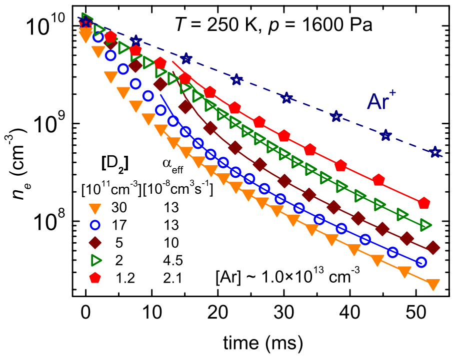

FIG. 2. (Color online) The subset of decay curves measured along the flow tube in the D_3^+-dominated afterglow plasma of He-Ar-D_2, as discussed in the text. The decay time corresponds to the position on the axis of the flow tube; the origin of the time scale is at port P2. Indicated are values of α_{eff} obtained at different deuterium densities. The decay curve measured in the Ar^+-dominated afterglow plasma in He-Ar is also plotted.

governed by ambipolar diffusion (i.e., with simple exponential decay).

In Fig. 3, the effective recombination rate coefficients α_{eff} obtained in FALP at 250 K and at two different He pressures are plotted as functions of deuterium density. Our previous data measured in the AISA experiment [16] at (230 ± 40) K, but at considerably lower pressure, are also plotted in Fig. 3. The previously measured results of Laube *et al.* [29] and Gougousi *et al.* [30] are also included in Fig. 3; both experiments were carried out at 300 K.

As can be seen from the plots in Fig. 3, there are three distinct regions of deuterium density:

(1) $[D_2]>10^{13}$ cm^{-3}; at these densities, the formation of D_5^+ ions and their fast recombination can influence the plasma decay. The process involving D_5^+ ions was studied previously so we will not discuss the details here (see Ref. [21]). We cannot exclude the D_2-assisted ternary recombination processes here; this process will be examined in a separate study.

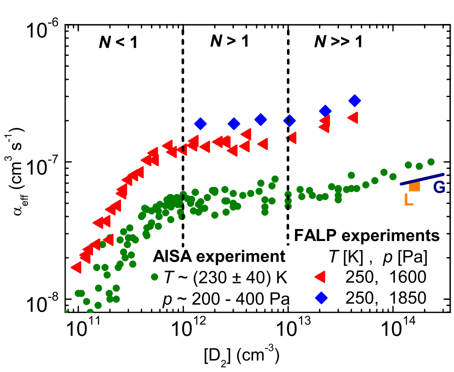

FIG. 3. (Color online) Examples of measured dependences of the effective recombination rate coefficient of electrons with D_3^+ ions on deuterium density. The measurements were carried out at different pressures at 250 K. Plotted are also the data obtained at 230 K in AISA experiment by Poterya *et al.* [16] and the data obtained at 300 K by Gougousi *et al.* [30] (FALP, full line indicated as G), and Laube *et al.* [29] (FALP, square indicated as L). Regions characterized by different average numbers N of "state changing collisions" are indicated as well.

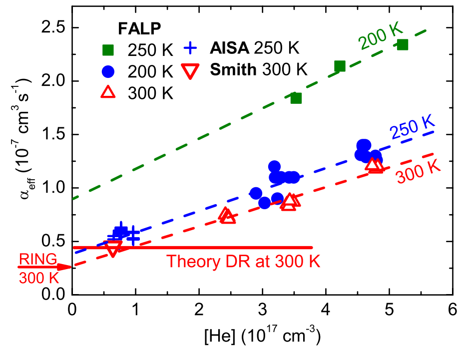

FIG. 4. (Color online) The dependences of the recombination rate coefficient (α_{eff}) on helium density and on temperature. Included are data obtained by Smith and Spanel [31]. The arrow indicates the value obtained by Larsson *et al.* [32] and Larsson and co-workers [33] in the CRYRING experiment, i.e., the value corresponding to the binary recombination rate coefficient at 300 K. The straight horizontal line indicates the value calculated for the binary dissociative recombination of D_3^+ ions at 300 K [11].

(2) 10^{12} cm$^{-3}<[D_2]<10^{13}$ cm^{-3}; in this region, the measured α_{eff} is nearly independent on $[D_2]$. As was already mentioned at $[D_2]>10^{12}$ cm^{-3}, the D_3^+ ion formed has several collisions with D_2 prior to its recombination with an electron. We assume that after these collisions the ions are in *p-o-m* equilibrium. We will call this the "saturated region" because of its independence of $[D_2]$.

(3) $[D_2]<10^{12}$ cm^{-3}; in this region, the measured α_{eff} increases with increasing deuterium density. At these low D_2 densities, the D_3^+ ions formed do not have enough collisions with D_2 to establish *p-o-m* equilibrium. The decay of the plasma due to recombination is faster than the rate of the approach to the *p-o-m* equilibrium, in this sense the afterglow plasma is changing along the flow tube. The deviation from equilibrium is greater if ions in different states (*p-o-m*) recombine with different rate coefficients. The theory indicates that the rate coefficients of binary recombination are state sensitive [10,11]; our recent calculations made for H_3^+ ions [17,18] show that also ternary recombination is very sensitive at low temperature to the internal state of the recombining ion. We can expect also that D_3^+ ions in different states will recombine with different rates.

The borders between regions can also depend on He pressure and temperature, but there is no doubt that between 10^{12} cm^{-3} and 10^{13} cm^{-3} the rate coefficient $\alpha_{eff}=\alpha_{eff}(T,[D_2],[He])$ is constant, independent of $[D_2]$. The rate coefficients measured in this "saturated region" at three different temperatures are plotted in Fig. 4 as functions of the helium density.

We briefly summarize the plotted data.

A. 300 K

(1) Open triangles ($\triangle$). The present data measured in the cryo-FALP experiment, the newest version of FALP designed to accommodate large variations in helium pressure

[18]. Some values were obtained in FALP by Novotny *et al.* [21].

(2) The open upside-down triangle (▽) is the value obtained by Smith and Spanel in 1993 (see Fig. 4 in Ref. [31]).

(3) Arrow (→). The arrow indicates value obtained in CRYRING experiment [32,33].

(4) The horizontal line indicates the calculated binary recombination rate coefficient of D_3^+ ions in *p-o-m* equilibrium [11].

B. 250 K

(1) Closed circles (●). The compilation of values obtained in different configurations of FALP in our laboratory (see, e.g., Refs. [21,34,35]).

(2) Cross symbols (+). Compilation from AISA measurements at (230 ± 40) K [16].

C. 200 K

(1) Closed squares (■). Present FALP data measured as a function of the pressure.

The experimental data plotted in Fig. 4 show that the measured recombination rate coefficient $\alpha_{eff} = \alpha_{eff}(T,[D_2],[He])$ depends linearly on helium density [He]. Below we will discuss a possible mechanism for this recombination; but at this point we can assume that the process has binary kinetics at very low [He] and with increasing [He] the helium-assisted ternary process contributes substantially to the overall recombination, i.e., to the deionization of the plasma. In this sense, we can write the following formula for the observed linear dependence:

$$\alpha_{eff} = \alpha_{bin}(T) + K_{He}(T)[He], \tag{2}$$

with the coefficients of binary recombination $\alpha_{bin}(T)$ and ternary (helium-assisted) recombination $K_{He}(T)$. The binary α_{bin} and ternary $K_{He}(T)$ recombination rate coefficients obtained are plotted in Fig. 5 as functions of temperature of the buffer gas. The contemporary theoretical values [11] and the data obtained in CRYRING experiments [32] are also plotted in Fig. 5. The agreement is good, but we must keep in mind the accuracy of the present values obtained in the limit $[He] \to 0$ and also the fact that the CRYRING experiment probably did not have internally cold ions. The values obtained for 300 K are $\alpha_{bin}(300\ K) = (2.7 \pm 0.9) \times 10^{-8}\ cm^3\ s^{-1}$; $K_{He}(300\ K) = (1.8 \pm 0.6) \times 10^{-25}\ cm^6\ s^{-1}$.

IV. DISCUSSION

The three-body recombination process with a neutral atom as a third body was previously described by Thomson [36] and by Bates and Khare [37]. The typical value for the three-body recombination rate coefficient with He as a third body at 300 K is of the order of $10^{-27}\ cm^6\ s^{-1}$ [38]. The ternary process we observe in the D_3^+ recombination is more efficient by a factor of 100; it suggests that the observed ternary process has a different origin. A similar fast ternary process was recently observed [17,18] in the H_3^+ recombination in the presence of He buffer gas. In Refs. [17,18], we have suggested a mechanism for the fast He-assisted recom-

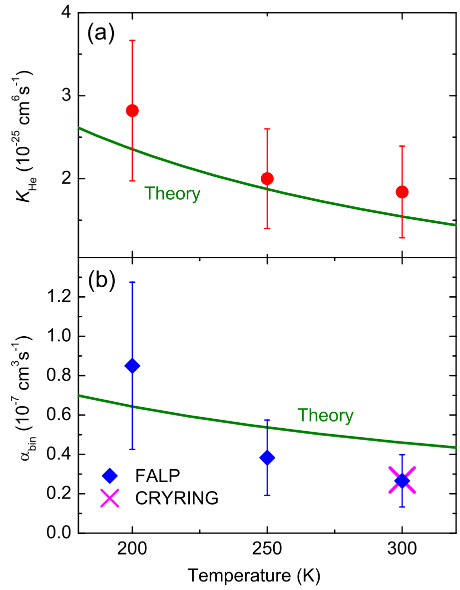

FIG. 5. (Color online) Panel (a): the measured rate coefficient $K_{He}(T)$ of ternary He-assisted recombination of D_3^+ ions with electrons. The values at 200, 250, and 300 K are calculated from the linear dependences plotted in Fig. 4. The solid line indicates the ternary recombination rate coefficient calculated in this work for thermal equilibrium. Panel (b): the measured binary recombination rate coefficient $\alpha_{bin}(T)$. Also plotted is the CRYRING value [32]. The calculated binary recombination rate coefficient for thermal equilibrium is indicated by the solid line [11].

bination of H_3^+ with electrons. The same model can be applied to the recombination of the D_3^+ plasma. In collisions between D_3^+ ions and electrons neutral Rydberg D_3^* molecules are formed. The lifetime of the molecules depends on the collision energy and internal excitation of the ion. The long-lived Rydberg molecule formed then collides with a He atom that makes the autoionization process of D_3^* impossible. The collisions that turn off the autoionization process are those that increase the orbital l and/or magnetic quantum number m of the Rydberg electron in D_3^* (l-changing collisions between D_3^* and He).

Previously, the l-changing collisions involving a Rydberg alkaline-earth-metal atom and a rare-gas atom have been observed experimentally by Gallagher *et al.* [39–41] and treated theoretically by Hickman [42,43] and Kaulakys [44]. The process of an l-changing collision in the present case of $D_3^*(np)$ is viewed as an electronic transition $np \to n'l$ $(l > 1)$ of the molecule caused by a time-dependent perturbation potential $V(t)$, which is created by the incident He atom. The main contribution to the amplitude of an l-changing electronic transition is accumulated at small distances $\tilde{r}$ between the electron and the He atom because the polarization potential behaves as $1/\tilde{r}^4$. The polarization of He due to the ionic core D_3^+ plays a smaller role. Therefore, the perturbation is the strongest when the helium atom crosses the Rydberg shell of D_3^*, where the electronic probability density is the largest. Because the time needed to cross the shell is comparable to $1/(E_{np} - E_{n\pm1,l})$, the transition amplitude for the l-changing collisions is relatively large. By making the above simplifications in the description of the process, we are able to calculate the transition amplitudes using a standard time-dependent perturbation formula. However, here we have not calculated the amplitudes explicitly for D_3^*, but instead use results calculated for Na^*+He l-changing collisions by Hickman [42,43] and Kaulakys [44], which should not be very different because the outer part of the highly excited Rydberg electronic states is the same for Na^* and D_3^*. (Hickman and Kaulakys both used the first-order Born approximation and replaced the e^--He scattering amplitude by the scattering length. Their calculation obtained generally good agreement with experimental data, although it tended to underestimate the l-changing cross section at high principal quantum numbers.)

Note that some puzzles remain in the literature, concerning l-changing collisions between atomic Rydberg states and rare-gas atoms. In particular, theory suggests that rate coefficients for this process should decrease at very high principal quantum numbers as n^{-3}. The available experiments, on the other hand, appear to suggest a behavior that is closer to *n independent* or in any case far slower decrease with n than theory predicts. For this reason, we are relying more on the experimental results than on the theory, for the l-changing collision rate coefficients needed in our current estimations. But this key point deserves further study.

Therefore, we took the value of 10^{-13} cm^2 for the cross section for l-changing D_3^*+He collisions [42–44]. The corresponding rate coefficient at 300 K is $k^l \approx 10^{-8}$ cm^3 s^{-1}. Using this rate coefficient at densities typical for our FALP experiment [He]$=5\times10^{17}$ cm^{-3}, we obtain averaged time between D_3^* and He collisions $\tau_{col}=200$ ps. If the lifetime τ^* of D_3^* molecule is longer or comparable with 200 ps then D_3^* can collide with He prior to its autoionization. Such collisions can influence the recombination process. Because the probability of such collisions is proportional to He number density, the rate coefficient of the overall process will be pressure dependent. In the low-pressure limit, we should then observe a linear dependence on the He density [45].

V. THEORY

A theoretical approach to estimate the ternary rate coefficient K^{3d} for recombination in a plasma has been developed for H_3^+ in our earlier paper [18]. Here we will only give the essential ingredients of the approach and discuss differences in our treatment of recombination in H_3^+ and D_3^+ plasmas.

We estimate the rate coefficient for He-assisted ternary recombination of D_3^+ plasma as a two-step process

$$D_3^+ + e^- \to D_3^*(np), \tag{3}$$

$$D_3^*(np) + \mathrm{He} \to D_3(nl) + \mathrm{He}, \tag{4}$$

where $D_3^*(np)$ indicates the neutral deuterium trimer molecule having a finite lifetime with respect to autoionization, with the outermost electron residing in an np Rydberg state. $D_3(nl)$ designates the deuterium trimer with the Rydberg electron having a different partial-wave state ($l>1$) with a very large or virtually infinite autoionization lifetime, such that it will dissociate and/or radiatively cascade into D+D +D or D_2+D products rather than autoionize back to D_3^+ and e^-. If the initial state of the $D_3^+ + e^-$ system is i and the intermediate state of $D_3^*(np)$ is j, the overall three-body rate coefficient can be expressed using the cross section σ_{ji} for the $i\to j$ inelastic collision between D_3^+ and e^-, the time Δt_{ji} of the $i\to j$ inelastic collision (an element of the delay-time matrix [19,18]), and asymptotic velocity v of the colliding D_3^+ ion and the electron

$$k^l \Delta t_{ji} v \sigma_{ji}(E). \tag{5}$$

The cross section σ_{ji} and the element Δt_{ji} of the delay-time matrix are expressed using the matrix element $S_{ji}(E)$ of the scattering matrix [18,19]. The ternary rate coefficient obtained in this manner is summed over all possible final states j. It turns out [18,19] that the resulting sum can be expressed as the diagonal element of the Smith's lifetime matrix $\hat{Q}$ [19] (the $\hat{Q}$ matrix is also known as the time-delay matrix),

$$\hat{Q} = -i\hbar \hat{S}^\dagger \frac{d\hat{S}}{dE}, \tag{6}$$

where the product of the matrices $\hat{S}^\dagger$ and $\frac{d\hat{S}}{dE}$ is the regular matrix product. Therefore, the ternary rate coefficient takes the following simple form (in a.u.):

$$K_i^{3d} = k^l \frac{\pi}{\sqrt{2E}} Q_{ii}, \tag{7}$$

where i corresponds to the initial state of the ion. The obtained coefficient strongly depends on the collision energy E between electrons and D_3^+ ions just because the $D_3^+ + e^-$ scattering matrix strongly depends on the energy due to the presence of autoionizing resonances in the $D_3^+ + e^-$ spectrum. For comparison with the plasma experiments, we perform a thermal average of the obtained ternary rate coefficient. In addition to the Maxwellian distribution over different collision energies E, the thermal average should also take into account the T-dependent population of different initial rotational states of the D_3^+ ion as well as different nuclear-spin states at a given temperature T. Summarizing, the thermal average is given by

$$\langle K^{3d} \rangle = \frac{2\sum_i \int_0^\infty K_i^{3d} w_i \exp\left(-\frac{E+E_i}{k_B T}\right)\sqrt{E}dE}{\sqrt{\pi (k_B T)^3}\sum_i w_i \exp\left(-\frac{E_i}{k_B T}\right)}, \tag{8}$$

where $w_i=(2I+1)(2N^++1)$ is the statistical weight of the initial state i of D_3^+ due to the angular momentum N^+ of the ion and its total nuclear spin I. Expressed in terms of the lifetime matrix element Q_{ii}, the thermally averaged rate coefficient becomes

$$\langle K^{3d} \rangle = \sqrt{\frac{2\pi}{(k_B T)^3}} \frac{k^l \sum_i \int_0^\infty Q_{ii} w_i \exp\left(-\frac{E+E_i}{k_B T}\right) dE}{\sum_i w_i \exp\left(-\frac{E_i}{k_B T}\right)}. \tag{9}$$

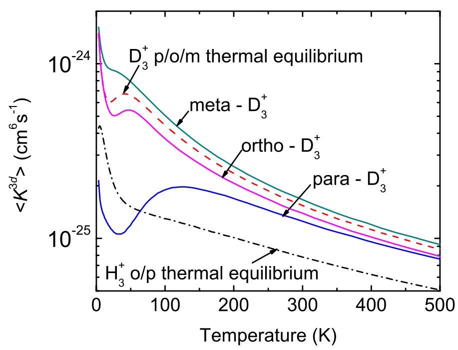

FIG. 6. (Color online) Calculated thermally averaged three-body rate coefficient K^{3d}. The rate coefficients calculated separately for ortho, meta, and para D_3^+ are very different. If the recombining plasma is not in thermal equilibrium with respect to the para, ortho, or meta ratio, the averaged rate coefficient could be very different from that shown (dashed). For comparison, we give also the thermally averaged rate coefficient K^{3d} for H_3^+ [18].

The total nuclear spin of D_3^+ can be 0, 1, 2, or 3. For the totally symmetric irreducible representation A_1 of the nuclear-spin function, two values of the total nuclear spin are allowed: $I=1$ and 3. So, the overall nuclear-spin statistical weight w_{ns} for the A_1 nuclear states is $7+3=10$. The A_1 nuclear-spin state is the ortho state for D_3^+. For the totally antisymmetric irreducible representation A_2, only one value $I=0$ is allowed, so the A_2 weight w_{ns} is 1. The A_2 nuclear-spin state is the para state for D_3^+. Finally, for the E irreducible representation, the states with $I=1$ and 2 are allowed, each of them comes in twice (E state is doubly degenerate). Therefore, the E weight w_{ns} is $3+5=8$. It is the meta nuclear-spin state of the D_3^+ ion. Because the calculations are performed for a particular nuclear-spin symmetry (or for a particular coordinate symmetry), not for a particular nuclear spin I, it is more convenient to represent w_i as a product $w_i=(2N^+ +1)w_{ns}$. The irreducible representation of the coordinate part of the total wave function (the rovibronic part) determines uniquely the irreducible representation of the nuclear-spin part and, therefore, the statistical weight of the nuclear-spin symmetry.

Figure 6 shows the theoretical ternary rate coefficient K^{3d} calculated using Eq. (9). The figure shows also the rate coefficients calculated separately for each of the nuclear-spin symmetries A_1 (o), A_2 (p), and E (m). For comparison, the He-assisted H_3^+ DR ternary rate coefficient obtained in our previous study [18] is also shown. The overall theoretical value for K^{3d} is in a reasonable agreement with experiment given the assumptions we used in the theoretical calculation: at 300 K the theoretical value for $K^{3d}=1.4\times10^{-25}$ cm^6 s^{-1}, the experimental value is $K^{3d}=1.8\times10^{-25}$ cm^6 s^{-1}. The most important assumption we made in the theoretical model is the value of the rate constant k^l for the l-changing collisions. The improved and possibly energy-dependent value of k^l should be the first step in an eventual improvement of the present theoretical model.

VI. CONCLUSIONS

Studying the recombination of the D_3^+-dominated afterglow plasma with electrons, we have observed a linear dependence of the overall recombination (deionization) rate coefficient on the density of helium buffer gas. From the measured dependence, we have obtained the binary and ternary recombination rate coefficients for temperatures between 200 and 300 K. The obtained binary recombination rate coefficient is in agreement with the value obtained in CRYRING experiment [32] and theoretical values [11]. The measured ternary rate coefficient is in fair agreement with the calculated value. Further studies of temperature dependences of the rate coefficients of binary and ternary recombination are in progress.

We would like to point out that the experiment shows that the ternary rate coefficients for H_3^+ [18] are comparable to the coefficients for D_3^+ at 300 K and larger at 200 K. The theoretical calculations show a different trend: $\langle K^{3d}\rangle(D_3^+) > \langle K^{3d}\rangle(H_3^+)$ (see Fig. 6). It suggests that the theory does not account for all details of ternary processes in H_3^+ and D_3^+ plasma recombination. One possibility is that H_2 (or D_2) dimers play a significant role in these processes.

We have deliberately excluded from our discussion the low ($[D_2]<10^{12}$ cm^{-3}) and high ($[D_2]>10^{13}$ cm^{-3}) deuterium densities. In particular, our discussion relates only to results obtained at deuterium densities sufficient to maintain the para, ortho, or meta equilibrium. Because the ternary rate coefficient is different for different nuclear-spin symmetries, at low deuterium densities the recombination process is strongly influenced by a nonthermal distribution of the ortho, para, and meta states of D_3^+. Further information and probably longer observation times for the plasma recombination are needed to understand the He-assisted recombination at low deuterium densities. At high deuterium densities, the collisions between D_3^+ and D_2 (including D_2-assisted recombination of D_3^+) influence the overall recombination process.

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