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COLLISION-INDUCED DISSOCIATION OF MOLECULAR HYDROGEN AT LOW DENSITIES

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ABSTRACT

Quasi-classical trajectory studies have been carried out on a chemically accurate H_4 potential-energy surface for $H_2 + H_2$ interactions to obtain cross sections for collision-induced dissociation (CID) from the $H_2(0, 0)$ ground vibration-rotation state. This is an important channel for dissociation, particularly in a low-density gas. These results are compared with corresponding calculations for the $H + H_2$ and $He + H_2$ systems. Collisions with the $H_2(0, 0)$ collision partner do not show the same dynamical elevation of threshold for CID seen previously for collisions with He. Despite the energetic threshold, $H_2(0, 0)$ is a much less effective collision partner in promoting CID than is H. Thermal rate coefficients for CID from the ground state are evaluated and compared to earlier approximations. A comparison with electron impact dissociation is also made.

Subject headings: ISM: molecules — molecular data — molecular processes

1. INTRODUCTION

Collision-induced dissociation (CID) of molecular hydrogen (H_2) is an important process in interstellar shocks (e.g., Hollenbach & McKee 1989). In neutral regions of the interstellar medium (ISM), the potentially important collision partners for H_2 are H, He, or another H_2. In regions with high fractional ionization, collisions with e^- and (streaming) ions like H^+ need to be considered, too (e.g., Hollenbach & McKee 1989; Draine, Roberge, & Dalgarno 1983). In a dense gas, dissociation often proceeds via ladder climbing: molecules are excited vibrationally and rotationally via successive collisions through a series of (v, j) states, and then dissociation occurs from these excited states. Since the ISM is not generally in local thermodynamic equilibrium, the relative populations of the (v, j) states cannot be described adequately with the Boltzmann distribution. Instead, the competing processes which can affect the populations—such as radiative emission and absorption, and collisional excitation, de-excitation, and dissociation—must be treated explicitly in the master equation, the solution of which describes the time evolution of state populations (e.g., Martin, Schwarz, & Mandy 1996). Particularly important, and often poorly known, are state-to-state collisional rate coefficients describing energy transfer and state-specific dissociation rate coefficients, collectively referred to as γ's (units: $cm^3\ s^{-1}$).

However, in situations where the density is sufficiently low that collisional frequency and consequent excitation are slow compared to radiative (via quadrupole emission) depopulation of the higher energy states, the collisional dissociation rate is determined only by dissociations directly from the ground states $H_2(0, 0)$ and $H_2(0, 1)$. The critical density below which this low-density limit is approached is 10^3–$10^4\ cm^{-3}$ (Martin et al. 1996) when the H atom is the dominant collision partner (Dove et al. 1987 find slightly higher critical densities when He is the collider). Knowledge of the CID rate coefficient in this limit, γ_l, together with the high-density limit, γ_h, can provide a basis for interpolating γ_{cid} to intermediate densities (with some knowledge of the critical density; see Lepp & Shull 1983; Martin et al. 1996). In cooler, more quiescent regions of the ISM, photolytic destruction of H_2 as the result of absorption of ultraviolet photons by these same ground states is often dominant over CID; see, e.g., Spitzer (1978).

Calculation of CID from the ground state $H_2(0, 0)$ is the focus of this paper. CID involving H and He colliders has been studied earlier by Dove & Mandy (1986a, 1986b) and Dove et al. (1986), respectively. Compared to H, they found that He is relatively inefficient in dissociating $H_2(0, 0)$: the collision between two closed-shell species tends to cause the molecular bond to stiffen, whereas a collision with an H atom weakens and loosens the molecular bond. The elevation of the dynamical threshold above the dissociation energy that was seen in the $He + H_2$ interaction was interpreted in terms of the repulsive nature of the HeH_2 interaction potential and the absence of an exchange channel in this potential. In subsequent work by Dove et al. (1990), it was demonstrated that, when an exchange channel is present and is accessible at or below the dissociation energy, there is no dynamic elevation of the dissociation threshold.

Dove & Mandy (1986a) speculated that if $H_2 + H_2$ collisions were of low efficiency in CID, similar to those of $He + H_2$, then H atoms might begin to dominate the dissociation behavior of low-density gas at quite low fractional abundance of H compared to H_2. However, while the H_4 potential is repulsive, there is an exchange channel that opens up for interaction energies comparable to the dissociation energy of an H_2 molecule (§ 3.1). On this basis, we anticipate that H_2 will in fact be a more effective collider than He in promoting CID.

To address this issue quantitatively, we have calculated γ_l for $H_2 + H_2$ collisions for the first time. This is part of a larger project to calculate state-to-state rate coefficients for collisional interactions in this system. The $H_2 + H_2$ system

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is one of the few four-center systems for which a chemically accurate ab initio potential is available (Keogh 1992; Boothroyd et al. 1991; Aguado, Suarez, & Paniagua 1994) and is both basic (prototypical) and fundamentally interesting from a molecular dynamics perspective. At the same time, we have made more extensive calculations for $H + H_2$ and $He + H_2$ to supplement the earlier results. Electron impact dissociation is reviewed for comparison in § 3.1.2.

2. METHOD OF CALCULATION OF CROSS SECTIONS

For $H_2 + H_2$, we ran fully three-dimensional quasi-classical trajectories (QCTs) using the potential energy surface of Keogh (1992), a multiparameter fit to the ab initio points of Boothroyd et al. (1991) with analytical derivatives (see also Keogh et al. 1998). Further details of the calculation are given in the subsections below. Additional QCTs have been carried out for H and He colliders, i.e., the three-body systems $H + H_2$ and $He + H_2$, using the potentials of Truhlar & Horowitz (1978, 1979) and Wilson, Kapral, & Burns (1974), respectively. Other details of the $H + H_2$ calculations were as given in Mandy & Martin (1991) and Dove & Mandy (1986a); the primary difference here for $H + H_2$ is greatly increased batch sizes approaching threshold, resulting in more accurately determined cross sections there. Trajectories for $He + H_2$ are described further in § 2.3.

2.1. *Four-Body Trajectories*

A new four-body trajectory code was developed, extending the three-body method employed by Mandy & Martin (1991, 1992, 1993), which had been derived from the original three-body code of Schreiber (1973). The initial vibrational and rotational energies of each hydrogen molecule were assigned to correspond precisely to quantum states, while the translational energy, E, was fixed at the desired value from the range of interest, in this case $0.1646–1.0E_h$ (energies are given in hartrees: $1E_h = 4.360 \times 10^{-11}$ ergs = 27.21 eV). The initial values of the remaining variables were Monte Carlo selected from appropriate distributions. These variables include the vibrational and rotational phase and the orientation of each molecule.

Stratified sampling was used for the impact parameter. The impact parameter strata were successive annuli of 1 a_0 width until the stopping criterion was encountered ($1\ a_0 = 0.5292 \times 10^{-8}$ cm). This stopping criterion was that no trajectory outcomes for the outermost 0.1 a_0 substratum were dissociative. At higher values of E, at least 1000 trajectories were run within each stratum of impact parameter. Because the cross section for dissociation decreases toward lower E (see § 3), the batch sizes were increased to improve the statistical accuracy. Near the apparent threshold, batches as large as 50,000 were used.

Following initialization of each trajectory, the coordinate system was transformed from that used for selection of initial conditions to one more appropriate for integration. The motion of the atoms was treated as completely classical, with the forces determined by the analytical derivatives of the interaction potential. The equations of motion were integrated using a variable-step Runge-Kutta integrator. Conservation of energy and momentum was monitored throughout the integration. The integration was stopped when at least four of the six molecular separations required to completely describe the system exceeded 12 a_0. On the basis of the shortest interatomic distance, the atoms are paired for analysis of final momenta and energy. For each pair, angular momentum is determined, then motion along the line of centers within the pair is considered. If the pair is bound, then continuously valued (v'', j'') quasi-classical quantum numbers are determined. These outcomes can subsequently be binned into quantized para and ortho states (as appropriate), and cross sections and statistical errors can be assigned (Mandy 1991; Mandy & Martin 1991).

Otherwise, the pair of atoms is regarded as dissociated (sometimes called classically unbound), the outcome of interest here. For that energy, the CID cross section $\sigma(E)$ is then determined. When the final state is H_2 and a dissociated pair, the bound pair can be examined to see if its atoms correspond to one of the original pairings in the target or collider; if not, exchange has occurred and the process can be called reactive-dissociative.

2.2. *Parallel Implementation*

The $H_2 + H_2$ trajectories are much more demanding computationally. Compared to either H_3 or HeH_2, the analytical H_4 potential energy surface and its derivatives are harder to evaluate, and so the four-body trajectories are individually 50–100 times more costly. The trajectory calculations were carried out in parallel, on a network of workstations (Keogh & Martin 1994) coordinated using Parallel Virtual Machine (PVM), public domain software from Oak Ridge National Laboratory. Among the features of this implementation (Martin 1997) are the following:

1. The Monte Carlo nature of the problem lends itself to a master-slave model.
2. It is coarse-grained parallel at the trajectory level.
3. The master determines a list of which trajectories to run, farms them out to the slaves one by one, keeps track of which have been completed, and archives the results.
4. There is low network traffic per trajectory: a few initial conditions and a few results.
5. The master-slave interaction is completely asynchronous.
6. Slaves are CPU-bound (using more than 95% of cycles on unloaded nodes), which leads to effective utilization of "idle" cycles.
7. Slaves have a low impact on other users of workstations: slaves run at low priority (UNIX "nice" 19), and the executable and PVM daemons are small (typically 3.4 Mb and 1.4 Mb, respectively).
8. Load-balancing software actively monitoring the load on each node can effectively idle a slave using various criteria.
9. The master is robust against slave slowdown or outright failure: when the list to be farmed out is exhausted and the master detects that a given trajectory has not been completed, another slave is given the same task.
10. Slaves can run concurrently on different architectures.

2.3. $He + H_2$ *Trajectories*

To supplement the earlier calculations (larger batch sizes and higher energies here), we carried out additional trajectory calculations for $He + H_2$ at translational energies between 0.319 and $0.637E_h$, with $0.0016E_h$ intervals below 0.458 and $0.0159E_h$ intervals above this energy. The batch size was 18,000 trajectories, with other details as given in Dove & Raynor (1978) and Dove et al. (1986).

As E increased within this range, we found that an increasing proportion of the trajectories failed, because of the unphysical behavior of the adopted analytic representation of the HeH_2 potential for compact conformations. At lower energies, the conformations of the atoms at the moment at which the trajectories failed were examined and compared with conformations of atoms in trajectories which ultimately led to dissociation. On this basis it was concluded that these failed trajectories were not likely to lead to dissociation and that the value of the dissociative cross section would not be affected. By $0.51E_h$, however, a larger range of conformations was present among failed trajectories so that we could no longer safely reach this conclusion. At this energy, the number of failed trajectories is 695 versus 876 dissociative (out of 18,000); if all of these failed trajectories were actually dissociative (surely an overestimate), the adopted cross section would increase by a factor of 1.8. For this reason the energy range reported for $He + H_2$ does not extend as high as for the other cases.

3. RESULTS

3.1. *Analytic Fits and the Threshold for CID*

Figure 1 shows the QCT cross section data for CID from the ground state, comparing the effects of the three neutral collision partners (data for the electron collider are described in § 3.1.2). The dashed curves are based on the empirical LeRoy (1969) class II functional form

$$\sigma(E) = a \frac{(E - E_0)^b}{E} \exp\left[-c(E - E_0)\right] , \qquad (1)$$

where E_0 is a dynamical threshold energy below which $\sigma = 0$, and parameters a, b, c, and E_0 are determined by a weighted, nonlinear, least-squares fit to the calculated QCT cross sections. We also experimented with determining the threshold based on only the lower energy cross sections and then using this threshold to redetermine a, b, and c from the full range of data. As can be seen, these fits provide an adequate description of the data over a wide energy range. The fitted parameters are given in Table 1 to sufficient precision that, when used in equation (1), they recover the curves shown in Figure 1 in the same units.

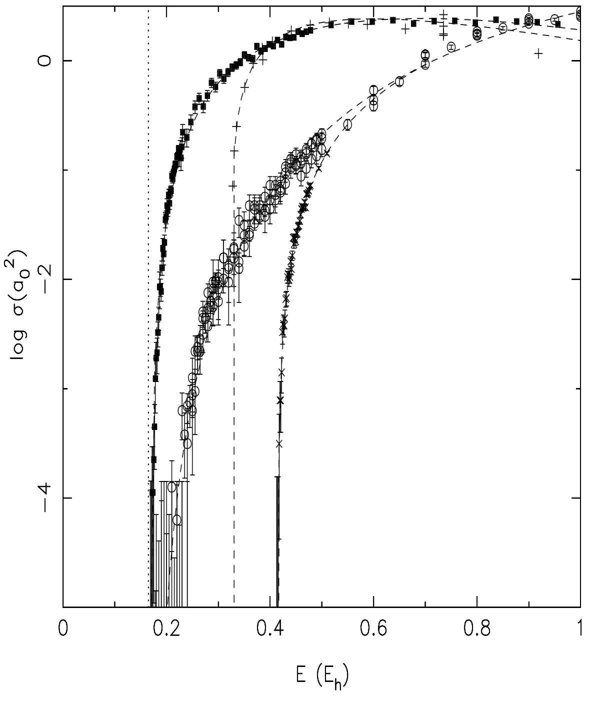

FIG. 1.—CID cross section for target $H_2(0, 0)$ with collision partners H (*solid symbols*, *left*), He (*crosses*, *right*), and $H_2(0, 0)$ (*open circles*) as a function of translational energy. Cross sections for He collision partner extend only to $0.5E_h$, beyond which the fitted curve [eq. (1)] is extrapolated to $0.7E_h$. Cross sections for electron impact excitation of triplet states of H_2 are shown by plus signs; above $0.5E_h$ the values become less reliable because of uncertain contributions by several higher states to the total. *Vertical line*: energetic threshold for dissociating one H_2 molecule. Threshold values are given in Table 1.

3.1.1. *Neutral Collision Partners*

For $H + H_2$, the threshold E_0 found is very close to the energetic limit of $0.1646E_h$, within the errors. For $H_2 + H_2$, the threshold also appears to be close to energetic, like the case with collision partner H. However, there is a dramatic difference in scale. The cross section with H increases much more steeply and is some 2 orders of magnitude higher in the 0.2–$0.3E_h$ range.

Most of the $H_2 + H_2$ dissociations observed in the lower part of the energy range shown were accompanied by the exchange reaction. Even some of those dissociations that did not show an exchange outcome might have resulted from very snarled trajectories; if there were an intermediate compact "transition state," statistically, this would produce both exchange and nonreactive products. Examination of the H_4 potential for certain compact conformations (Mandy, Martin, & Keogh 1998b) shows local minima in the interaction regions, such as would be associated with a long-lived reaction complex.

At all energies considered for $H_2 + H_2$, many more reactive (exchange) interactions leaving two bound molecules occurred (4C reactions) than did dissociations, with a somewhat lower apparent dynamical threshold than for dissociation. Reactive interactions have been shown to be accompanied by substantial energy redistribution (Mandy, Martin, & Keogh 1998a).

CID for $He + H_2$ clearly has a significantly elevated dynamical threshold, as found earlier by Dove et al. (1986). Note that, even if all of the aforementioned failed trajectories had been counted as dissociative (surely an extreme), the threshold would still be $0.33E_h$. While the fitted function approximates the computed cross sections well, the extrapolation to higher energies should be used with caution.

3.1.2. *Electron Impact Dissociation*

Energetic electrons can excite the electronic states of H_2, the lowest of which, $b\,^3\Sigma_u^+$, is repulsive, going to the same

TABLE 1

FITTING PARAMETERS[a] FOR $\sigma(E)$ FOR FOUR COLLISION PARTNERS

Partner	a	b	c	E_0
H	54.1263	2.5726	3.4500	0.1680
$H_2(0, 0)$	40.1008	4.6881	2.1347	0.1731
He	4.8152	1.8208	−0.9459	0.4146
e^-	11.2474	1.0948	2.3182	0.3237

[a] See eq. (1) and text for units adopted.

dissociation limit as the ground state $X\,{}^1\Sigma_g^+$. The higher triplet states like $a\,{}^3\Sigma_g^+$ and $c\,{}^3\Pi_u$ radiatively decay to $b\,{}^3\Sigma_u^+$, and so their excitation also leads to dissociation. Since the energy of the $b\,{}^3\Sigma_u^+$ state is a decaying function of the internuclear separation, the (ill-defined) threshold energy for excitation can be approximated as the relative energy of $b\,{}^3\Sigma_u^+$ evaluated at the outer turning point (the edge of the so-called Franck-Condon region) of the ground (v, j) state (0, 0), which is $0.32E_{\rm h}$ (see Kolos & Wolniewicz 1965). The energy difference to the first (v, j) state of $a\,{}^3\Sigma_g^+$ is somewhat higher, $0.43E_{\rm h}$ (see Kolos & Wolniewicz 1968), and marginally higher still ($0.44E_{\rm h}$) for $c\,{}^3\Pi_u$.

Some cross sections for CID by electrons are summarized in Figure 1. For the $b\,{}^3\Sigma_u^+$ excitation, we adopt the results of Corrigan (1965) at low energies, joining these with other theoretical and experimental values at intermediate energies, as summarized by Khakoo et al. (1987; see also Rescigno & Schneider 1988). At even higher energies, above about $0.5E_{\rm h}$, contributions from excitation of $a\,{}^3\Sigma_g^+$ and $c\,{}^3\Pi_u$ become important; this introduces increases as illustrated by the plotted points at $0.73E_{\rm h}$, but the values are more uncertain than for the $b\,{}^3\Sigma_u^+$ excitation (Khakoo & Trajmar 1986).

A process that does not appear to have been considered is excitation of the lowest singlet states, $B\,{}^1\Sigma_u^+$ and $c\,{}^1\Pi_u$. Some fraction of the time (branching ratio ∼10%), these radiatively decay to the vibrational continuum of $X\,{}^1\Sigma_g^+$, causing spontaneous radiative dissociation—the same role they play in photodestruction of H_2 in the ISM. The threshold for excitation of $B\,{}^1\Sigma_u^+$ is approximately $0.43E_{\rm h}$, if evaluated for the $v = 3$ state, which just overlaps the Franck-Condon region of (0, 0) (see Kolos & Wolniewicz 1965; $0.41E_{\rm h}$ otherwise). However, the excitation cross sections of Khakoo & Trajmar (1986) suggest that the fractional contribution by the singlets would become important only above $1E_{\rm h}$, above the range of most interest here.

Electrons can also promote dissociation through collisional ionization of H_2 (threshold $0.57E_{\rm h}$) followed by dissociative recombination, but we do not consider this branch here, just as we have not for the other collision partners.

We have fitted the cross section data in Figure 1 using equation (1), giving emphasis to the lower energy behavior, since we are interested in the lower temperature rate coefficients. The fitting parameters are in Table 1; note the value of E_0.

3.2. *Thermal Rate Coefficients*

To compute thermal rate coefficients $\gamma(T)$, QCT calculations of $\sigma(E)$ at many E are integrated over E, using a Maxwellian distribution for the appropriate temperature T. The translational distribution depends on E/kT, where k is the Boltzmann constant ($3.167 \times 10^{-6} E_{\rm h}$ K^{-1}). At translational energies relevant to dissociation ($E \approx 0.2E_{\rm h}$) and temperatures typical of what might be encountered in shocked regions in the ISM ($T \approx 5000$ K), $E/kT \approx 12.6$, far beyond the peak in the Maxwellian weighting function at $E/kT = 1$. This shows that, especially for lower temperatures, it is the energy range corresponding to the exponentially decaying Maxwellian tail that is important, and the resulting value of $\gamma(T)$ is very sensitive to the threshold energy E_0 and the form of $\sigma(E)$ near this threshold.

Mandy (1991) calculated the integral for $\gamma(T)$ using a piecewise linear fit to $\sigma(E)$ for H + H_2 and then evaluating analytic subintegrals; errors in σ can be propagated. This integration is carried out for many values of T, and an analytic fit to γ as a function of T can be found for ease of use in simulations (e.g., Martin & Mandy 1995).

An alternative used here is to fit the LeRoy class II function as above, and then find γ from the analytic integral of this function:

$$\gamma(T) = d\left(\frac{8kT}{\pi\mu}\right)^{1/2} \frac{a(kT)^{b-1}\Gamma(b+1)\exp(-E_0/kT)}{(1+ckT)^{b+1}}\,, \quad (2)$$

where μ is the reduced mass of the colliding pair (in grams), Γ is the gamma function, and, given the other choices of units adopted, the scale factor $d = 1.849 \times 10^{-22}$ to give γ the usual units, cm^3 s^{-1}. This alternative was checked against the results of Martin & Mandy (1995) using the same cross sections and found to give good agreement.

In Figure 2 we show rate coefficients generated from the fits and equation (2). Results for certain temperatures are given in Table 2. Recall that the γ's for the lowest values of T are the most sensitive to the threshold behavior of σ. The values for He + H_2 above 10,000 K are becoming uncertain, because they rely on extrapolation of the cross section to higher energies (with the extrapolation shown in Fig. 1, the rate coefficients would approach those found for H_2 + H_2).

3.3. *Comparison with Other Results*

Since the H + H_2 calculations were done, improved H_3 potentials have become available (Boothroyd et al. 1991,

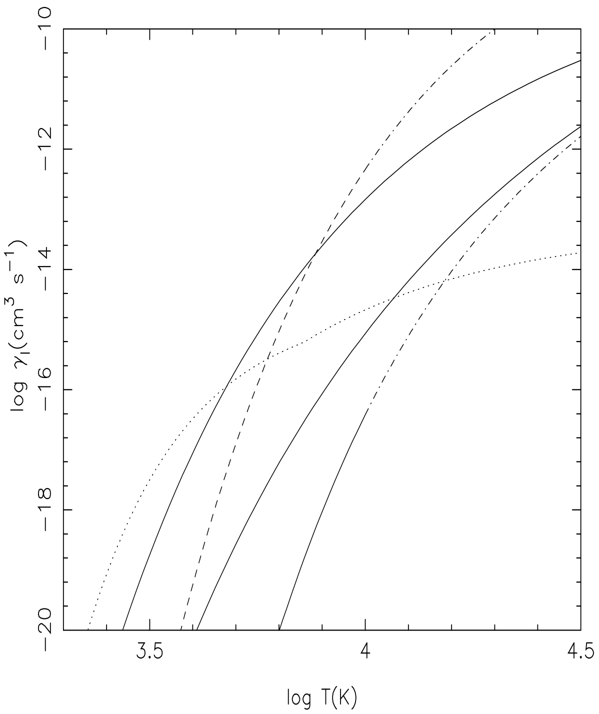

FIG. 2.—Thermal rate coefficients for CID from H_2(0, 0). *Solid curves*: new results for collision partners H (*upper*), He [*lower*; *dash-dotted extension* above 10,000 K, where γ_l is more uncertain owing to extrapolation of $\sigma(E)$], and H_2(0, 0) (*middle*). *Dashed curve*: dissociation via electron impact [*dash-dotted extension* above 10,000 K, where γ_l is rendered uncertain by $\sigma(E)$ at higher energies]. *Dotted curve*: analytic form from Lepp & Shull (1983) for H_2 + H_2.

TABLE 2

RATE COEFFICIENTS[a] FOR DISSOCIATION FROM $H_2(0, 0)$ FOR FOUR COLLISION PARTNERS

T (K)	H	$H_2(0, 0)$	He	e^-
1000	3.2×10^{-36}	3.8×10^{-41}	1.2×10^{-69}	1.5×10^{-53}
1400	2.4×10^{-29}	9.4×10^{-34}	3.2×10^{-53}	8.8×10^{-41}
2000	4.2×10^{-24}	5.0×10^{-28}	7.7×10^{-41}	3.5×10^{-31}
3000	6.5×10^{-20}	2.4×10^{-23}	4.0×10^{-31}	1.1×10^{-23}
4500	5.2×10^{-17}	5.4×10^{-20}	1.4×10^{-24}	1.2×10^{-18}
6000	1.7×10^{-15}	3.5×10^{-18}	3.0×10^{-21}	4.0×10^{-16}
7800	2.1×10^{-14}	8.1×10^{-17}	6.7×10^{-19}	2.3×10^{-14}
10000	1.5×10^{-13}	9.9×10^{-16}	3.8×10^{-17}	4.6×10^{-13}
14000	1.2×10^{-12}	1.7×10^{-14}	2.6×10^{-15} [b]	9.9×10^{-12} [c]
20000	6.2×10^{-12}	2.0×10^{-13}	7.3×10^{-14} [b]	1.0×10^{-10} [c]
30000	2.6×10^{-11}	1.9×10^{-12}	1.2×10^{-12} [b]	6.2×10^{-10} [c]

[a] Units $cm^3\ s^{-1}$.

[b] Uncertainty owing to high-energy extrapolation of $\sigma(E)$.

[c] Uncertainty relating to contributions to $\sigma(E)$ from several higher states at high energies.

1996); however, the impact on the dissociative cross sections is not significant. Our rate coefficients γ_l for $H + H_2$ are close to those used in Martin et al. (1996) and to the low-density limit cited by Mac Low & Shull (1986). An earlier functional form proposed by Lepp & Shull (1983) is not accurate, as discussed by Dove & Mandy (1986a), Dove et al. (1987), and Martin et al. (1996). Lepp & Shull (1983) also proposed an equation for $\gamma_l(T)$ for $H_2 + H_2$, similar to that for $H + H_2$; as expected, the comparison in Figure 2 reveals this to be unsuitable, too.

The new cross sections for $He + H_2$ are in accord with those presented by Dove et al. (1986) in the same energy range above threshold. Our results for γ_l supersede those of Dove et al. (1987, their Table 2 and eq. [4]), which were based on rather few trajectories (Dove & Raynor 1978), as pointed out by Rusk (1983). The new results are orders of magnitude smaller.

For $e^- + H_2$, rate coefficents generated from equation (2) are plotted in Figure 2 and given in Table 1. Hollenbach & McKee (1989) give a slightly simpler expression based on the results of Corrigan (1965) only, with the same threshold energy; for this temperature range the predicted values are close to ours.

4. DISCUSSION

Whether or not a ground-state H_2 molecule behaves the same as a He or H atom as a collision partner depends on the energy and type of transition; this is rooted in fundamental differences in the shapes of the relevant portions of the potential energy surfaces. Of the three neutral collision partners considered, only He has CID interactions with a dynamical threshold significantly elevated above energetic. This provides further support for the view (Dove et al. 1986, 1990 and references therein) that the existence of an exchange channel is important in keeping the dynamical threshold for dissociation close to energetic. Note that the exchange channel is not nearly as readily accessible for $H_2 + H_2$ as it is for $H + H_2$, but the important thing here is that it is open for energies relevant for CID.

The above comments on the comparative behavior of collision partners apply to CID involving ground state H_2. For other types of transitions, like energy transfer, and for those involving excited (v, j) states of H_2, the situation can be more complex (Mandy et al. 1998a).

The different dependences of $\sigma(E)$ seen in Figure 1 are reflected in the corresponding γ's. In particular, γ_l is higher for the H collision partner than for H_2 because of the higher σ at each energy over the relevant range. The γ_l for the He collision partner is the smallest because of the dynamically elevated threshold. Thus in the ISM, He will not be important for CID from the ground state and is not a good surrogate for the H_2 collision partner, either. In a neutral gas that is purely molecular, $H_2 + H_2$ collisions alone are relevant, but it can be seen that even a tiny fraction of H relative to H_2 in the gas could have a dramatic effect, at least in this low-density limit. Compared to the case of collision partner H, $\gamma(T)$ for electron CID rises later because of the higher E_0, whereas at higher T the coefficient is higher, despite similar $\sigma(E)$ at higher energies, because of the lower reduced mass. High fractional ionization and high temperature clearly increase the importance of dissociation by electrons.

Because ortho-para interconversion of H_2 requires that exchange occurs via collision, at low density the population of the other ground state, ortho $H_2(0, 1)$, may be "frozen in" at a significant value, reflecting the earlier history of the gas. Thus, dissociation from $H_2(0, 1)$ also makes an important contribution to the low-density rate of dissociation. Our examination of results for target $H_2(0, 1)$ in collision with H, He, $H_2(0, 0)$, and $H_2(0, 1)$ shows that the cross sections and rate coefficients are close to those observed for target $H_2(0, 0)$. The difference in energy between these two ground states, $0.00054E_h$, is small compared to the threshold energy for dissociation.

At low densities there is another route to dissociation from the ground state, involving excitation to one of the high-lying quasi-bound states from which dissociative tunneling then occurs (see, e.g., Martin et al. 1996). Because the excitation energy of the quasi-bound states is just above the bond-dissociation energy, this can be an effective alternative at low temperature. In fact, for $H + H_2$ it is dominant for $T < 4500$ K (Dove & Mandy 1986a; Martin et al. 1996). For $H_2 + H_2$, excitations of quasi-bound levels from $H_2(0, 0)$ should not show a dynamic elevation of threshold, but there is elevation in the case of $He + H_2$ (Mandy et al. 1998a). Compared to direct CID, we expect this alternative route to be significant for both of these collision partners, too.

Assessing the rate of dissociation at high density requires master-equation calculations to elucidate the contributions of ladder climbing. Such master-equation solutions have been carried out for H_2 infinitely dilute in H atoms (Martin et al. 1996) and infinitely dilute in He atoms (Dove et al. 1987). In both cases, dissociation from excited states becomes increasingly important as the density is increased, with the critical density dependent on the collider. Since we have shown that He is not a good surrogate for an H_2 collision partner for either energy transfer (Mandy et al. 1998a) or CID, similar studies must be carried out explicitly to understand the case where the only colliders are molecular. This will require a calculation of rate coefficients for all transitions of $H_2 + H_2$ as an essential preliminary.

Detailed studies of the $He + H_2$ interaction will require an improved HeH_2 potential energy surface. Toward this end we have made, with A. I. Boothroyd, extensive ab initio computations of interaction energies to which a new analytic fit will be made. Further work is also needed on electron impact excitation from other than the ground (v, j) state.

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