ANALYTIC TEMPERATURE DEPENDENCES FOR A COMPLETE SET OF RATE COEFFICIENTS FOR COLLISIONAL EXCITATION AND DISSOCIATION OF H_2 MOLECULES BY H ATOMS

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ABSTRACT

Analytic expressions for the temperature dependences for a new complete set of rate coefficients for collisions of H_2 with H are presented. The rate coefficients describe both state-to-state transitions (excitation and de-excitation) and collision induced dissociation. The temperature range for the fits was 450 K to 20,000 K to ensure a smooth behavior across the entire range where the underlying data are most accurate, about 600 K to 10,000 K.

Subject headings:

ISM: molecules – molecular processes – molecular data

1. INTRODUCTION

Evaluation of several fundamental processes involving H_2 (e.g., in interstellar shocks and photodissociation regions) requires a detailed knowledge of the populations of the (v, j) vibration-rotation states of the molecule (e.g., Martin et al. 1996 and references therein). Since the interstellar medium 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, including collisional excitation, deexcitation, and dissociation (CID), must be treated explicitly. Mandy & Martin (1993, 1996) have described calculations of a new complete set of rate coefficients for collisions of H_2 with H, including both state-to-state transitions and CID. In § 2 we review the development of these rate coefficients at a finite set of temperatures and the expected range of validity. There are significant differences in these rate coefficients compared to earlier estimates based on various more approximate calculations. Examination of the complete results has called into question the assumption that only a few types of collisional transition (limited Δv and Δj) are important.

In many complex astrophysical applications the physical conditions and populations change in time and/or space, requiring collisional rate coefficients as a function of temperature. The main focus of this *Letter* in § 3 is to fit analytic expressions encapsulating the temperature dependence of each rate coefficient, so that the complete set can be readily exploited. In § 4 we conclude with a discussion which includes a cautionary comparison with one earlier rate coefficient scaling relation and a description of the data available for electronic distribution.

2. COLLISIONAL RATE COEFFICIENTS

In the calculations reported we have considered only H atoms as collision partners. All 348 (v, j) states of H_2 in its electronic ground state are included. As displayed in Figure 1 of Martin et al. (1996), these consist of manifolds of j states for $v = 0$ to 14. Within each manifold, quantum numbers j can range from 0 to j_{max}, with the actual value of j_{max} depending on the value of v (j_{max}= 38 for $v = 0$, j_{max}= 4 for $v = 14$). Let n_k be the population of a (v, j) state with energy E_k. For the 348 states, the rate of population change due to collisions with H atoms at density $n_{\rm H}$ is

$$\frac{dn_k}{dt} = n_{\rm H} \sum_{l \neq k} (\gamma_{kl} n_l - \gamma_{lk} n_k) \, , \tag{1}$$

where we adopt the matrix-motivated convention that subscript kl represents a transition *to* state k *from* state l (i.e., $kl \equiv k \leftarrow l$) and γ_{kl} is a collisional rate coefficient. Let n_{349} represent the population that has dissociated. Neglecting recombination (Martin et al. 1996) equation 1 is then supplemented by

$$\frac{dn_{349}}{dt} = n_{\rm H} \sum_{l=1,348} \gamma_{349,l} n_l \, . \tag{2}$$

2.1. Calculation of the Collisional Rate Coefficients

The interaction potential energy surface for H + H_2 is well known for the ground electronic state (Liu 1973; Siegbahn & Liu 1978; Truhlar & Horowitz 1978; Varandas et al. 1987; Boothroyd et al. 1991, 1996). The rate coefficients γ_{kl} reported here were determined from cross sections which had been calculated with the quasiclassical trajectory (QCT) method using the LSTH potential energy surface (for details see Mandy & Martin 1993, 1996 and references therein).

Outcomes of H + H_2 collisions fall into three classes that can be distinguished in QCT calculations: (i) non-reactive (referred to as *nr*), in which an inelastic collision leaves

the original H_2 molecule in a different (v, j) state which must be of the same nuclear spin parity (Δj even); (ii) exchange (referred to as *ex*), in which the atomic H collision partner combines with one of the H atoms of the target diatomic to form an new H_2 molecule in some (v, j) state (among such collisions are those with Δj odd, which change the parity); and (iii) dissociation (CID) in which the molecular bond is severed leaving three H atoms. All of these processes are included explicitly here. There are 60,222 non-zero coefficients γ_{nr}, 120,756 non-zero coefficients γ_{ex}, and 348 non-zero coefficients for CID (stored in row 349 of γ_{nr}). These rate coefficients have been evaluated at 22 temperatures between 100 and 100,000 K (181,326 coefficients per temperature).

The final γ_{kl} in equation 1 is the sum of γ_{nr} and γ_{ex}.

2.2. Accuracy

In the QCT method, a statistical limit to the accuracy of the final rate coefficients is determined by the size of the batches of trajectories run to find the cross section at each energy. For fixed batch sizes, there are consequently larger *fractional* errors for cross sections that are small. Cross sections for a given transition tend to be smaller for energies near the (energetic) threshold for the transition and this leads to larger fractional errors for low temperature rate coefficients where the Maxwell-Boltzmann distribution for the translational energies samples only the low energy cross sections. Some transitions (e.g., transitions with large energy jumps) have lower overall probability, and so larger fractional errors for the rate coefficients. For applications like equation 1 this is acceptable: the dominant transitions have the lowest fractional errors.

In finding the temperature dependence, we fit $\log_{10} \gamma(T)$ with the errors in $\gamma(T)$ transferred to the equivalent fractional error (*dex*). These errors are neither distributed in a normal distribution nor entirely independent from temperature to temperature. The

rms (average) statistical error for the $\sim 2 \times 10^6$ data considered was 36% (20%). Fitted data were weighted according to the errors, but to the avoid undue emphasis on the higher temperature rate coefficients for a given transition, the weight was capped corresponding to a fractional error of 7%.

In addition, there are systematic errors in the rate coefficients arising from errors in the underlying potential energy surface. Comparisons of various revised surfaces and limited comparisons of cross sections and rate coefficients (for transitions of relatively low energy) based on them indicate that the LSTH calculations should be quite accurate (Mandy & Martin 1991, 1992; Keogh et al. 1992; Sun & Dalgarno 1994; Lepp, Buch & Dalgarno 1995; Boothroyd et al. 1996). There are other systematic errors, such as neglect of quantum effects like tunneling at low energy or zero-point energy, and the influence of coupling to an electronically excited surface at high energy; these set the temperature range over which the rate coefficients can be considered adequate.

2.2.1. Temperature Range for the Fits

As discussed by Mandy & Martin (1993) and Martin et al. (1996) some caution must be exercised in using the rate coefficients at the high end of the temperature range, above $T \simeq 10^4$ K. We limit our analytic fits to $T \leq 20,000$ K, which provides a smooth functional representation through 10^4 K and somewhat higher. Because of the rapid dissociative cooling, a higher temperature in the gas would be of short duration in many astrophysical applications. If the higher temperature were maintained, the H_2 would be largely removed since collisional dissociation is rapid. In addition the role of electronic excitation of the atoms and molecules would need to be considered. Caution must also be exercised at the low end of the temperature range. Following our previous discussions, QCT calculations should be reliable to as low as ~ 600 K. We limit our analytic fits to $T \geq 450$ K, which

provides a smooth functional representation through 600 K and somewhat lower. The restricted range for the fits therefore contained 13 of the original 22 temperatures.

3. ANALYTIC FITS OF THE TEMPERATURE DEPENDENCE

There are a number of possible parametrizations of the rate coefficient, an elementary one being a modification of the Arrhenius equation (in logarithmic form):

$$\log_{10}\gamma(T) = A + B\log_{10}T - C/T \ . \tag{3}$$

In explorations fitting with this form over the temperature range 450 K to 20,000 K we found an rms deviation of 22% (non-reactive and exchange transitions are again considered separately). Fitting over the more restricted range 600 K to 10,000 K reduced the rms to 11%. Comparing the size of the deviations of the fits from the data with the calculated errors of the original QCT data, neither fit was regarded as a satisfactory representation since they systematically degraded the data beyond its original quality.

To maintain the quality, a simple extension of equation 3 that was adopted is

$$\log_{10}\gamma(t) = a + bz + cz^2 - d\left(\frac{1}{t} - 1\right) \ , \tag{4}$$

where $t = T/4500$ K and $z = \log_{10}t$. This gave a notably improved rms of 8.8% (5.5% fitting over the more restricted range). Where the original data are of higher accuracy, γ is a smoother function of T and the fit is correspondingly more accurate. The archived matrices contain a, b, c and d, stored with sufficient precision to reconstruct the original fit. Note that a is the fitted prediction of $\log_{10}\gamma$ at 4500 K.

We tried other four-parameter (including non-linear) forms, finding none more satisfactory. An advantage of equation 4 is that by inclusion of the d/t term detailed balance is well preserved explicitly (see § 4.2.1). A potential disadvantage of a higher-order

fit is poorer interpolation and extrapolation properties. With 4 parameters and 13 temperatures in the fit interpolation is good and extrapolation is not necessary (and is in fact to be discouraged) given that the adequately broad fitted temperature range is coincident with the range of validity of the QCT calculations.

The final γ_{kl} required for astrophysical applications (equation 1) is the sum over non-reactive and exchange components. When either the γ_{nr} or γ_{ex} component dominates, it will have a lower rms in its fit; the less dominant component, being smaller and having larger fractional errors in the original data, will have a larger rms. Therefore, comparisons of γ_{kl} with the summed original data show a lower rms than when γ_{nr} and γ_{ex} are compared separately. Based on the archived fits, this reduction in rms is quite remarkable, to typically 0.5% (1.0% at 450 K, 0.2% at $T \geq 14,000$ K). This suggests that a fit to the original sum might be sought, but we have not carried this out since we wanted primarily to represent the original data. In general γ_{nr} and γ_{ex} have different temperature dependences (often the curves cross), and so one could not expect as accurate a fit using four parameters rather than eight.

Given the finite numbers of trajectories used in the QCT cross section calculations, state-to-state transitions with low probability sometimes end up with a zero rate coefficient. However, because of the large batches of trajectories actually run, only 464 out of the possible 181,326 rate coefficients γ_{nr} and γ_{ex} are zero at all T throughout the fitting range (the majority of these γ_{nr}). For a further 90 transitions the computed QCT rate coefficients were zero for $T \leq 4500$ K so that a fit was not deemed advisable (only five remaining fiducial temperatures); these data have been examined individually and in the fitted representation these coefficients are also set, conservatively, to zero everywhere. These 554 cases come as 277 downward and upward pairs and are never among the dominant transitions (which have small Δv and Δj) from the states involved; rather they are at least three orders of magnitude smaller. For the downward transition of the pair both the upper limits for the

QCT rate coefficients and the non-zero data where present are $\sim 10^{-14}$ cm^3 s^{-1} (the upper limits also obey detailed balance).

Of the 121,104 (summed) transitions in the final γ_{kl} there actually remain only 44 with $\gamma_{kl} = 0$ from the original data and 6 more that are zero taking into account cases where a fit was inadvisable. There were also 84 cases where for one of the components, γ_{nr} (mostly) or γ_{ex}, a fit was inadvisable; for these cases the other component (γ_{ex} or γ_{nr}) is larger at low temperatures and so the summed γ_{kl} is accurate there. For a few of these cases at the highest temperatures this is no longer true; for these the QCT results indicate that the component not fit and thus set to zero in the results of the analytic fits actually dominates the sum, so that γ_{kl} is underestimated. At 20,000 K, there are 22 elements [e.g., for $(13,2) \rightarrow (0,0)$] that are underestimated by more than a factor 2; however, since these particular rate coefficients are at least three orders of magnitude smaller than those for the dominant transitions from those states, this deficiency of the analytic fits should cause little problem in numerical simulations.

There were 118 intermediate cases with zero values of the rate coefficient for some $T < 4500$ K for which fits were carried out (an average of 7.6 fiducial temperatures used each). For the downward transition of the 59 pairs the upper limits for the rate coefficients at low temperatures are again $\sim 10^{-14}$ cm^3 s^{-1}. Most are non-reactive transitions characterized by high j and low j'; they are again never the dominant transitions from those states. Examination of all of these cases shows that the fits not only represent the non-zero data well but also extrapolate to reasonable small values (less than the upper limits) at the low temperatures at which the original rate coefficient is zero. In the summed combination γ_{kl} many of these are not the dominant component. In fact there are only 24 of the 118 transitions at 450 K for which the rate coefficient is overestimated by more than a factor 2; these transitions involve a high-lying usually quasibound state [e.g., $(8,20) \rightarrow (2,0)$]. Even these overestimated rate coefficients are at least three orders of magnitude smaller than

those for the dominant transitions from these states and so again this deficiency should not compromise numerical simulations.

4. DISCUSSION

4.1. Scaling Relations

Our collisional rate coefficients for the H + H_2 system fully describe rotational and vibrational excitation, and the related processes of interconversion of vibrational and rotational energy, ortho-para interconversion, and collisionally induced dissociation, all of astrophysical interest. In the absence of such detailed calculations of rate coefficients, a major challenge in many simulations has been the treatment of the multi-quantum (v, j) transitions. Often this has been attempted using few available rate coefficients and scaling relations.

In Mandy & Martin (1993) we gave rate coefficients for all transitions among the states with total energy (relative to the potential energy minimum of H_2) less than 1 eV. In the $v = 0$ manifold this included states with $j \leq 9$ while for the $v = 1$ manifold, states with $j \leq 5$ were considered. We presented a comparative discussion in the context of previous estimates of the rate coefficients and some scaling relations. The present fitted complete set of coefficients will be valuable for exploring a variety of potential scaling relations over the whole energy range (Mandy & Martin 1996).

This is illustrated here using an exemplary though arbitrary formula given by Sternberg & Dalgarno (1989) for exoergic transitions with $\Delta j = -2\Delta v$ (our complete results indicate that transitions of this diagonal type are not the sole important ones in vibrational deexcitation):

$$\gamma(vj \rightarrow v'j') = \frac{2j'+1}{2j+1} \, \frac{3.4 \times 10^{-10}}{(v-v')^2} \, \left(\frac{T}{1000 \text{ K}}\right)^{1/2} . \tag{5}$$

In absolute value these predictions can be much too large. For example, at 1000 K the predicted rate coefficient for $(3,0) \rightarrow (2,2)$ is 1.7×10^{-9} cm^3 s^{-1} whereas $\gamma_{kl} = 8.6 \times 10^{-12}$ cm^3 s^{-1}; the same comparison at 4000 K gives 3.4×10^{-9} cm^3 s^{-1} versus 1.4×10^{-11} cm^3 s^{-1}. That normalization issue aside we can look at the ratios of related rate coefficients relative to this for various Δj: $(2,0) \rightarrow (1,2)$, $(1,0) \rightarrow (0,2)$, $(2,2) \rightarrow (1,4)$, $(1,4) \rightarrow (0,6)$, $(3,0) \rightarrow (1,4)$, $(2,2) \rightarrow (0,6)$, and $(3,0) \rightarrow (0,6)$. From equation 5 these ratios are 1.0, 1.0, 0.36, 0.29, 0.45, 0.13, and 0.29, respectively, independently of temperature whereas from γ_{kl} the ratios are 0.62, 0.24, 0.40, 0.07, 0.69, 0.24, and 0.61 at 1000 K and 0.96, 0.93, 1.1, 0.82, 0.78, 0.73, and 0.80 at 4000 K. Thus the suggested scaling based on the quantum numbers is not adequate (nor is the agreement generally better at other temperatures). Equation 5 predicts a temperature scaling with index 0.5. Comparing the γ_{kl} for the above transitions at 4,000 K and 1,000 K we find the index ranges from 0.37 to 2.1.

4.2. Applications using the Electronic Distribution

Electronic files of the fitting parameters for γ_{nr} and γ_{ex} are available from the authors via anonymous ftp (currently ftp.cita.utoronto.ca, file cita/pgmartin/h2hdist/readme); or contact the authors by e-mail for up-to-date instructions. There are two matrices nr.dat and ex.dat of dimension {4, 349, 349}. The first dimension corresponds to the four parameters a, b, c, and d of equation 4, the second to the final state, and the third to the initial state as in equations 1 and 2. The particular choice for ordering of the states (column or row index 1 – 349) is described by Martin et al. (1996). The size of each archived matrix is about 4 MB, but in compressed form shrinks to 0.7 MB and 1.2 MB, respectively. An auxiliary file of the H_2 energy levels is available (ecol.dat).

Two FORTRAN programs are available as well. One (h2hone.f) reconstructs the γ_{nr}

and γ_{ex} rate coefficients for a requested transition at a chosen temperature. The other (h2hall.f) generates the entire matrix γ_{kl} (including the negative diagonal element; Mandy & Martin 1993) at a chosen temperature in anticipation of astronomical applications; this takes 0.75 s for successive temperatures on a DEC ALPHA computer (150 MHz DEC 3000). Both programs have been compiled and tested in various UNIX environments (SunOS 4.1.3_U1; SGI IRIX 4.0.5H; DEC OSF1 V3.2). These programs also demonstrate by example auxilliary functions such as manipulation of (v, j) to column index and vice versa and use of ecol.dat. A readme file summarizes instructions and details sample output to validate the programs.

4.2.1. Detailed Balance

For physically meaningful results, the collisional rate coefficients must obey detailed balance (microscopic reversibility; Mandy & Martin 1993) to machine accuracy. Detailed balance is obeyed by both the original QCT rate coefficients γ_{nr} and γ_{ex} and those reconstructed from the analytic fits, but only to a finite accuracy dependent on the number of significant figures recorded in the archives (fractional errors in detailed balance comparisons about 0.1% and 0.3%, respectively). Thus for the most precise applications, when the matrix γ_{kl} is being generated the upward coefficient γ_{kl} $(E_k > E_l)$ should be calculated from the downward coefficient γ_{lk} using detailed balance; this procedure is incorporated in the program h2hall.f.

4.3. Conclusions

Over the past two decades computational speeds have improved to the extent that it should be possible to include a full treatment of the (v, j) populations of H_2 in models of

astrophysically interesting environments, such as shocks and photodissociation regions. The steady-state models by Martin et al. (1996) illustrate this possibility for time-dependent calculations and show that a full simulation is a desirable goal compared to approximate treatments. Over the same time there have been significant advances in the computation of the potential energy surface for H + H_2 and in the calculation of state-to-state (and CID) cross sections, to the point that a full set of rate coefficients is now available for the H + H_2 interaction. The analytic fits for the temperature range 450 – 20,000 K and the electronic distribution described here now make these generally available for incorporation in further studies. These rate coefficients need to be extended by quantum calculations to lower temperatures, which is not insurmountable since there only transitions among the lowest (v, j) states are important (which transitions can be gauged approximately by modest extrapolation of our γ_{lk}).

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