ROTATIONAL QUENCHING RATE COEFFICIENTS FOR H$_2$ IN COLLISIONS WITH H$_2$ FROM 2 TO 10,000 K

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ABSTRACT

Rate coefficients for rotational transitions in H$_2$ induced by H$_2$ impact are presented. Extensive quantum mechanical coupled-channel calculations based on a recently published (H$_2$)$_2$ potential energy surface were performed. The potential energy surface used here has been demonstrated to be more reliable than surfaces used in previous work. Rotational transition cross sections with initial levels of $J \leq 8$ were computed for collision energies ranging between 10^{-4} and 2.5 eV, and the corresponding rate coefficients were calculated for the temperature range $2 \leq T \leq 10,000$ K. In general, agreement with earlier calculations, which were limited to 100–6000 K, is good, although discrepancies are found at the lowest and highest temperatures. Low-density-limit cooling functions due to para- and ortho-H$_2$ collisions are obtained from the collisional rate coefficients. Implications of the new results for nonthermal H$_2$ rotational distributions in molecular regions are also investigated.

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

Online material: color figures, machine-readable table

1. INTRODUCTION

Collision-induced energy transfer involving H$_2$ molecules plays an important role in many areas of astrophysics, since hydrogen is the most abundant molecule in the interstellar medium (ISM), dominating the mass of both dense and translucent molecular clouds. Because H$_2$ is a homonuclear molecule and lacks a dipole moment, its infrared emission is weak and it is difficult to observe directly. Furthermore, because of the low mass of the hydrogen atom, the rotational levels of molecular hydrogen are widely spaced and require relatively high temperatures, $T \geq 100$ K, in order for even the lowest levels to be appreciably excited via thermal collisions. Nevertheless, with the current sensitivity of detectors deployed on space-based observatories, such as the *Spitzer Space Telescope* and the former *Infrared Space Observatory* (*ISO*), the detection and mapping of the pure rotational lines of H$_2$ in a significant sample of galaxies is now possible (Neufeld et al. 2006; Fuente et al. 1999). These observations, as well as others from the ultraviolet (Meyer et al. 2001; Boissé et al. 2005; France et al. 2005, 2007) to the near-infrared (Burton et al. 1998; McCartney et al. 1999; Allers et al. 2005), probe shock-induced heating and cooling and UV and X-ray irradiation of gas in the ISM of galactic and extragalactic sources and star-forming regions.

Since the H$_2$-H$_2$ system constitutes the simplest diatom-diatom collision system and one in which all atomic constituents are quantum mechanically indistinguishable, early work, notably by Green and coworkers, carried out a succession of theoretical studies on rotational relaxation in H$_2$+H$_2$ collisions (Green 1975; Ramaswamy et al. 1977, 1978; Green et al. 1978). The calcu-

lation of the relaxation cross sections involves the quantum mechanical scattering of the heavy particles on a potential energy surface (PES) that is computed using quantum chemistry techniques, accounting for the electronic motion for all relevant nuclear configurations of the constituent colliders. The availability of more realistic (H$_2$)$_2$ potential surfaces has enabled considerable progress to be made toward obtaining a more reliable set of state-to-state collisional cross sections and rate coefficients. To date, the most comprehensive studies have been made by Flower (1998) and Flower & Roueff (1998). Within the rigid rotor approximation, Flower & Roueff have made use of the (H$_2$)$_2$ interaction potential from Schwenke (1988) in a quantal coupled-channel method to determine the rate coefficients for rotational transitions in H$_2$+H$_2$ collisions. Rotational levels of $J \leq 8$ and kinetic temperatures of $T \leq 1000$ K were employed, and the results were compared with those reported by Danby et al. (1987), which were based on an older potential surface.

Accurate determinations of rate coefficients for state-to-state transitions in small molecular systems such as the H$_2$ molecule require a quantum mechanical description of the scattering process. A full quantum calculation of rovibrational transitions in the H$_2$-H$_2$ system is computationally challenging. So far, only a few studies have been reported that include both rotational and vibrational degrees of freedom of the H$_2$ molecules. Pogrebnya & Clary (2002) reported vibrational relaxation of H$_2$ in collisions with H$_2$ using a coupled-states approximation implemented within a time-independent quantum mechanical approach. Panda et al. (2007) and Otto et al. (2008) employed a time-dependent quantum mechanical approach and reported rotational transition cross sections in ortho-H$_2$+para-H$_2$ and para-H$_2$ collisions. More recently, Quéméner et al. (2008) reported a full-dimensional quantum scattering calculation of rotational and vibrational transitions in the H$_2$-H$_2$ system that does not involve any dynamics approximations. All these calculations adopted the six-dimensional H$_4$ PES developed by Boothroyd et al. (2002). While this PES is useful for benchmarking full-dimensional quantum scattering codes for the H$_2$-H$_2$ system, comparisons with experimental data have shown (Lee et al. 2006; Otto et al. 2008) that the PES predicts rotational transition rate coefficients between the $J = 0$ and

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$J = 2$ levels that are too small and that it is not appropriate for accurate determinations of rotational transition rate constants in the H_2-H_2 system.

Since full-dimensional quantum calculations of four-atom systems are computationally demanding, especially for excited rotational levels, the rigid rotor approximation is often employed. The adequacy of the rigid rotor approximation for pure rotational transitions in H_2-H_2 collisions was recently demonstrated by Otto et al. (2008), who reported cross sections for rotational excitations in para-H_2 using the rigid rotor model and a full-dimensional quantum calculation. While these calculations have been performed using the Boothroyd et al. (2002) PES, we believe that the conclusions are valid for the H_2-H_2 system in general.

The accuracy of collisional data for astrophysical applications is limited by the uncertainty in the PES and the approximations employed in the dynamics calculations. It is a nontrivial task to judge the impact of the uncertainties in the collisional data that are associated with the choice of the PES. Accurate determination of the potential energy in the interaction region to the requisite level of accuracy of $\sim 10^{-3}$ hartress (or $\sim 10\,K$) remains a challenge, as mentioned above. This is especially important at low temperatures, where small uncertainties in the interaction potential translate into larger errors in the cross sections and rate constants. A further difficulty arises from fitting a limited number of ab initio potential energy points in order to obtain a surface over all configurations that are sampled in the scattering calculations. Unphysical behavior in the fitted PES can result, particularly when bridging explicitly calculated energies at intermediate internuclear separations to long-range asymptotic forms.

A reliable $(H_2)_2$ rigid rotor PES was computed by Diep & Johnson (2000). The accuracy of this PES for rotational transitions in H_2 has recently been demonstrated by comparing computed rate coefficients for $J = 0 \rightarrow 2$ rotational excitation against experimental results (Maté et al. 2005; Lee et al. 2006; Otto et al. 2008). Thus, we believe that the PES by Diep & Johnson (2000) could be employed to provide reliable values of rate constants for rotational transitions in the H_2+H_2 system. Since the H_2+H_2 collision system is of astrophysical significance, it is crucial to establish whether the cross sections and rate coefficients for rotational energy transfer based on this PES are in agreement with the earlier data. Therefore, we adopted this PES in the present quantum mechanical close-coupling calculations to obtain the rotational transition cross sections with initial levels of $J \leq 8$ for collision energies ranging from 10^{-4} to 2.5 eV. The corresponding rate coefficients were computed for the temperature range of $2 \leq T \leq 10,000$ K. The present rate coefficients are compared with the results of Flower (1998) and Flower & Roueff (1998), which are, to the best of our knowledge, the only comprehensive calculations available for rotational de-excitation rate coefficients. We also present H_2-H_2 cooling functions in the low-density limit and test the new rate coefficients in simulations of UV-irradiated molecular gas. Atomic units are used throughout unless otherwise specified; i.e., distances are in units of bohrs (a_0) and energy is in units of hartrees (E_h). Recall that $1\,a_0 = 0.529177\,\text{Å}$, while $1\,E_h = 27.2114$ eV $= 219474.635156$ cm^{-1} $= 627.51$ kcal mole^{-1}.

2. COMPUTATIONAL DETAILS

We carried out quantal coupled-channel calculations for collisions of H_2 with H_2 using a fixed bond length of 1.449 a_0 (0.7668 Å). The rigid rotor H_2 target and projectile energy levels were calculated using a rotational constant of $B = 60.853$ cm^{-1}. To solve the coupled-channel equations, we used the hybrid modified log-derivative Airy propagator (Alexander & Manolopoulos 1987) in the general-purpose nonreactive scattering code MOLSCAT

TABLE 1
H_2-H_2 INTERACTION ENERGY

R (bohr)	Flower (1998)	Diep & Johnson (2000)	Difference
Linear Configuration			
3.0........................	0.06546	0.061703	0.00376
3.5........................	0.02836	0.027103	0.001257
4.0........................	0.01168	0.011378	0.000302
4.5........................	0.004593	0.004525	0.000068
5.0........................	0.001687	0.001660	0.000027
Parallel Configuration			
3.0........................	0.03906	0.037810	0.00125
3.5........................	0.01679	0.016355	0.000435
4.0........................	0.006942	0.006629	0.000313
4.5........................	0.002761	0.002488	0.000273
5.0........................	0.001021	0.000827	0.000194

NOTE.—H_2-H_2 interaction energy, in units of hartrees, for the linear [$(\theta_1, \theta_2, \phi_{12}) = (0, 0, 0)$] and parallel [$(\theta_1, \theta_2, \phi_{12}) = (\pi/2, \pi/2, 0)$] configurations.

developed by Hutson & Green (1994). The log-derivative matrix is propagated to large intermolecular separations, where the numerical results are matched to the known asymptotic solutions to extract the physical scattering matrix. This procedure is carried out for each partial wave. We have checked that the total integral cross sections are converged with respect to the number of partial waves, as well as the asymptotic matching radius (e.g., $R = 40\,a_0$) for all channels included in the calculations.

In addition to the partial wave convergence, we have checked that the results are optimized with respect to other parameters that enter into the scattering calculations. In particular, the parameters used for the analytical expression for the Diep & Johnson (2000) PES,

$$V(R, \theta_1, \theta_2, \phi_{12}) = \sum_{l_1, l_2, l} V_{l_1, l_2, l}(R)\, G_{l_1, l_2, l}(\theta_1, \theta_2, \phi_{12}), \quad (1)$$

where $V_{l_1, l_2, l}(R)$ are the radial expansion coefficients and $G_{l_1, l_2, l}(\theta_1, \theta_2, \phi_{12})$ are the bispherical harmonics as defined in the Appendix of Green (1975). The angles θ_1 and θ_2 denote the two angles in the plane, and ϕ_{12} is the relative torsional angle. We used 10 quadrature points each for integration along the angular coordinates θ_1, θ_2, and ϕ_{12}. From the Diep & Johnson fit to their numerical PES, the expansion coefficients $V_{l_1, l_2, l}(R)$ are determined. They noted that only the $V_{0,0,0}(R)$, $V_{2,0,2}(R)$, $V_{0,2,2}(R)$, and $V_{2,2,4}(R)$ terms make significant contributions to the potential. Explicit forms of $G_{0,0,0}$, $G_{2,0,2}$, $G_{0,2,2}$, and $G_{2,2,4}$ are given in Diep & Johnson (2000).

In Table 1, we show a comparison between the PES adopted by Flower (1998), the Schwenke (1988) potential, and the Diep & Johnson (2000) $(H_2)_2$ PES for the linear [$(\theta_1, \theta_2, \phi_{12}) = (0, 0, 0)$] and parallel [$(\theta_1, \theta_2, \phi_{12}) = (\pi/2, \pi/2, 0)$] configurations, respectively. Although the two potentials show reasonable agreement for both configurations, the analytic PES of Schwenke (1988) for $(H_2)_2$ is known to be accurate only for pairs of hydrogen molecules with intermolecular separations not greater than $\sim 5\,a_0$. The discrepancy may be attributed to the improved accuracy in the Diep & Johnson PES, which incorporates the correct long-range behavior.

The present calculations consider the hydrogen molecules to be indistinguishable. Symmetric basis sets were used for

para-para and ortho-ortho collisions, whereas, for para-ortho collisions, asymmetric basis sets were chosen on the basis of the order of the energy spectrum. The scattering cross sections for rotational transitions were computed for collision energies ranging between 10^{-4} and 2.5 eV. Four de-excitation cases with $\Delta J_1 = -2$ were considered (i.e., para-para and para-ortho; ortho-para and ortho-ortho). Note that a sufficiently large, but truncated basis set has been used to optimize the computation time and minimize the loss of numerical accuracy (i.e., to $\lesssim 5\%$) in the scattering cross section calculations. Further details about the calculations can be found in Lee et al. (2006).

Rate coefficients for state-to-state rotational transitions were obtained by averaging the appropriate cross sections over a Maxwellian distribution of the relative kinetic energy E_k of the H$_2$ molecules at a given temperature T:

$$k_{J_1 J_2 \to J_1' J_2'}(T) = \frac{A}{(1 + \delta_{J_1 J_2})(1 + \delta_{J_1' J_2'})}$$
$$\times \int_0^\infty dE_k \, \sigma_{J_1 J_2 \to J_1' J_2'}(E_k) E_k e^{-\beta E_k}, \quad (2)$$

where $A = (8/\mu\pi\beta)^{1/2}\beta^2$, $\beta = (k_B T)^{-1}$, k_B is the Boltzmann constant, and μ is the reduced mass of the collision system. Here we have adopted the definition of the cross section for indistinguishable particles as given by Green (1975). This definition differs from that adopted by Flower & Roueff (1998), which was given by Zarur & Rabitz (1974). As discussed by Danby et al. (1987) for single rotational excitation transitions, the cross section defined by Green (1975) must be divided by 2 if $J_1 = J_2$ or $J_1' = J_2'$ in order to prevent double counting in the determination of the production rate of J_1' or J_2'. The factor of $(1 + \delta_{J_1 J_2})(1 + \delta_{J_1' J_2'})$ in the denominator of equation (2) accounts for this.

3. RESULTS

3.1. Comparison of Rate Coefficients

Figure 1 shows a comparison between the present theoretical results and the experimental rate coefficients of Maté et al. (2005) for the $(0, 0) \to (2, 0)$ excitation transition between 50 and 300 K, where we have used the notation (J_1, J_2). The experimental and current theoretical rate coefficients are in good agreement, as was shown previously in Lee et al. (2006). The theoretical results obtained by Flower (1998), which used the older PES of Schwenke (1988), also shows good agreement with the measured and new calculated rate coefficients.

Figures 2a and 2b show the rotational de-excitation rate coefficients $\Delta J_1 = -2$ and $\Delta J_2 = 0$ for para-para and ortho-ortho collisions, respectively. For the para-para case, the current rate coefficients for most transitions are found to be similar to those obtained by Flower (1998) and Flower & Roueff (1998), but for the important $(2, 0) \to (0, 0)$ transition, Flower & Roueff's result is $\sim 10\%$ smaller for temperatures less than 1000 K.[7] On the other hand, the $(8, 0) \to (6, 0)$ transition rate coefficients from Flower (1998) and Flower & Roueff (1998) are larger compared to the current results, and the agreement appears to deteriorate as the temperature increases above ~ 400 K. The $(4, 0) \to (2, 0)$ transition, however, is in excellent agreement, but only below ~ 1000 K.

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[7] We note that the rate coefficients from Flower (1998) are limited to temperatures between 100 and 1000 K, while those given in Flower & Roueff (1998) extend from 1000 to 4500 K, but only for para-H$_2$ colliders. We supplement these in Figs. 2 and 3, and in the discussion throughout, with additional data given between 1500 and 6000 K on D. Flower's Web site at http://ccp7.dur.ac.uk/cooling_by_h2/node1.html.
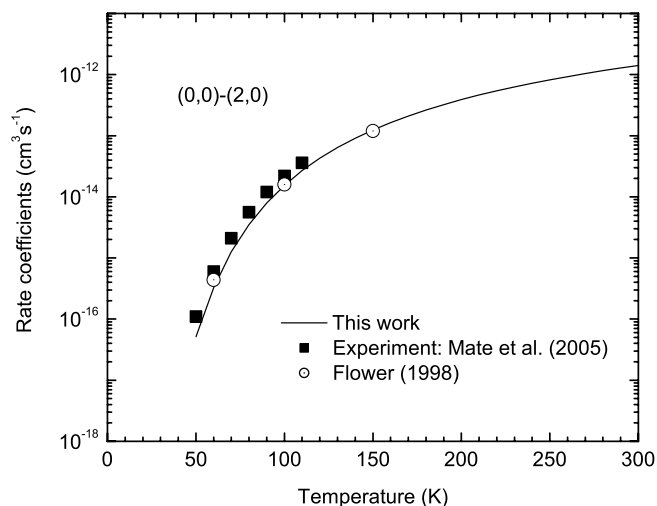

Fig. 1.—Rate coefficients for $(0, 0) \to (2, 0)$ rotational excitation in indistinguishable H$_2$+H$_2$ collisions as a function of temperature. The solid curve denotes the present result, which uses the Diep & Johnson (2000) PES. The filled squares represent the experimental data from Maté et al. (2005). The open circles represent the theoretical results of Flower (1998).

Likewise, for the ortho-ortho transitions, the rate coefficients of Flower & Roueff are similar to the current results, except at the highest temperatures.

Figures 3a and 3b show the rotational de-excitation rate coefficients for ortho-para and para-ortho collisions, respectively. Reasonable agreement was observed, except for the $(8, 1) \to (6, 1)$ transition, where the results of Flower & Roueff (1998) tend to be significantly larger than the present calculations. This behavior is essentially identical to that seen for the $(8, 0) \to (6, 0)$ transition shown in Figure 2a. Discrepancies are also noted for all of the transitions at the highest temperatures.

3.2. Rate Coefficient Data and Fitting

Numerical values for the rate coefficients are given in Table 2. We have also fitted the computed rate coefficients to an analytical form similar to that introduced by Le Bourlot et al. (1999). The adopted form used here is

$$k_{J_1 J_2 \to J_1' J_2'}(T) = 10^{a+b/t_1+c/t^2} + 10^{e+(f/t_2)^h}, \quad (3)$$

where $t = T/1000 + \delta t$, $t_1 = d(T/1000) + \delta t$, and $t_2 = g(T/1000) + \delta t$, with $\delta t = 1$. The fit coefficients a–h, a Fortran routine to return the rate coefficient k following input of the temperature T and the set of initial and final quantum numbers, the numerical data for the rate coefficients, and the numerical data for the cross sections can all be obtained online.[8] The fits are valid between 2 and 10,000 K and were performed for exothermic $\Delta J_1 = -2$ transitions. Rate coefficients for endothermic transitions can be obtained by detailed balance, which is implemented in the Fortran routine.

Because the accuracy of the PESs for values of l_1, l_2, and $l \geq 4$ (see eq. [1]) is uncertain, we did not explicitly compute the rate coefficients for $\Delta J_1 < -2$ transitions, except for two $\Delta J_1 = -4$ cases: $(4, 0) \to (0, 0)$ and $(5, 1) \to (1, 1)$. The rate coefficients for these processes are typically a factor of ~ 50 smaller than the $\Delta J_1 = -2$ rate coefficients for the same initial state. Transitions with $\Delta J_1 < -4$ are expected to have even smaller rate
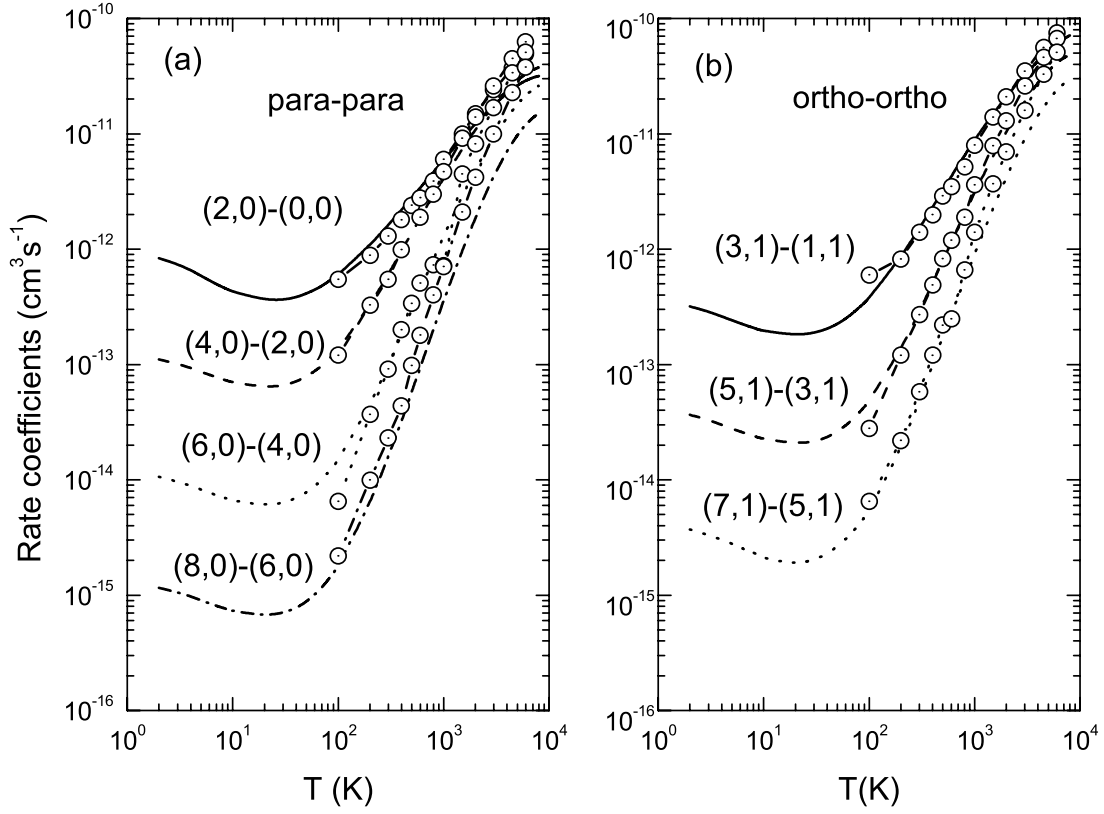
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[8] See http://www.physast.uga.edu/ugamop/.

FIG. 2.—Temperature dependence of rotational state-resolved rate coefficients for H_2+H_2 collisions. (*a*) Para-para and (*b*) ortho-ortho collisions. Circles denote theoretical results from Flower (1998) and Flower & Roueff (1998). [*See the electronic edition of the Journal for a color version of this figure.*]
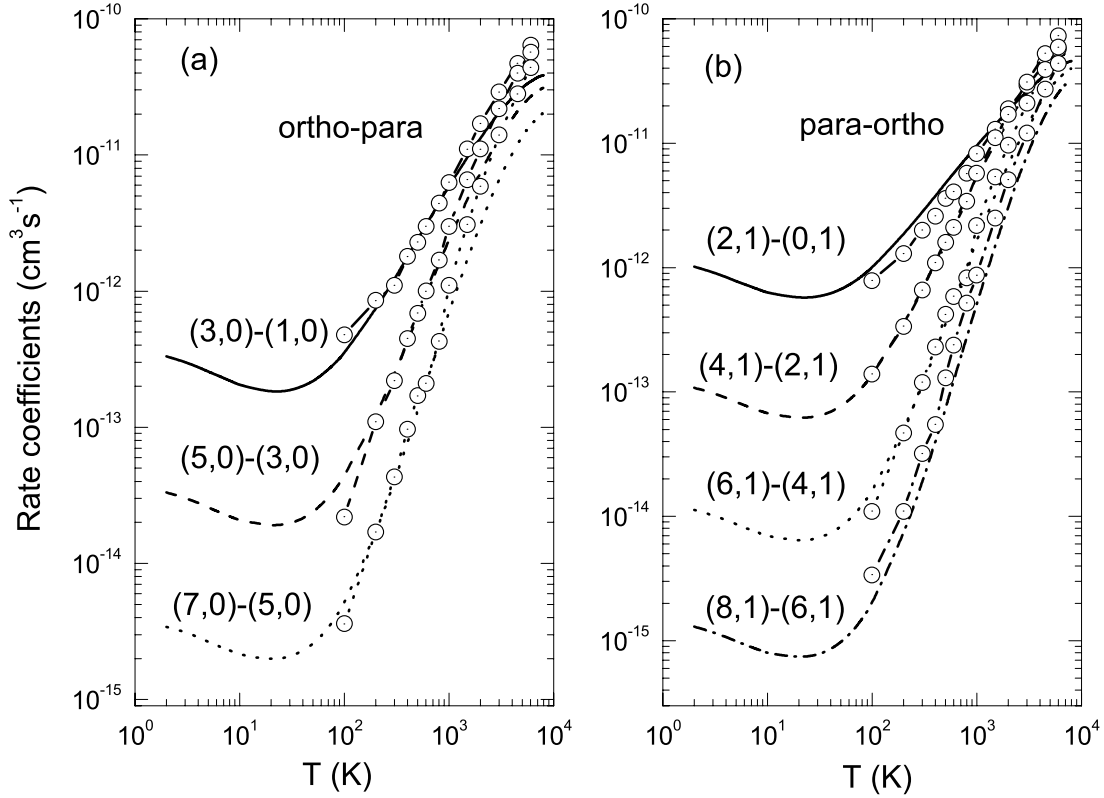

FIG. 3.—Same as Fig. 2, but for ortho-para and para-ortho collisions. [*See the electronic edition of the Journal for a color version of this figure.*]

TABLE 2
Rotational De-excitation Rate Coefficients

v_1	J_1	v_1'	J_1'	v_2	J_2	v_2'	J_2'	T (K)	k^{a} (cm^3 s^{-1})
0	2	0	0	0	0	0	0	2.0	8.365($-$13)
0	2	0	0	0	0	0	0	3.0	7.416($-$13)
0	2	0	0	0	0	0	0	4.0	6.531($-$13)

Notes.—Rotational de-excitation rate coefficients as a function of temperature for H$_2$($v_1 = 0$, J_1) due to collisions of H$_2$($v_2 = 0$, $J_2 = 0$ or 1). Table 2 is presented in its entirety in the electronic edition of the *Astrophysical Journal*. A portion is shown here for guidance regarding its form and content.
  $^{\mathrm{a}}$ The notation $A(-B)$ refers to $A \times 10^{-B}$.

coefficients. While these two rate coefficients have been fitted, we estimate all other $\Delta J_1 < -2$ transitions with a version of the modified exponential energy gap law (MEGL; Steinfeld et al. 1991). With the MEGL, the rate coefficients for $\Delta J_1 < -2$ transitions are obtained by scaling the $\Delta J_1 = -2$ rate coefficients with the following relation:

$$k_{J_1 J_2 \to J_1' J_2'}(T) = k_{J_1 J_2 \to J_1 - 2, J_2'}(T) \frac{2(J_1 - 2) + 1}{2J_1' + 1}$$
$$\times \exp[-\beta(T)\Delta/T]\left(\frac{1 + \alpha\Delta/T}{1 + \alpha\gamma\Delta/T}\right)^2, \quad (4)$$

where $\Delta = \left[E(J_1 - 2) - E(J_1')\right]/k_B$ is the difference in rotational binding energies in units of K and a value of $\alpha = 2$ is usually adopted. We find that the $(4, 0) \to (0, 0)$ transition is fitted with $\gamma = 2/3$ and $\beta(T)/T = 1/300$, the latter being nearly temperature-independent.

4. ASTROPHYSICAL APPLICATIONS

In order to investigate the effect of the new rate coefficients in astrophysical environments, we show in Figure 4 low-density-limit cooling functions given by

$$\frac{\Lambda(T)}{n_{H_2}(J_1)n_{H_2}(J_2)} = k_{J_1 J_2 \to J_1' J_2}(T)h\nu_{J_1' J_1}, \quad (5)$$

where $\Lambda(T)$ is the cooling rate in units of erg cm^{-3} s^{-1}, $n_{H_2}(J)$ is the number density of H$_2$ in rotational state J, and $h\nu_{J_1' J_1}$ is the emitted photon energy. Here we consider transitions among the lowest four rotational states and plot the cooling rate due to para-H$_2$ collisions on H$_2$($J_1 = 0$, 1) and the total cooling rate for a statistical distribution of ortho- and para-H$_2$; i.e., ortho : para = 3 : 1, following the prescription given by Glover & Abel (2008). The new cooling functions are compared to those obtained by Glover & Abel (2008), based on the H$_2$-H$_2$ rate coefficients of Flower & Roueff (1998), which are indicated to be valid for the range $100 < T < 6000$ K. The two sets of cooling functions are generally in agreement to within $\sim$20% for $T < 2000$ K, including cooling due to ortho-H$_2$ collisions (*not shown*). The level of agreement reflects differences in the collisional rate coefficients shown in Figures 2 and 3. However, above $\sim$2000 K the cooling functions of Glover & Abel (2008) are seen to depart significantly from the current results, which is due to the divergence in the two sets of rate coefficients at the higher temperatures.

In a further test, we include the full set of H$_2$-H$_2$ rate coefficients in a model of a molecular photodissociation region (PDR) using the spectral simulation code Cloudy (Ferland et al. 1998).
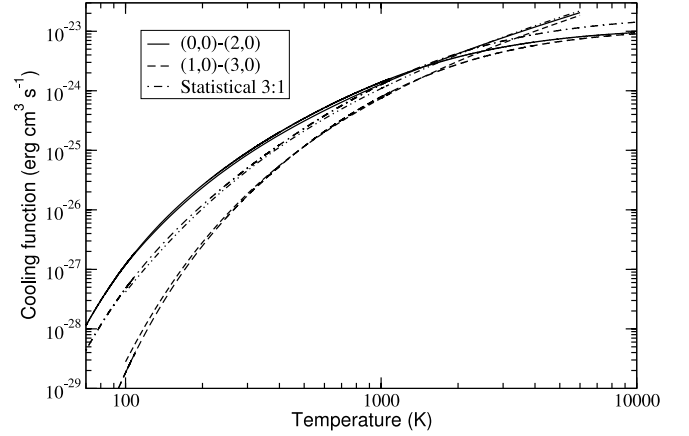

Fig. 4.—Low-density-limit cooling function of H$_2$ due to H$_2$+H$_2$ collisions. Thick lines show the present results. Thin lines are from Glover & Abel (2008), based on the rate coefficients of Flower & Roueff (1998). Solid lines indicate para-para collisions, dashed lines indicate para-ortho collisions, and dot-dashed and double-dot–dashed lines indicate the statistical ortho-para population.

Model V3 of the PDR code comparison study (Röllig et al. 2007) is adopted, in which the total density is taken to be constant at $10^{5.5}$ cm^{-3} and the intensity of the incident far-ultraviolet (FUV) radiation field is 10 times that of the standard Draine (1978) FUV field. Other model parameters of the molecular region are given in Röllig et al. (2007). A nearly complete description of the electronic, vibrational, and rotational radiative and collisional properties of the H$_2$ molecule was included as described by Shaw et al. (2005). Figure 5a gives the H and H$_2$ number densities and the temperature structure of the cloud as a function of depth. We note that in a strongly irradiated PDR, the rotational (and vibrational) levels are typically not in thermal equilibrium, but are usually overpopulated (e.g., Shaw et al. 2005). Therefore, even though the gas temperature is less than 100 K, the H$_2$ rotational levels are significantly populated.

In Figure 5b, the effect of the new H$_2$-H$_2$ rate coefficients is shown by plotting the ratio of the rotational populations $n(v = 0, J)$ determined from two separate models. In the numerator, the standard set of H$_2$-H$_2$ rate coefficient fits given in Le Bourlot et al. (1999) are adopted, while in the denominator the current H$_2$-H$_2$ rate coefficients are used. H$_2$-H and H$_2$-He collisions are also included and are taken from the recent calculations of Wrathmall et al. (2007) and T.-G. Lee et al. (2008, in preparation) and used in both models. Since the rate coefficients from the two calculations are in general agreement, most levels do not experience a significant change in population. However, differences are seen for cloud depths greater than $\sim$10^{10} cm, which corresponds to an increase in the total H$_2$ abundance and decreases in the H abundance and the gas temperature. The abundance changes maximize the effect of H$_2$ colliders, reducing the importance of H collisions, although He collisions are still important. As such, while the discrepancies in the H$_2$-H$_2$ rate coefficients are maximized above $\sim$1000 K, their effects at these high temperatures will be masked by the more important roles of H and He collisions. However, as the temperature decreases below 100 K and the H$_2$ collisions become more important, the discrepancies are related to the fact that the Le Bourlot et al. (1999) fits were not intended to be valid below 100 K. The largest differences, of $\sim$50% and $\sim$20%, are those for the $J = 3$ and $J = 4$ populations, respectively. These differences are related to the increase in the rate coefficients to populate the levels as shown in Figures 3a and 2a, respectively, for temperatures less than 200 K. As the temperature falls further, below $\sim$20 K, discrepancies in the $J = 2$
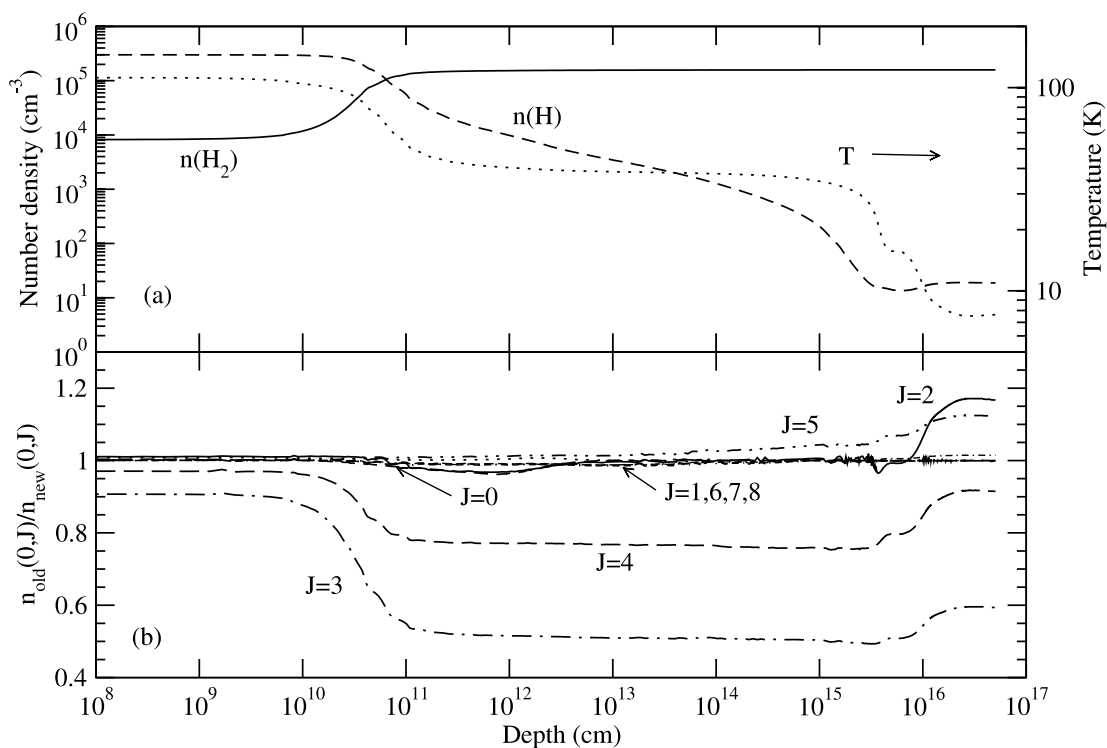
FIG. 5.—(a) Total H and H₂ abundances and the gas temperature as a function of depth into a model molecular photodissociation region. See text for model parameters. (b) Effect of the new H_2-H_2 rate coefficients on the H₂ rotational populations in the model molecular photodissociation region. Ratio of the values of n_{H_2} ($v = 0$, $J = 0-8$) obtained with the standard Le Bourlot et al. (1999) rate coefficient fits (based on Flower 1998) to those obtained by replacing the H_2-H_2 rate coefficients with the current calculations. See text for details.

and $J = 5$ populations also become significant since the current rate coefficients reach a minimum near this temperature, while the fits of Le Bourlot et al. (1999) go to constant values.

5. SUMMARY

We have performed an extensive quantum mechanical coupled-channel calculation, based on a demonstratedly reliable $(H_2)_2$ potential energy surface, to obtain rotational transition cross sections with initial levels of $J \leq 8$. Collision energies ranging between 10^{-4} and 2.5 eV were considered. We have computed the corresponding rate coefficients for the temperature range from 2 to 10,000 K and have compared our results with the previous works of Flower (1998) and Flower & Roueff (1998), which were based on an older potential energy surface. We conclude that in some cases, the improvement made in the new potential energy surface and the larger number of basis functions used in the present scattering calculations led to significant changes in the resulting state-to-state cross sections and rate coefficients. Implementation of the new H_2-H_2 rate coefficients in calculations

of the low-density-limit cooling function and in the rotational level populations in a molecular photodissociation region result in some differences compared to the use of the rate coefficients from Flower & Roueff. Complete tabulations of rate coefficients are available electronically upon request, on the Web,[9] and from the *Astrophysical Journal* electronic tables.

[9] Available at http://www.physast.uga.edu/ugamop/.

REFERENCES

Alexander, M. H., & Manolopoulos, D. E. 1987, J. Chem. Phys., 86, 2044
Allers, K. N., Jaffe, D. T., Lacy, J. H., Draine, B. T., & Richter, M. J. 2005, ApJ, 630, 368
Boissé, P., Le Petit, F., Rollinde, E., Roueff, E., Pineau des Forêts, G., Andersson, B.-G., Gry, C., & Felenbok, P. 2005, A&A, 429, 509
Boothroyd, A. I., Martin, P. G., Keogh, W. J., & Peterson, M. J. 2002, J. Chem. Phys., 116, 666
Burton, M. G., Howe, J. E., Geballe, T. R., & Brand, P. W. J. L. 1998, Publ. Astron. Soc. Australia, 15, 194
Danby, G., Flower, D. R., & Monteiro, T. S. 1987, MNRAS, 226, 739
Diep, P., & Johnson, J. K. 2000, J. Chem. Phys., 112, 4465 (erratum 113, 3480)
Draine, B. T. 1978, ApJS, 36, 595
Ferland, G. J., Korista, K. T., Verner, D. A., Ferguson, J. W., Kingdon, J. B., & Verner, E. M. 1998, PASP, 110, 761
Flower, D. R. 1998, MNRAS, 297, 334
Flower, D. R., & Roueff, E. 1998, J. Phys. B, 31, 2935
France, K., Andersson, B.-G., McCandliss, S. R., & Feldman, P. D. 2005, ApJ, 628, 750
France, K., McCandliss, S. R., & Lupu, R. A. 2007, ApJ, 655, 920
Fuente, A., Martine-Píntado, J., Rodríguez-Fernández, N. J., Rodríguez-Franco, A., & De Vicente, P. 1999, ApJ, 518, L45
Glover, S. C. O., & Abel, T. 2008, MNRAS, 388, 1627
Green, S. 1975, J. Chem. Phys., 62, 2271
Green, S., Ramaswamy, R., & Rabitz, H. 1978, ApJS, 36, 483
Hutson, J. M., & Green, S. 1994, MOLSCAT, Version 14 (distributed by Collaborative Computational Project 6; Daresbury Laboratory: UK Eng. Phys. Sci. Res. Council), http://www.giss.nasa.gov/tools/molscat/
Le Bourlot, J., Pineau des Forêts, G., & Flower, D. R. 1999, MNRAS, 305, 802

Lee, T.-G., Balakrishnan, N., Forrey, R. C., Stancil, P. C., Schultz, D. R., & Ferland, G. J. 2006, J. Chem. Phys., 125, 114302

Maté, B., Thibault, F., Tejeda, G., Fernández, J. M., & Montero, S. 2005, J. Chem. Phys., 122, 064313

McCartney, M. S. K., Brand, P. W. J. L., Burton, M. G., & Chrysostomou, A. 1999, MNRAS, 307, 315

Meyer, D. M., Lauroesch, J. T., Sofia, U. J., Draine, B. T., & Bertoldi, F. 2001, ApJ, 553, L59

Neufeld, D. A., et al. 2006, ApJ, 649, 816

Otto, F., Gatti, F., & Meyer, H.-D. 2008, J. Chem. Phys., 128, 064305

Panda, A. N., Otto, F., Gatti, F., & Meyer, H.-D. 2007, J. Chem. Phys., 127, 114310

Pogrebnya, S. K., & Clary, D. C. 2002, Chem. Phys. Lett., 363, 523

Quéméner, G., Balakrishnan, N., & Krems, R. V. 2008, Phys. Rev. A, 77, 030704

Ramaswamy, R., Green, S., & Rabitz, H. 1977, J. Chem. Phys., 66, 3021

Ramaswamy, R., Rabitz, H., & Green, S. 1978, Chem. Phys., 28, 319

Röllig, M., et al. 2007, A&A, 467, 187

Schwenke, D. 1988, J. Chem. Phys., 89, 2076

Shaw, G., Ferland, G. J., Abel, N. P., Stancil, P. C., & van Hoof, P. A. M. 2005, ApJ, 624, 794

Steinfeld, J. I., Ruttenberg, P., Millot, G., Fanjoux, G., & Lavorel, B. 1991, J. Phys. Chem., 95, 9638

Wrathmall, S. A., Gusdorf, A., & Flower, D. R. 2007, MNRAS, 382, 133

Zarur, G., & Rabitz, H. 1974, J. Chem. Phys., 60, 2057