RAT E COEFFICIENTS FOR D(1s) + H⁺ ⇌ D⁺ + H(1s) CHARGE TRANSFER AND SOME
ASTROPHYSICAL IMPLICATIONS

DANIEL WOLF SAVIN
Columbia Astrophysics Laboratory, 550 West 120th Street, Columbia University, New York, NY 10027; savin@astro.columbia.edu
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ABSTRACT

We have calculated the rate coefficients for D(1s) + H⁺ ⇌ D⁺ + H(1s) using recently published theoretical cross sections. We present results for temperatures T from 1 K up to 2 \times 10^5 K and provide fits to our data for use in plasma modeling. Our calculations are in good agreement with previously published rate coefficients for 25 \leq T \leq 300 K, which covers most of the limited range for which those results were given. Our new rate coefficients for T \gtrsim 100 K are significantly larger than the values most commonly used for modeling the chemistry of the early universe and of molecular clouds. This may have important implications for the predicted HD abundance in these environments. Using our results, we have modeled the ionization balance in high-redshift QSO absorbers. We find that the new rate coefficients decrease the inferred D/H ratio by \lesssim 0.4%. This is a factor of \gtrsim 25 smaller than the current \gtrsim 10% uncertainties in QSO absorber D/H measurements.

Subject headings: atomic data — atomic processes — early universe — ISM: molecules — plasmas — quasars: absorption lines

1. INTRODUCTION

Deuterium plays an important role in addressing several fundamental questions in astrophysics. The deuterium abundance is a key constraint for models of big-bang nucleosynthesis. Primordial D/H measurements provide the most sensitive probe of the baryon-to-photon density ratio η. This, in combination with the cosmic microwave background measurement of the photon density, can be used to determine the cosmological baryon density (Burles & Tytler 1998; Lemoine et al. 1999; Tytler et al. 2000). Deuterium may also be important in the formation of structure in the postrecombination era of the early universe. HD is the second-most abundant primordial molecule after H₂, and cooling radiation from it may play a role in the formation of the first collapsing objects (Puy et al. 1993; Stancil et al. 1998). This is also a major source of HD (Black & Dalgarno 1973; Dalgarno, Black, & Weisheit 1973; Watson 1973). This is also an important source of HD in the early universe (Stancil et al. 1998).

In the early universe, these are two of the most important processes involving deuterium (Galli & Palla 1998). In molecular clouds, the process in equation (1), followed by the exothermic reaction

\[ H_2 + D^+ \rightarrow HD + H^+ , \]

is a major source of HD (Black & Dalgarno 1973; Dalgarno, Black, & Weisheit 1973; Watson 1973). This is also an important source of HD in the early universe (Stancil et al. 1998).

Recently, Igarashi & Lin (1999) and Zhao, Igarashi, & Lin (2000) have carried out cross section calculations for reactions (1) (σ₁) and (2) (σ₂) using a hyperspherical close-coupling method. This technique is free from the ambiguities associated with the conventional Born-Oppenheimer approach. Here we use their results to produce CT rate coefficients for reactions (1) (σ₁) and (2) (σ₂). In § 2 we describe how we evaluated σ₁ and σ₂. Our results are presented in § 3 and compared with previously published calculations. Some astrophysical implications are discussed in § 4.

2. CALCULATION OF THE RATE COEFFICIENTS

We consider only capture from and into the 1s level of hydrogen and deuterium. The reason for this is twofold. First, in the sources discussed in § 1, neutral hydrogen and deuterium are expected to be found essentially only in their ground state. Second, at the low temperatures (i.e., low collision energies) relevant for these sources (T \lesssim 3 \times 10^4 K [i.e., k_B T \lesssim 3 eV]), CT into the 1s level is predicted to be over 4 orders of magnitude greater than capture into other levels. CT into higher levels does not become important until collision energies of \gtrsim 10^5 eV (Ait et al. 1994).

We use the results of Igarashi & Lin (1999) and Zhao et al. (2000) for σ₁(E) and σ₂(E) at center-of-mass energies E from 2.721 \times 10^{-8} to 2.721 eV (A. Igarashi 2001, private communication). Because the binding energy of D(1s) is slightly larger than that of H(1s), reaction (1) is endothermic, with a threshold of 3.7 meV (43 K). Hence, σ₁ is predicted to be smaller than σ₂ at all energies, but particularly at low energies. As E increases, σ₁ and σ₂ converge,
and for $E \gtrsim 2.72$ eV, the two are predicted to lie within $\lesssim 0.1\%$ of one another (Zhao et al. 2000; A. Igarashi, private communication). The energy dependences for $\sigma_1$ and $\sigma_2$ allow us to extend the results of Igarashi and collaborators to higher energies. We do this using the calculated cross sections of Dalgarno & Yadav (1953) for the related reaction

$$H^+ + H(1s) \rightarrow H(1s) + H^+ .$$  

(4)

First, to extend the data for $\sigma_2$, we multiply the energy scale of Dalgarno & Yadav by $\mu_{HD}/\mu_{HH}$, where $\mu$ is the reduced mass for the HD and HH systems. This effectively matches the velocity scale for each data set. Then, we multiply the results of Dalgarno & Yadav by a factor of 0.959 to set it equal to the results of Igarashi and collaborators at 1.333 eV. Next, for energies between 1 and $\approx 2.72$ eV, we fit the ratio of $\sigma_1/\sigma_2$ from Igarashi to the formula

$$\frac{\sigma_1}{\sigma_2} = 1 - \frac{A}{E} - \frac{B}{E^2},$$  

which yields $A = 2.692 \times 10^{-3}$ and $B = 7.936 \times 10^{-4}$. We calculate $\sigma_1$ for energies above $\approx 2.72$ eV using the scaled cross sections of Dalgarno & Yadav multiplied by equation (5).

We use the resulting data for $\sigma_1$ and $\sigma_2$ from energies of $2.721 \times 10^{-8}$ to $10^3$ eV to evaluate the rate coefficients $\alpha_1(T)$ and $\alpha_2(T)$ as a function of the gas temperature $T$. Rate coefficients are calculated numerically using the desired cross section times the relative velocity, and convolving these results with the appropriate Maxwellian distribution (taking the reduced mass into account). Cross sections for energies not calculated by Igarashi and collaborators or by Dalgarno & Yadav (1953) are evaluated using a spline interpolation method (Press et al. 1992) for $\sigma(E)$ versus log ($E$).

3. RESULTS AND COMPARISONS

Our calculated results for $\alpha_1(T)$ and $\alpha_2(T)$ are given in Table 1 from 1 K up to $2 \times 10^8$ K. These results are also plotted in Figure 1 from 1 to 30,000 K. As expected, the rate coefficient for the endothermic reaction (1) decreases dramatically for $T \lesssim 10^5$ K. The rate coefficient for reaction (2) decreases slowly with decreasing temperature down to $T \approx 15$ K. Below this, $\alpha_2$ begins to increase with decreasing temperature. We attribute this to the rapid increase in $\sigma_2$ with decreasing collision energy (see Fig. 2 of Igarashi & Lin 1999).

We have fitted our calculated CT rate coefficients using the formula

$$\alpha(T) = aT^b \exp \left(-c/T\right) + dT^e.$$

(6)

The best-fit values are listed in Table 2. The fits for $\alpha_1$ and $\alpha_2$ are accurate to better than 6% and 4%, respectively, for $2.7 \leq T \leq 2 \times 10^5$ K.

Several other groups have carried out detailed calcu-
models of the early universe have been published. For these

| Rate Coefficient | a (cm⁻³ s⁻¹) | b (K) | c (cm⁻³ s⁻¹) | d |
|------------------|--------------|-------|--------------|---|
| α₁ | 2.00E-10 | 0.402 | 37.1 | -3.31E-17 | 1.48 |
| α₂ | 2.06E-10 | 0.396 | 33.0 | 2.03E-09 | -0.332 |

lations for σ₁ and σ₂. Davis & Thorson (1978) published
results for and Davis & Thorson (1978) published
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results for from 3.7 to 8 eV. Results for σ₁ and σ₂ were reported by Hunter & Kuriyan (1977) for energies from 10⁻³ to 7.5 eV, by Hodges & Breig (1993) from 10⁻³ to 10 eV, and by Esry et al. (2000) from ≈3.7 meV to 8 eV.

In general, the calculations of Igarashi and collaborators are in good agreement with these measurements. The most significant difference is for energies above 10⁻³ eV, for which the results of Hunter & Kuriyan (1977) can fall as much as 15% below those of Igarashi and collaborators (Igarashi & Lin 1999; Zhao et al. 2000; A. Igarashi 2001, private communication). This is partially due to the accidental overlap of minima in the oscillating cross sections with the energy points published by Hunter & Kuriyan (1977).

There have been a couple of experimental measurements of σ₁. We are unaware of any experimental results for σ₂. Absolute measurements of σ₁ have been carried out by Newman et al. (1982) for energies between ≈0.1 and 10 eV. The theoretical results of Zhao et al. (2000) and Esry et al. (2000) are in good agreement with these measurements. Relative measurements for σ₁ have been carried out by Wells et al. (2001) for energies between threshold and 1 eV. Good agreement was found with the calculations of Esry et al. (2000) between ≈0.02 and 1 eV. Uncertainties in background subtraction limit the reliability of the experimental results below 0.02 eV.

Using the results of Hunter & Kuriyan (1977), Watson et al. (1978) calculated α₁ and α₂ for a number of temperatures between 10 and 300 K. These results are listed in Table 1 and are also plotted in Figure 1. For T ≥ 50 K, the results of Watson et al. agree with ours to better than 5%. At 25 K, their results differ from ours by ≈8% and at 10 K by ≈30%. The differences for T ≤ 25 K are most likely due to the uncertainty associated with extrapolating the results of Hunter & Kuriyan (1977) to energies below those published (Watson et al. 1978).

Galli & Palla (1998) fit the results of Watson et al. (1978) for α₁ and α₂. The resulting fitted rate coefficients are plotted in Figure 1. Between 10 and 300 K, these fitted rate coefficients agree with our results not quite as well as the results of Watson et al. Agreement with our results becomes progressively worse the further one extrapolates these fitted rates outside this temperature range.

Watson (1976) presented an estimate for α₁ and α₂, which we plot in Figure 1. These estimated rate coefficients are in poor agreement with our results here, differing significantly in both the values and temperature dependences of α₁ and α₂.

4. SOME ASTROPHYSICAL IMPLICATIONS

4.1. The Early Universe

Recently, results from a number of different chemical models of the early universe have been published. For these models, Puy et al. (1993) and Stancil et al. (1998) used the estimated rate coefficients of Watson (1976). Galli & Palla (1998) used their fits to the results of Watson et al. (1978). For redshifts z ≳ 50, above which the gas temperature is predicted to be ≳ 50 K (Puy et al. 1993), the rate coefficients used by Puy et al. and Stancil et al. (1998) begin to differ significantly from our newly calculated results. At z ≈ 400 (T ≈ 1000 K; Puy et al. 1993), the rate coefficients used by them are a factor of ≳ 3 smaller than our results. In contrast, the extrapolated rate coefficients used by Galli & Palla (1998) are only ≳ 22% smaller. Determining the full implications of our new rate coefficients will require rerunning updated versions of these various chemical models of the early universe.

4.2. Molecular Clouds

Modeling studies of molecular clouds have been carried out recently by Millar, Bennett, & Herbst (1989), Pineau des Forêts, Roueff, & Flower (1989), Heiles, McCullough, & Glassgold (1993), Rodgers & Millar (1996), and Timmermann (1996). These studies have all used the results of Watson (1976) for α₁ and α₂, and hence significantly underestimate these two rate coefficients for T ≥ 100 K. Because reaction (1) followed by reaction (3) is predicted to be a major source of HD in molecular clouds (Black & Dalgarno 1973; Dalgarno, Black, & Weisheit 1973; Watson 1973), underestimating α₁ could in turn lead to an underestimate in the amount of HD produced in these clouds.

4.3. High-Redshift QSO Absorption Systems

Observations of high-redshift QSO absorption systems are used to infer the primordial D/H ratio. These studies are carried out assuming that the D/H ratio is identical to that of D/H (Burles & Tytler 1998). Here we investigate the validity of this assumption in light of the different values for α₁ and α₂.

The D/H ratio inferred from these observations is given by

\[ \frac{n_D}{n_H} = \frac{f_{D_i} N(D_i)}{f_{D_i} N(H_i)}, \]  

where \( n_D \) is number density of deuterium, N(D) is the column density of D, and f₁₀ is the abundance of D relative to the total abundance of D. Similar definitions exist for H and H. We can write \( f_{D_i} \) as

\[ \frac{1}{f_{D_i}} = 1 + \frac{n_D n_{H_i}}{n_D n_{H_i}}. \]

A similar expression can be written for \( f_{H_i} \).

Currently, there are believed to be six reliable measurements of D/H in high-redshift QSO absorbers (Pettini & Bowen 2001). These measurements all assume \( f_{D_i} = f_{D_i} \text{.} \) To determine the validity of this assumption, we evaluate

\[ \frac{f_{D_i}}{f_{D_i}} = 1 + \frac{n_D n_{H_i}}{n_D n_{H_i}}. \]  

using our new results for α₁ and α₂.

At the inferred temperatures in these six absorbers (\( T \approx 1.1 \times 10^6 \) K), the gas is predicted to have an insignificant abundance of molecules (Petitjean, Srianand, & Ledoux 2000). The ionization balance of deuterium in these
QSO absorbers can therefore be written
\[
\frac{n_{D_{II}}}{n_{D_1}} = \frac{\beta_{D_1} + n_e C_{D_1} + n_{H II} \alpha_{D+H^+} + \sum_{X^+} n_{X^+} \alpha_{D+X^+}}{n_e R_{D_1} + n_{H I}\alpha_{D+H^+} + \sum_X n_X \alpha_{X+H^+}}.
\]  

In the numerator on the right hand side (RHS) of this equation, \( \beta_{D_1} \) is the photoionization (PI) rate of \( D \) due to the radiation field and accounts for further ionization due to the resulting nonthermal photoelectrons, \( n_e \) is the electron density, \( C_{D_1} \) is the electron impact ionization (EII) rate coefficient due to thermal electrons, \( \alpha_{D+H^+} \) is the rate coefficient for \( D + H^+ \) collisions producing \( D^+ \), and similarly for \( \alpha_{D+X^+} \), where \( X^+ \) represents a \( q \)-times charged ion of \( X \), and the sum over \( X^+ \) includes the ions of all elements except for those of hydrogen and deuterium. Here, \( \alpha_{D+H^+} \) and \( \alpha_{D+X^+} \) are purely CT rate coefficients. This is because collisions that leave both colliding particles in an ionized state are predicted to be insignificant at the temperatures of interest (Janev, Presnyakov, & Shevelko 1985). In the denominator on the RHS, \( R_{D_1} \) is the radiative-recombination (RR) rate coefficient for \( D II \, \alpha_{D+H^+} \) is the CT rate coefficient for \( H + D^+ \) collisions producing \( D \), and similarly for \( \alpha_{D+X^+} \).

The PI rates and EII and RR rate coefficients for deuterium and hydrogen are expected to be essentially identical (Galli & Palla 1998; Stancil et al. 1998). The differences in the energy-level structure of deuterium and hydrogen have an insignificant effect on these processes. Thus, in equation (10) we can substitute
\[
\beta_{H I} = \beta_{D_1}, \quad C_{H I} = C_{D_1},
\]  

and
\[
R_{H II} = R_{D_1}.
\]

Next, we add and subtract
\[
n_{D_{II}} \alpha_{H^+D^+} + \sum_{X^+} n_{X^+} \alpha_{H^+X^+}
\]

to the numerator on the RHS of equation (10) and
\[
n_{D_1} \alpha_{D+H^+} + \sum_X n_X \alpha_{X+H^+}
\]
to the denominator. We note that using equation (10), we get \( n_{H_{II}}/n_{H_I} \) by interchanging all charge states of \( H \) (and vice versa). Hence, we can rewrite equation (10) as
\[
\frac{n_{D_{II}}}{n_{D_1}} = \frac{n_{H_{II}}}{n_{H_I}} \left( \frac{1 + \gamma_1}{1 + \gamma_2} \right),
\]  

where
\[
\gamma_1 = \alpha_{D+H^+} - \frac{n_{D_{II}}}{n_{H_{II}}} \alpha_{H^+D^+} + \sum_{X^+} n_{X^+} \left( \alpha_{D+X^+} - \alpha_{H^+X^+} \right),
\]
\[
\gamma_2 = \alpha_{H^+D^+} - \frac{n_{D_{II}}}{n_{H_{II}}} \alpha_{D+H^+} + \sum_X n_X \left( \alpha_{X+D^+} - \alpha_{X+H^+} \right),
\]  

and
\[
\delta = \frac{n_e}{n_{H_I}} R_{H II} + \frac{n_{D_{II}}}{n_{H_{II}}} \alpha_{D+H^+} + \sum_X n_X \frac{\alpha_{X+H^+}}{n_{H_I}}.
\]

We can simplify \( \gamma_1 \) and \( \gamma_2 \). First we note that \( \alpha_{D+H^+} = \alpha_1 \) and \( \alpha_{H^+D^+} = \alpha_2 \), and at the temperatures of interest, \( \alpha_1 \approx 3 \times 10^{-9} \) cm\(^3\) s\(^{-1}\). Now, to a first approximation, \( n_{D_{II}}/n_{H_{II}} \) and \( n_{D_{II}}/n_{H_I} \) are equal to the primordial D/H value that we take to be \(\approx 2 \times 10^{-5}\) (from Pettini & Bowen 2001). Hence, the second term in equations (17) and (18) is roughly 5 orders of magnitude smaller than the first term and can be dropped.

At energies important for \( T \approx 1.1 \times 10^4 \) K, we note that \( \sigma_1 \approx \sigma_2 \). Similarly, we expect at these temperatures \( \sigma_{D+X^+}(v) \approx \sigma_{H^+X^+}(v) \) and \( \sigma_{D+H^+}(v) \approx \sigma_{H^+H^+}(v) \), where \( v \) is the relative velocity. As a result, we have \( \sigma_{D+X^+}(\mu_{HX})^{1/2} \approx \sigma_{H^+X^+}(\mu_{HX})^{1/2} \) and \( \sigma_{D+H^+}(\mu_{HX})^{1/2} \approx \sigma_{H^+H^+}(\mu_{HX})^{1/2} \). Here, \( \mu_{HX} \approx 1 \) and \( \mu_{OX} \approx 0 \) are the reduced masses. For those ions in which CT is important in photoionized plasmas (e.g., QSO absorbers), we estimate that \( \alpha_{D+X^+}, \alpha_{H^+X^+}, \alpha_{X+D^+}, \) and \( \alpha_{X+H^+} \), will all be \( \lesssim 10^{-9} \) cm\(^3\) s\(^{-1}\) (Kingdon & Ferland 1996). The expressions in the parentheses in the third term in equations (17) and (18) are thus \( \lesssim 4 \times 10^{-10} \) cm\(^3\) s\(^{-1}\). Furthermore, we note that the metallicity in these absorbing systems are \( \approx 10^{-2} \) solar (Pettini & Bowen 2001) and that we expect \( n_{X^+}/n_{H_{II}} \) and \( n_{X^+}/n_{H_I} \) to be within a couple of orders of magnitude of these reduced abundances. As a result, we can also drop the third term in equations (17) and (18). With these approximations, we can rewrite equation (16) as
\[
\frac{n_{D_{II}}}{n_{D_1}} \approx \frac{n_{H_{II}}}{n_{H_I}} \left( \frac{\alpha_1}{\alpha_2} \right) \left( 1 + \delta/\alpha_1 \right) \left( 1 + \delta/\alpha_2 \right).
\]  

For typical QSO absorption systems, we estimate that \( \delta/\alpha_1 \approx \delta/\alpha_2 \approx 0.15 \), and as \( \alpha_1 \) and \( \alpha_2 \) differ by \( \lesssim 0.4\% \) at \( T \approx 1.1 \times 10^4 \) K, equation (20) reduces to
\[
\frac{n_{D_{II}}}{n_{D_1}} \approx \frac{n_{H_{II}}}{n_{H_I}} \left( \frac{\alpha_1}{\alpha_2} \right).
\]

Because \( \sigma_1 \) has a threshold, in contrast to \( \sigma_2 \), the ratio \( \alpha_1/\alpha_2 \) will always be less than 1. For the temperature of interest here, we have
\[
\frac{n_{D_{II}}}{n_{D_1}} \approx 0.996 \frac{n_{H_{II}}}{n_{H_I}}.
\]  

Substituting these results into equations (7) and (9), we find
\[
\frac{n_D}{n_H} = \left\{ \begin{array}{ll}
0.996N(D I)/N(H I) & n_{H_{II}} \gg n_{H_I}, \\
1.000N(D I)/N(H I) & n_{H_{II}} \ll n_{H_I}.
\end{array} \right.
\]

The uncertainty in the above factor of 0.996 depends on the accuracy of the theoretical cross sections we have used here. Verifying the accuracy of these cross sections will require further theoretical and experimental studies. However, we note that the variation of \( \approx 0.4\% \) in \( n_D/n_H \) is a factor of \( \gtrsim 25 \) smaller than the current \( \gtrsim 10\% \) uncertainties in QSO absorber D/H measurements. Thus, it is likely to be some time before the subtle differences in reactions (1) and (2) become important for primordial D/H measurements.

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